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SELECTED ASPECTS OF PROVIDING THE CHEMMOTOLOGICAL RELIABILITY OF THE ENGINEERING

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S45 **Selected aspects of providing the chemmotological reliability of the engineering: Monograph** / Sergii Boichenko, Olexander Aksionov, Petro Topilnytskyi, Andrii Pushak, Kazimierz Lejda / under the general editorshipof prof. Sergii Boichenko. – K.: Center for Educational Literature, 2019. – 342 p.

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The Monograph selectively represents the Aspects of providing the Chemmotological Reliability of the Transport through the investigation of the Quality Parameters of Fuel and Lubricants. Is devoted to the Modern Problems of of Rational use of Traditional and Alternative Fuels, Lubricants and other operational materials during exploitation of Transport.

BASIC ABBREVIATIONS

PC – ProfiLab software
ETC – electron transport chain
DM – decision makers
ICAO – International Civil Aviation Organization
CAAF – Conference on the Use of Alternative Fuels
MEA – more electric planes
ODS – Oil dispersed systems
ARPD – asphalt-resin-paraffin deposits
PPVO – product of processing of vegetable oils
PA – polycyclic arenes
MAC – maximum allowable concentrations
TWUO – tar from West-Ukrainian oil
EPC – European Pellet Council
EIPS – European Industry of Pellet Suppliers
IBTC – International Biomass Torrefaction Council
CIR – coumarone-indene resin
AER – air excess ratio
DTA – differential-thermal analysis
IBP – initial boiling point
EBP – end boiling point
WPhF – wide phenolic fraction
EMF – electromagnetic field
MF – magnetic field
L – lubricants
IATA – International Air Transport Association
CamO – camellina oils
JF – jet fuel
FAEE – fatty acids ethyl esters
FlP – flash point
ASTM – American Society for Testing and Materials
DERD – Directorate of Engine Research and Development
KMKO – Complex of Methods for Qualitative Assessment
GDP – gross domestic product
EGR – exhaust gas recirculation
ECH – engine cylinder head
EG – exhaust gas
PM – particles mater
ER – emission reduction
ID – indicator diagram
CPG – cylinder-piston group
OBD – On-Board Diagnostic
GPS – Global Positioning System
EASA – European Aviation Safety Agency
CAA – Civil Aviation Authority
FAME – fatty acid methyl esters
MIC – Microbial Induced Corrosion
TCA – tricarboxylic acid
IPCC – Intergovernmental panel on Climate Change
BFFM2 – Boeing Fuel Flow Method 2
EE – engine emission
EAPA – European Asphalt Pavement Association
PMB – polymer modified bitumen
SBS – styrene-butadiene-styrene
SIS – styrene-isoprene-styrene
SEBS – styrene-ethylene / butylene-styrene
TE – Thermoplastic elastomers
EPL – Environmental Protection Law
OOU – obszar ograniczonego użytkowania (in Polish), noise zone (in English)

«Not the mind from the books,
but the books from the mind were created»
Grigorii Skovoroda

Introduction

Transport sector is an important component of the economy that have an impact on the development and prosperity of the population.

Rational use of fuels and lubricants, energy efficiency, environmental safety are included into the list of the most important problems of the modern world. Solving these problems determines in a great manner the sustainable development of the world economy and keeping comfort conditions for human being.

Efficiency, reliability of operation of vehicles, rational use of operational materials depend on their correct selection. According to its quality operational materials must conform to both the model and operating conditions of vehicles. The use of poor quality materials leads to a decrease in the durability and reliability of machinery and machine parts; the use of materials of higher quality than required causes unreasonable increase in costs.

The knowledge of machinery suggest not only the knowledge of construction, kinematic, dynamic, and temperature characteristics but also physico-chemical properties of constituent materials that are necessary for analyzing and forecasting of physico-chemical processes during use of a Fuels or a Lubricants. Thus, the efficiency and reliability of vehicles operation depends not only on their structural characteristics, but also on the optimal selection of Fuels and Lubricants, Technical Liquids and other Operational Materials.

Work professional activity of specialists dedicated to petroleum refinery, organizing of storage, transportation and distribution of products, assurance of correspondence between the properties of Fuels, Lubricants, Technical liquids and the conditions of operation of technology and engines aimed at obtaining maximum technical, economical, ecological and social effects is called **usage** of Fuels, Lubricants and Technical liquids.

To **know** Fuels, Lubricants and Technical liquids is to clearly understand the interconnection of quality parameters with physico-chemical and energy processes, occurring in the process of their use under specific conditions, and also the connection with their chemical and group composition.

The **knowledge** of technology suggest not only the knowledge of construction, kinematic, dynamic, and temperature characteristics but also physico-chemical properties of constituent materials that are necessary for analyzing and forecasting of physico-chemical processes during use of a Fuel or a Lubricant.

The study of the essence, regularity (tendens) and connections of phenomena and the processes of use of Fuels, Lubricants, Technical liquids in Aviation Technology with the help of special methodological tools is the base of **Aviation Chemmotology**.

Aviation Chemmotology is a part of Chemmotology that studies and solves the problems of ensuring the necessary quality and application requirements of Fuels and Lubricants used in Aviation Technology.

Chemmotological reliability is a reliability of technology depending on the Quality of Fuels and Lubricants (the ability of technology to maintain good reliability when operated with Fuels and Lubricants grades that are of a economically reasonable quality level).

This monograph as an intergative scientific work of many scholars is a striking example of the representation of these aspects and really illustrates the modern consolidated work of scientists and practitioners, trends in the development of scientific schools of different universities, different countries and science in general. Because, as is know, science does not have borders. Scientific achievements are global civilizational heritage.

Chapter 1

THEORETICAL ASPECTS OF CHEMMOTOLOGY, CHEMICAL TECHNOLOGY AND ENGINEERING

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1.1 THE PROBLEMS OF FORMATION OF ASPHALT-RESIN-PARAFFIN DEPOSITS. PREVENTION AND UTILIZATION

Olena Tertyshna, Kostiantyn Zamikula, Oleh Tertyshnyi

Oil dispersed systems (ODS) contain asphaltenes, resins and paraffins which can promote the formation of asphalt-resin-paraffin deposits (ARPD) on the surfaces of process equipment.

The rate of deposits formation is influenced by the oil composition, namely, the ratio of paraffins, resins and asphaltenes, and by the hydrodynamic and temperature conditions of its transportation, storage and processing [1]. Asphaltenes, peptized and stabilized by resins, are characterized by high melting points (~300 °C) and are partly in the solid state in oil. They do not form a joint crystals or solid solutions with hydrocarbons, and serve only as centers of aggregation and crystallization. Resins in oil form true solutions and are located in the dispersion medium. Part of the resin, the pour point of which is close to the pour point of hydrocarbons, crystallizes forming mixed crystals or solid solutions. The other part forms the solvate shell around the solid particles.

Asphaltenes behave as coagulants, resins – like peptizers, preventing the merging of crystals and the formation of spatial grid [1].

ARPD formation and growth are promoted by the temperature gradient which occurs in the near-wall layer of pipeline and heat exchangers as a result of raw material cooling.

Typically, deposits are removed without prior analysis of the reasons of their formation and accumulation in various units of industrial equipment [2]. The creation of a well-founded kinetic model of ARPD formation and growth will allow to develop ways of deposition minimization, and in the future it will allow to prevent their formation.

The kinetics of deposits formation from oil sample, which was taken from the storage tank at the refinery, was investigated. Oil characteristics of the content of potentially solid components are presented in Table 1.

ARPD formation was studied using a method of «coldfinger test».

A glass of oil (200 ml) was placed in a thermostatic bath, where with stirring at a speed of 120 Rev/min it was heated to the temperature of 30, 40 and 50 °C. The copper tube («coldfinger») with the surface of 744.45 mm^2 was cooled with running water to a temperature of 10 °C. Preliminarily weighed and degreased tube was placed in the center of the glass with oil so that it was at the height of 3 cm from the bottom. The tube was removed from the oil after 5 min and weighed. To remove stuck deposit hot water was ran through the tube, and then ARPD was collected. Small intervals of exposure (5 min) were adopted to minimize the influence of thermal resistance of the deposit layer.

Table 1

Oil characteristics

Characteristic	Value
1	*2*
Asphaltenes (A)	0,1
Paraffins (P)	1,0
Resins (R)	15,9

Table 1 continue

1	*2*
Ratio P/(A+R)	0,06
Ratio R/(P+A)	14,45
Density, $\cdot 10^{-3}$, kg/m^3	843,4
Viscosity, Pa·sec	1,096·
Pour point, ^{0}C	-18

Processing of experimental data was performed using logarithmic (1) and exponential (2) kinetic models, which were chosen to describe the kinetics of ARPD formation from the condensate [3].

$$\frac{dm}{d\tau} = k_{1\log} \cdot k_{2\log}^{-m}, \tag{1}$$

$$\frac{dm}{d\tau} = k_{1\exp} - k_{2\exp} \cdot m, \tag{2}$$

where m – deposit mass; $k_{1\log}, k_{1\exp}, k_{2\log}, k_{2\exp}$ – rate constants; τ – deposition time.

The constants $k_{1\log}, k_{1\exp}$ correspond to the deposit formation on the tube at the initial moment of time. The values of the constants $k_{2\log}, k_{2\exp}$ were selected on the principle of best approximation of experimental data using the built-in genfit function for nonlinear regression of the general form in Mathcad.

The average particle size of the sample solution was determined by the photoelectrocolorimetric method on the KFK-3 colorimeter at two wavelengths of light 530 and 680 nm.

We assumed that the particles of the dispersed phase were spherical and calculated their average diameter d_n (nm) by the formula:

$$d_n = 6000/(\rho \cdot S), \tag{3}$$

where ρ is the density of the dispersed phase particles, $\rho = 1{,}2$ g/cm^3 [4]; S is the specific interphase surface, m^2/g, which was calculated by the equation:

$$S = 8.08 \cdot 10^3 \cdot \frac{\lg D_{\lambda 1} - \lg D_{\lambda 2}}{\lambda_1 - \lambda_2}, \tag{4}$$

where $D_{\lambda 1}$ and $D_{\lambda 2}$ are the optical densities at wavelengths λ_1 and λ_2.

Formation and sedimentation of AS were accelerated by centrifugation of the petroleum solution in toluene (solvent) with *n*-hexane (precipitant) for 12 minutes. The rotational velocity of the centrifuge was 4000 rpm. The stability factor was determined, which is the ratio of the concentrations of components (or characteristics) of the petroleum dispersion system after centrifugation in two layers, separated from each other at a certain distance in the direction of the deposition forces [4].

The stability factor was calculated by the formula:

$$F = \frac{D_1}{D_2}, \tag{5}$$

where D_1, D_2 are the optical densities of the upper and lower layers, respectively, at a wavelength of 680 nm.

The mechanism of the PPVO action was estimated from the results of the IR spectral analysis of samples of the pure petroleum and the petroleum with additives on the spectrometer Spectrum BX II in the range of 400–4000 cm^{-1}. The spectral coefficients were determined by the ratio of the characteristic absorption bands [4].

Dynamics of the deposit formation from the oil sample depending on the temperature difference between the oil and the tube surface is presented in Table 2.

Table 2

Mass of the deposit on the tube surface

Temperature gradient, ^{0}C	Duration of test, min					
	5	10	15	20	25	30
	Mass of the deposit, mg					
20	1,45	2,8	4,1	5,15	5,86	6,1
30	1,87	3,53	4,93	6,13	7,1	7,4
40	2,73	5,27	7,53	9,53	10,15	10,25

The results of the experiment showed that at the initial stage (15–20 min) the main mass of the deposit forms on the tube and it is about 83–93 % of all deposit mass. After twenty minutes of experiment, the rate of deposit accumulation reduced markedly. One of the reasons of slow deposit accumulation is exhaustion of the oil bulk relatively potentially solid components.

The results of the calculation of the rate constants for both equations at three values of temperature gradient are presented in Table 3.

Table 3

The constants of kinetic models of ARPD deposition from oil

ΔT, °C	$\frac{dm}{d\tau} = k_{1\log} \cdot k_{2\log}{}^{-m}$		$\frac{dm}{d\tau} = k_{1\exp} - k_{2\exp} \cdot m$		T*, °C
	$k_{1\log}$	k_{2log}	$k_{1\exp}$	k_{2exp}	
20	0,379	1,181	0,356	0,039	-0,93
30	0,477	1,159	0,440	0,045	-0,70
40	0,806	1,138	0,720	0,053	-0,56

Here T^* is the dimensionless temperature parameter corresponding to the driving force of the sedimentation process:

$$T^* = \frac{T_c - T_w}{T_{oil}} \qquad (6)$$

where T_c, T_w, T_{oil} are the pour points of oil, of the tube surface and of the oil in the glass, respectively (°C).

If taking into account that in the selected experimental conditions T_c, T_w are constant, the parameter T^* only depends on the temperature of oil heating.

From Table 3 it is seen that the values of the constants k_1 are close for both models, while the constants k_2 differ considerably. Such comparison allows to make clear the mechanism of deposition directly on the surface at initial time points and in the process of their accumulation. At small values of the constant k_1 the rate of instantaneous deposition from oil is rather low, for which the value of $R/(A+P)$, i.e. the ratio of peptizator (resin) to the amount of potentially solid crystallizable components ($P+A$), is sufficiently large.

Using the found values of constants the direct problem of modeling the kinetics of ARPD formation in accordance with equations (1) and (2) was solved. The comparison of calculated and experimental values of the deposit mass is presented in Fig.1.

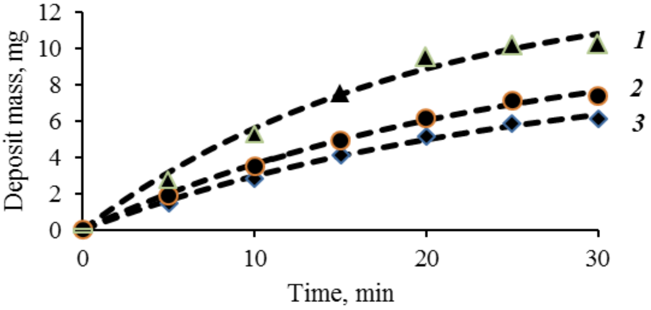

Fig. 1. Dynamics of ARPD accumulation from oil at the temperature difference between the oil and the surface of the tube, ΔT, °C: *1* – 40; *2* – 30; *3* – 20. Points correspond to experimental data, dashed lines are the calculated curves according to the equations (1), (2)

The analysis of Fig. 1 shows that both the logarithmic and the exponential models give almost full coincidence with experimental data. Model verification was performed by the least-squares method (Table 4).

Table 4

The results of the calculation of deviations of experimental and calculated values of the deposits accumulation rate

	Logarithmic model			Exponential model		
ΔT, °C	20	30	40	20	30	40
Sum of squared deviations	0,238	0,204	1,622	0,163	0,122	1,066

Comparison of deviations shows that when using the exponential model the discrepancy between the experimental and calculated data is minimal. Therefore, to describe the kinetics of the process of the deposits formation the exponential equation is more accurate.

The dependence of the rate constants $k_1 = f(T^*)$ and $k_2 = f(1/T^*)$ for both models are linear and described by the equations given in Table 5.

Table 5

The relation of the rate constants with temperature parameter T^*

Logarithmic model	Exponential model
$k_{1\log} = 0{,}893T^* + 0{,}130$	$k_{1\exp} = 1{,}02T^* + 0{,}388$
$k_{2\log} = 1{,}294/T^* - 0{,}261$	

Substitution of the values of the constants from Table 5 in the equation (2) for the exponential model as more accurate, allows to obtain the kinetic equation relating the rate of the deposits growth with temperature factor T^*:

$$\frac{dm}{d\tau} = 1{,}02T^* + 0{,}388 - 1{,}294/T^* - 0{,}261 \cdot m \tag{7}$$

To assess the influence of the layer thickness of the deposit formation on the deposition rate, the dynamics of single (20 min) formation of the deposit were compared with cumulative (with intermediate unloading every 5 minutes) formation (Fig. 2).

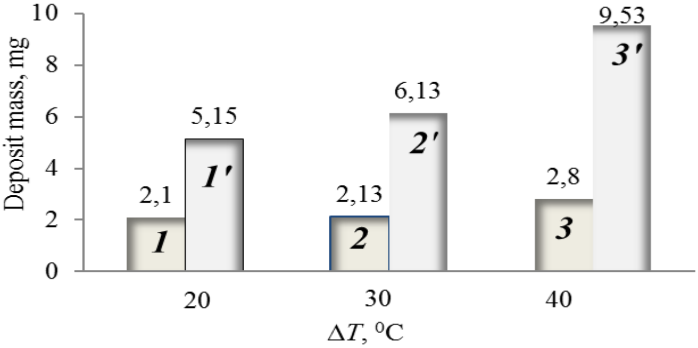

Fig. 2. The mass of the deposit formed at single (*1*, *2*, *3*) and cumulative (*1'*, *2*', *3*') formation of the deposit (20 min) from oil depending on the temperature gradient of oil and the tube Δ*T*

It is seen that the mass of the deposit obtained during continuous deposition is 2.5–3 times less than during its regular removal. This is due to the changes in temperature of the process. It is natural that the growth of ARPD layer on the surface of the tube prevents heat transfer between the cooled surface and the tube, distorting the true temperature gradient set in the experiment. The results of the model thermal calculations performed in accordance with the methods [2] are given in table 6.

Table 6

The temperature regime of ARPD deposition, depending on the hydrodynamics and the layer thickness of the deposit at the temperature of the tube 10 °C

Oil temperature, ^{0}C	Heat-transfer coefficient, W/m^2·K		Deposit layer thickness, м	Heat resistance of the deposit δ/λ, m^2·K/W	Heat-transfer coefficient K_T,W/m^2·K	Actual difference between oil and the tube, ^{o}C
	from the wall side, α_1	from oil, α_2				
1	*2*	*3*	*4*	*5*	*6*	*7*
Turbulent regime						
30	500	300	-	-	187	12
			0,001	0,005	97	6,1
			0,002	0,01	65	4,1
40	500	300	-	-	187	18
			0,001	0,005	97	9
			0,002	0,01	65	6,3
50	500	300	-	-	187	25
			0,001	0,005	97	12,6
			0,002	0,01	65	8,5

Table 6 continue

Laminar regime + natural convection						
1	*2*	*3*	*4*	*5*	*6*	*7*
30	10	60	-	-	8,6	2,7
			0,001	0,005	8,2	2,6
			0,002	0,01	7,9	2,5
40	10	60	-	-	8,6	4,2
			0,001	0,005	8,2	4,0
			0,002	0,01	7,9	3,8
50	10	60	-	-	8,6	5,6
			0,001	0,005	8,2	5,3
			0,002	0,01	7,9	5,1

Data shown in Table 6 indicate that in the turbulent regime the increase in the thickness of the deposit on the surface of the tube to 1 mm cuts the actual temperature difference by half, and when the layer thickness is 2 mm – by three. Under conditions of laminar flow and natural convection the temperature difference is only 2.5–5.6 degrees. It is obvious that the temperature rise in the surface layer of the deposit slows down the process of formation of ARPD solid particles and their accumulation. The conditions corresponding to the turbulent regime under actual conditions can be observed when operating heat transfer equipment. Natural convection occurs when transporting oil products through pipelines and during storage in tanks and containers.

The next stage of the study was the search for effective and inexpensive ways to combat the formation of ARPD and the directions for their processing.

The product of processing of vegetable oils (PPVO) have been used as asphaltene precipitation inhibitorfrom ODS [5, 6].

PPVO is a by-product of the production of biodiesel fuelcomponents [5,6]. The additive was synthesized in the laboratory according to the chemical modification technique by glycerolysis of rapeseed and castor oil with composition (% by weight): rapeseed – 75–80 % and castor – the rest: $CH_3–(CH_2)_5–{}^{12}CH(OH)–CH_2–CH{=}CH–(CH_2)_7–O–CH_2–CH(OH)–CH_2–O–C(O)R',R''$, where R, R', R'' are $C_{17}H_{33}$; $C_{17}H_{31}$; $C_{17}H_{29}$ radicals of any combination. Industrial additives were commercial inhibitors Pachem P-501; Pachem-P-505; Pachem PS-603/X [7].

PPVO was added to the petroleum at the concentrations of 0.07, 0.09 and 0.1 % v/v. Industrial additives were dosed in quantities according to the manufacturer's recommendations for their use: Pachem P-501– 0,07 % v/v, Pachem-P-505–0,07 % v/v, Pachem PS-603 / X – 0,1 % v/v.

The results of the additives influence on the petroleum stability were estimated by changing the average diameter of particles of the dispersed phase with the use of KFK-3 photocolorimeter at the wavelengths of 680 nm by measuring the optical density of the petroleum-toluene mixture (in the ratio of 1:1) with PPVO.

The effectiveness of the additive action on the aggregative stability of the petroleum is presented in Fig. 3,4.

Sediment formation was observed only in the case of the pure petroleum. Determination of the average diameter of the disperse particles in the upper and lower layers of the petroleum samples after centrifugation (Fig. 3) showed that the additives prevent or significantly decrease coagulation. In the pure petroleum under the action of centrifugal force the average particle size of the disperse phase is more than 225 nm. When using the additives, the difference in diameters in the upper and lower layers is insignificant and the lowest value is achieved when using 0.09 % v/v PPVO (sample 3). The average size of the disperse particles in the lower layer correlates with the stability factor – from 0.344 for the pure petroleum to 0.692 with PPVO (sample 3).

The effectiveness of the PPVO additive corresponds to the effectiveness of known proven industrial additives.

Blank column – lower layer of the centrifugate;shaded column – upper layer of the centrifugate.

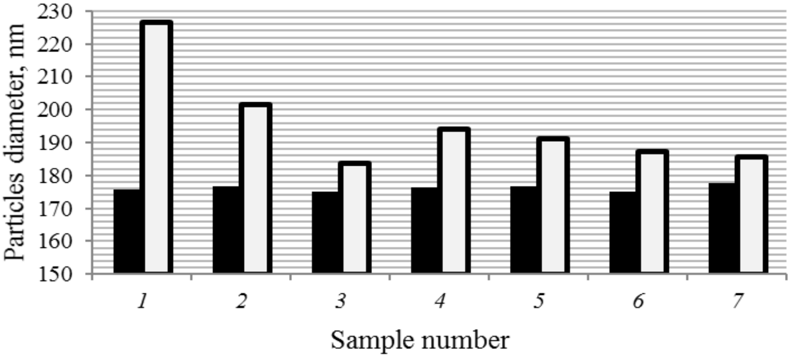

Fig. 3. The value of the disperse particles diameter in the upper and lower layers of the centrifugate of the petroleum solution samples, nm:
1 – pure petroleum; petroleum with the additive:*2* – 0.07 % PPVO; *3* – 0.09 % PPVO; *4* – 0.12 % PPVO; *5* – 0.07 % Pachem P-505; *6* – 0,07 % Pachem P-501; *7* – 0,1 % Pachem PS-603/X

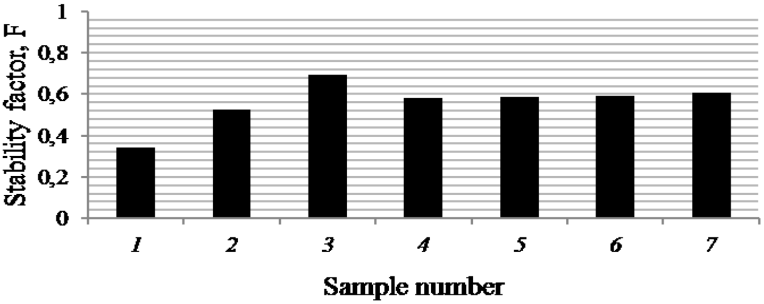

Fig. 4. The value of the stability factor of the petroleum samples:
1 – pure petroleum; petroleum with the additive: *2* – 0.07 % PPVO; *3* – 0.09 % PPVO; *4* – 0.12 % PPVO; *5* – 0.07 % Pachem P-505; *6* – 0,07 % Pachem P-501; *7* – 0,1 % Pachem PS-603/X

IR spectral analysis of the petroleum sample (Fig. 5) showed the presence of paraffin structures of normal and iso-structure, the presence of long paraffin chains (absorption bands are 1462, 1377, 727 cm^{-1}). The presence of aromatic structures (absorption bands are 1605, 1032, 810, 873 cm^{-1}) is noted. The absorption bands of 742, 810, 873, 1032 cm^{-1} indicate the presence of condensed bi-, tri-, and polycyclic aromatic structures in the petroleum. Carbonyl group C–O is absent, petroleum is not oxidized. Sulfoxide group (SO) is present in the absorption band of 1030 cm^{-1}. A strong peak is observed in the region of 2850–2950 cm^{-1}, which indicates the presence of aliphatic CH bonds.

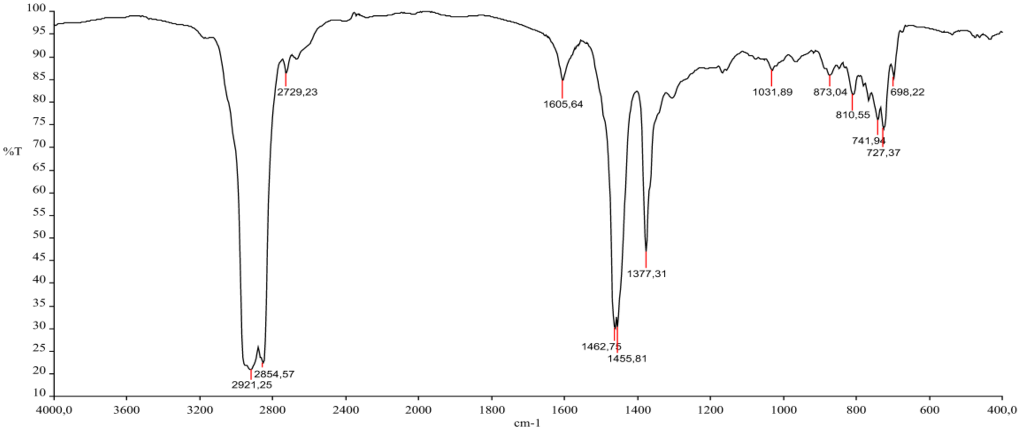

Fig. 5. IR spectra of the pure petroleum

In the IR spectrum of the PPVO (Fig. 6) the peak at about 1750 cm^{-1} are related to valence vibrations of carbonyl groups of aliphatic carboxylic acid esters. The vibrations of the C–O–O at the region of 1300–1000 cm^{-1} confirm the presence of esters. The peak at 3474 cm^{-1} is related to glyceride OH groups.

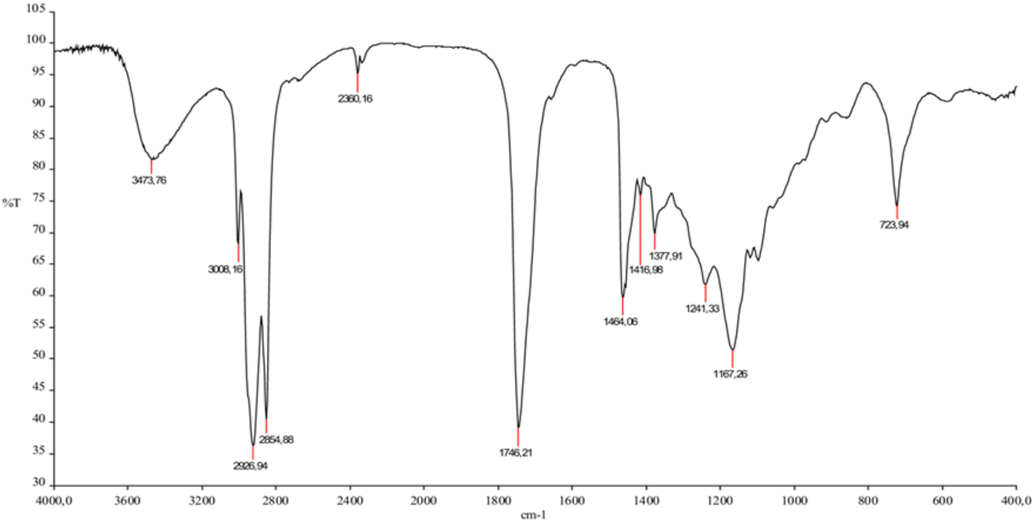

Fig. 6. IR spectra of PPVO

In the petroleum sample with PPVO additive the presence of any new chemical compounds was not found. It is clear from infrared spectrum (Fig 7) that this sample is just the mixture of the above mentioned substances.

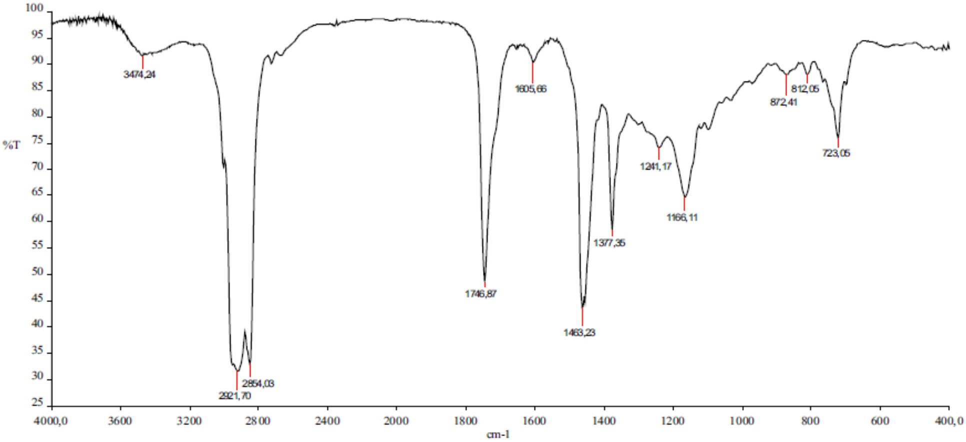

Fig. 7. IR spectra ofthe petroleum with 0.09 % PPVO.

With IR spectral analysis it was established that industrial additives Pachem-P -505 and Pachem-P-501 contain aromatic and alkyl groups, carboxylic acid esters, and also free carboxylic acids. Pachem-PS-603X differs in the increased content of aromatic and alkyl groups, and absence of carboxylic acids. As in the case of PPVO when adding these industrial agents any chemical interaction was not registered.

Apparently the active substances of the additives are surface-active agent. And they are glycerides of fatty acids.

In attempt to estimate quantitatively the influence of additives components on the stabilizing action we used the method of quantitative analyses of hydrocarbonic fragment in petroleum based on IR spectroscopy [8]. The method is considered as most informative for petroleum systems and uses the following absorption bands as characteristic: 727 cm^{-1} (alkane structures with $(CH_2)_x$, $X \geq 4$), 1377 cm^{-1} (branched alkane structures), 1605 cm^{-1} (aromatic structures). It should be noted that fragments concentration in different samples found as the surface under the peaks in the IR spectra cannot be compared owing to the different layer thickness of the samples. Petroleum samples can be compared for the following coefficients: branching coefficient C_b is the ratio of optical density 1377 cm^{-1} (D_{1377}) to optical density 727 cm^{-1} (D_{727}); aliphatic coefficient C_{al} is the ratio of D_{1377} and D_{727} sum to D_{1605}; aromaticity coefficient C_{ar} is the ratio of D_{1605} to D_{727}.

The results for the studied samples with the additives are presented in Table 7.

Table 7

Results of the quantitative analysis of IR spectra of the samples

Petroleum sample	C_b	C_{ar}	C_{al}	F
Pure petroleum	2,06	0,59	5,20	0,35
Petroleum + 0.07 % Pachem P-505	2,49	0,56	6,17	0,59
Petroleum + 0.07 % Pachem P-501	1,86	0,57	5,00	0,59
Petroleum + 0.1 % Pachem PS-603X	2,22	0,65	4,96	0,6
Petroleum + 0.07 % PPVO	1,94	0,57	6,17	0,52
Petroleum + 0.09 % PPVO	2,61	0,53	6,44	0,7

Taking into account nanometer size of the dispersed phase it is clear that IR spectra show only the composition of the dispersion medium because of the infrared radiation diffraction on the nanoparticles.

There are not clear correlation between stability factor and one of the coefficients, but the best value of stability factor F corresponds to the increase of aliphaticy and branching and the decrease of aromaticity coefficients for the Petroleum + PPVO systems. As C_{ar} changes insignificantly, C_{al} and C_b increase by a different value, we inferred that amount of soluble aromatic compound and aliphatic $(CH_2)_x$ groups in the dispersion medium grows in an almost equal degree, whereas amount of branched alkane structures rises in a greater degree.

We can assume that PPVO additive acts as a surfactant displacing natural petroleum surfactants from the particles surface into the dispersion medium and the mechanism of action of Pachem additives differs.

One of the directions of utilization of oil deposits is proposed to add them to the raw materials of the process of visbreaking – tar, the physico-chemical characteristics of which are given in Table 8 [9].

ARPD organic part addition to the tar on light products output and residue quality in the visbreaking process.

The visbreaking process was carried out at the temperature of 713 K and the volume rate of material feed of 3,0 h^{-1}. The product was distillated at atmospheric pressure to obtain petrol (overpoint – 453 K) and gas-oil fraction (453–623 K) and the residue with the beginning of boiling point above 623 K.

Table 8

Physical and chemical characteristics of the visbreaking raw materials

Parameter	Tar sample	ARPD
Density at 293 K, kg/m^3	997	940
Molecular weight	790	670
Sulfur content, % wt.	2,4	1,3
Cokeability, % wt.	17,3	-
Pour point, K	304	301
Kinematic viscosity, mm^2/sec		
at 353 K at 373 K	518 245	960 316
Organic part, % мас.	100	95,8
Hydrocarbon type content, % wt:		
paraffins	10,2	27,1
aromatics	53,3	33,18
resins	28,4	11,1
asphaltenes	6,1	16,5

The laboratory-scale plant (Fig. 8) was used for the investigation of the effect of ARPD samples were diluted at a ratio of 1:3 with oil solvent C155/200 (GOST 3134–78), heated to the temperature of 323–328 K and filtered. The organic part of ARPD containing in the filtrate was separated from petroleum solvent by simple distillation. The tar with the temperature of 343–373 K and organic part of ARPD in a certain proportion were mixed in the raw material block. The temperature of the blended material in the reactor block was kept in the range of 423–453 K with the use of electric heating.

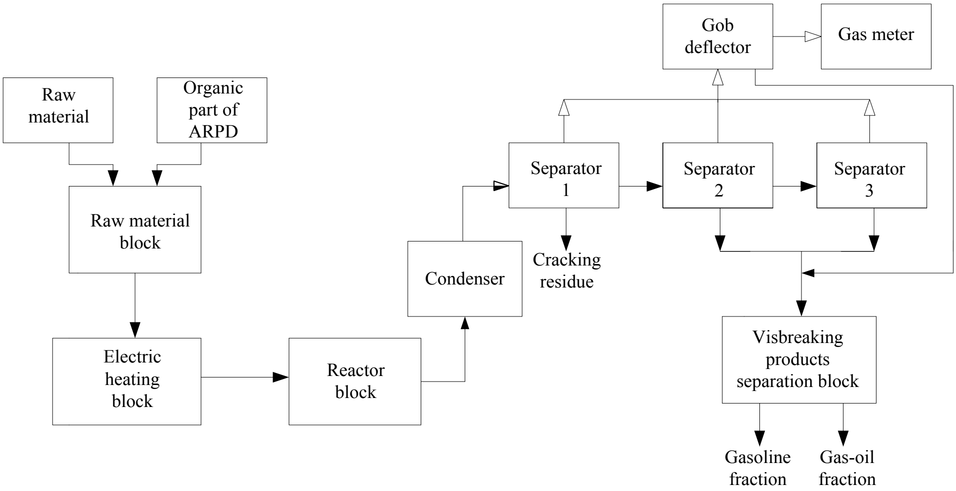

Fig. 8. Block diagram of the laboratory-scale plant of visbreaking process with the use of ARPD organic part

The mixture of the tar with ARPD organic part was sent to the heating block by means of a dosing pump. ARPD-tar mixture was heated in the furnace to the process temperature (430–450 °C) and sent to the reactor block where visbreaking process proceeded. The temperature in the reactor was maintained within 430–450 °C with the use of an additional electric heating, pressure was no more than 0,3 MPa. Sampling of light vapor fractions which was produced in the process was carried out through a straight condenser. The resulting condensate was collected in series-connected separators and the gas fraction was directed through the gas outlet to the gas meter.

In all experiments the amount of gasoline and gasoil, gas and distillation residue was measured, and the material balance was calculated. The physical and chemical properties of oil products were estimated: determination of kinematic viscosity, hydrocarbon composition of heavy oil residues (determination was performed in an oil refinery laboratory), cocking, sulfur, density,pour point, fractional composition, molecular weight, refractive index.

Generalized results of the study of the influence of ARPD content on the qualitative characteristics of the raw material mixture are shown in Fig. 9.

The study was conducted by adding 10, 20, 30 and 40 % (wt.) ARPD to the tar. The fractions yield was measured and kinematic viscosity of the raw material and visbreaking residue was determined. After each experiment the amount of coke in the reactor was controlled.

ARPD influence on the quality indicators of visbreaking raw material was estimated by the change of the disperse characteristics of the mixture, kinematic viscosity, pour point, density depending on the content, the yield of light distillates, coking degree and qualitative indicators of residue.

The change in the dispersion characteristics of the raw material mixture was estimated on the average diameter of the particles of the dispersed phase, the method of determination of which is described above.

In the whole range of ARPD content in tar from 0 to 40 % the decrease of density and pour point is observed which corresponds to the properties of the original components. The influence of ARPD content on the dynamic of change of the dispersed particles size, viscosity and pour point becomes apparent at the 20 % threshold crossing. When the part of ARPD is more than 20 %, intensive aggregation of particles, lowering of the pour point and viscosity increase are observed. This is due to the growing influence of asphaltenes on the aggregative stability of colloid-disperse system.

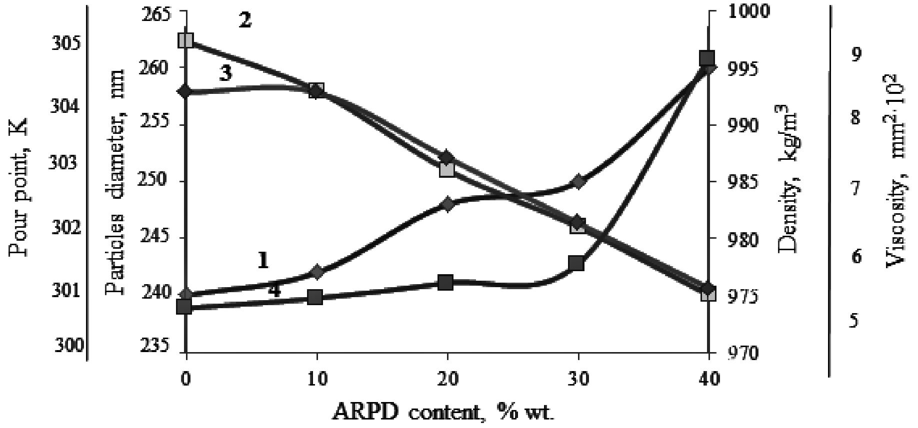

Fig. 9. Dependence of the characteristics of raw material mixture on ARPD content:
1 – particles diameter, nm; *2* – density, kg/m^3; *3* – pour point, К; *4* – viscosity, mm^2/sec at 353 K.

The influence of ARPD on viscosity and the amount of visbreaking products are summarized in Table 9 and Fig. 10.

Table 9

The results of laboratory investigation of visbreaking process

Material/parameter	Mixture number				
	1	*2*	*3*	*4*	*5*
	Mixture composition, % wt.				
Tar	100	90	80	70	60
ARPD	0	10	20	30	40
	Products yield				
Hydrocarbon gas	2,3	2,9	3,7	4,1	4,3
Gasoline fraction (over point – 453 K)	3,0	3,8	4,7	5,0	5,2
Gasoil fraction (453–623 K)	6,7	8,4	10,7	11,6	15,1
Visbreaking residual > 623 K	86,8	84,2	80,9	79,0	74,4
Coking (visually)	negligible	negligible	negligible	considerable	substantial

When adding 10 % wt. of ARPD there was observed slightly increased yield of distillate fractions, insignificant cocking, and insignificant change of viscosity of the cracking residue compared to the residue after tar visbreaking. The increase of the deposits amount in raw material to 20 % is accompanied by increased output of gasoline and gas-oil fractions, low change of viscosity of visbreaking residue which meets normative requirements.

There was observed the significant increase of cocking, viscosity growth of the feedstock and a significant increase in viscosity of visbreaking residue when adding 30 and 40 % of ARPD.

These results are explained by the changes in the composition of the initial mixture of hydrocarbon raw materials. Addition of ARPD increases the relative content of asphaltenes and paraffins, decreases the amount of resins and aromatic compounds (Table 7). Asphaltenes can be conversed relatively poorly during visbreaking, while resins are converted into lighter hydrocarbons which have characteristics of distillates. The higher asphaltenes content in raw material and the less resin content in it, the less reduction in viscosity of the visbreaking residue is.

The increase in viscosity of the visbreaking residue is due to the formation of consolidation products. At the same time, the feature of aromatic hydrocarbons is their tendency to reactions of consolidation with the formation of condensed aromatic hydrocarbons. Products of consolidationare the source material for the formation of resin-asphalt and coke-like substances. Raw material with high content of aromatic hydrocarbons is the least desirable for the processing with the aim to obtain light products – it requires a strict regime of the process and has a significant tendency to cocking.

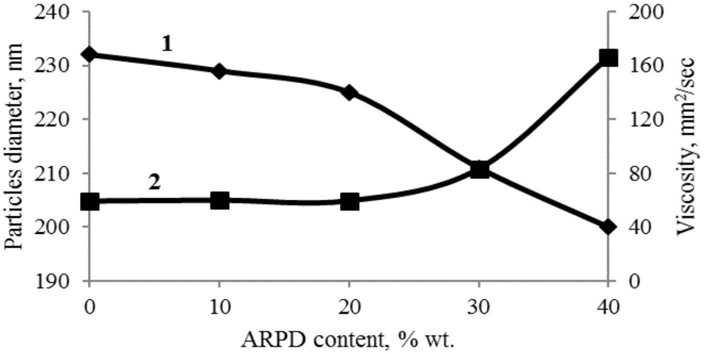

Fig. 10. Dependence of the characteristics of cracking residue on ARPD content:
1 – particles diameter, nm; *2* – viscosity of visbreaking residue at 353 K, mm^2/sec

It was experimentally establish that ARPD addition to raw materials of visbreaking up to 20 % by weight does not significantly increase the relative content of asphaltenes and aromatic compounds, does not influence aggregative stability of raw material and does not significantly affect the qualitative and quantitative characteristics of the final products of the process.

As a result of laboratory simulation of the visbreaking process with a remote reactor when ARPD is added to raw material the industrial visbreaking process scheme was proposed. For that the block of pretreatment of heavy oil deposits was included in the existing technological scheme. Solvent is heated in the heat exchanger T-1, it moves to the mixer M-1 where ARPD is added after heating in the heat exchanger T-2 by gasoil. After the mixer the homogenized mixture is filtered and goes to the column K-1, where solvent is distilled off the top outlet, and ARPDgoes from the bottom. Modernized scheme of thermal destruction of blended raw material is shown in Fig. 11.

Hot tar (363 K) from the preliminary oil distillation plant is mixed with water vapor and pretreated ARPD, then it passes the tube space of the heat exchanger T-3 and is fed to the coil pipe of the furnace P where is heated to the temperature of 703–723 K. The use of water vapor as a turbolator prevents coagulation and consolidation of the main cocking components – asphaltenes. After the furnace the raw material is subjected to visbreaking in the cocking-chamber under the pressure of 4,2 MPa. The product mixture is sent to the fractionating column K-2. Before the column inlet the mixture is cooled by means of cold gas-oil, supplied to the line. Gas-gasoline mixture gets out of the column top and it is cooled in the heat exchanger T-4 to the temperature of 318 K with cold water. In the separator C-2 the gas-product mixture is separated into fat gas and gasoline fraction. A part of gasoline returns into the column for irrigation. The outlet for gas-oil fraction is in the middle part of the column. Then gas-oil is cooled in the water heat exchanger T-2, the part of it returns as recirculat to the inlet of raw material into the column. The visbreaking residue is taken from the bottom of the column.

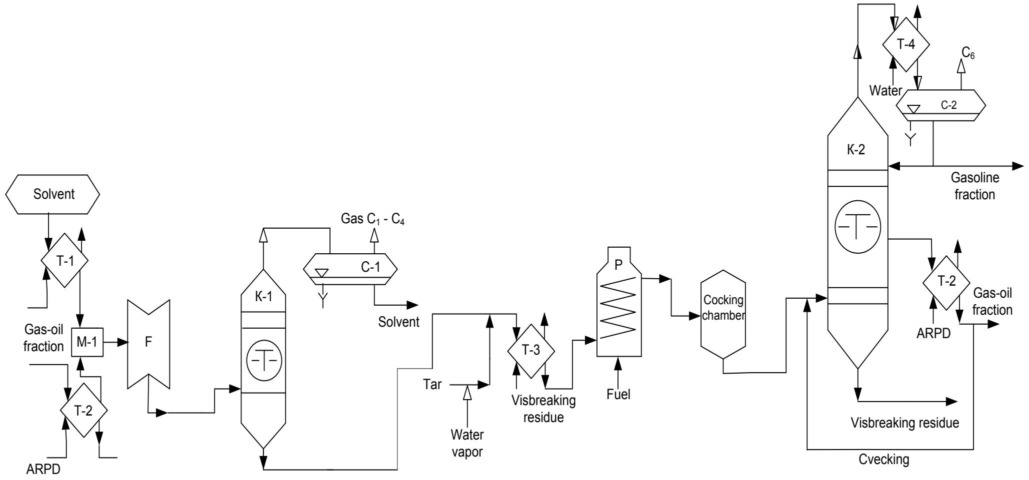

Fig. 11. Joint scheme of tar visbreaking process with addition of organic part of ARPD.
T-1, 2, 3, 4, 5, 6 – heat exchangers; F – vacuum filtration unit; C-1, 2 – separators;
K-1, 2 – rectification columns; P – furnace, M – mixer

The rate of the deposits formation on metal surfaces when the values of the temperature gradient are 20–45 °C with the greatest certainty is described by the exponential kinetic equation, the numerical parameters of which depend on the ratio of the temperatures of oil, the tube and oil pour point.

It is shown that when the deposit layer thickness is 1 mm the temperature gradient decreases, causing reduction of the rate of deposit accumulation by 2,5–3 times compared with the clean tube.

The ability of an additive PPVO made from oils of vegetable origin to the increase of the petroleum stability factor from 0.34 to 0.692 has been demonstrated.

The optimal concentration of PPVO was 0.09 % v/v.

The stabilizing action mechanism of the additive, which consists in the adsorption of theadditive’s polar parts on the paraffin surface with the simultaneous formation of nonpolar alkyl chains, which are guided in the dispersion medium and thus create repulsion forces between the aggregates, is established.

Analysis of IR spectra of experimental samples showed that the use of plant additives and industrial additives and their effects are not accompanied by chemical interaction with the oil dispersed medium.

It was developed the basis of the process of tar visbreaking with asphalt-resin-paraffin deposits, which are partly waste product, into the fuel fractions.

A laboratory-scale plant for the study of the processes of thermal decomposition of heavy oil residues was made.

Optimal conditions of visbreaking of blended raw materials, with fuel fractions and boiler fuel as the product, were determined.

A basic technological scheme of industrial plant of tar visbreaking with addition of 20 % wt. asphalt-resin-paraffin deposits was proposed.

РЕФЕРАТ

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ПРОБЛЕМИ ФОРМУВАННЯ АСФАЛЬТО-СМОЛО-ПАРАФІНОВИХ ВІДКЛАДЕНЬ. ЗАПОБІГАННЯ ТА УТИЛІЗАЦІЯ

Утворення і накопичення асфальто-смоло-парафінових відкладень (АСПВ) призводить до зменшення пропускної здатності трубопроводів, скорочує корисну ємність резервуарів, знижує ефективність роботи теплообмінної апаратури.

Актуальним завданням є вивчення процесу утворення АСПВ для подальшої розробки методів зниження їх кількості та шляхів переробки органічної частини АСПВ.

Об'єкт дослідження – нафта, присадки різних типів, гудрон та відклади донного накопичення резервуару зберігання нафти.

Мета роботи – встановлення кінетичних параметрів процесу формування АСПВ залежно від температури середовища і її хімічного складу, вивчення впливу присадок на дисперсні характеристики нафти, розробка ефективної технології вісбрекінгу із залученням до сировини АСПВ.

Ключові слова: асфальто-смоло-парафінові відклади, кінетика, присадка, вісбрекінг, утилізація.

РЕФЕРАТ

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ПРОБЛЕМЫ ФОРМИРОВАНИЯ АСФАЛЬТО-СМОЛО-ПАРАФИНОВЫХ ОТЛОЖЕНИЙ. ПРЕДОТВРАЩЕНИЕ И УТИЛИЗАЦИЯ

Образование и накопление асфальто-смоло-парафиновых отложений (АСПО) приводит к уменьшению пропускной способности трубопроводов, сокращает полезную емкость резервуаров, снижает эффективность работы теплообменной аппаратуры.

Актуальной задачей является изучение процесса образования АСПО для дальнейшей разработки методов снижения их количества и путей переработки органической части АСПО.

Объекты исследования – нефть, присадки различных типов, гудрон и отложения донного накопления резервуара хранения нефти.

Цель работы – установление кинетических параметров процесса формирования АСПО в зависимости от температуры среды и ее химического состава, изучение влияния присадок на дисперсные характеристики нефти, разработка эффективной технологии висбрекинга с привлечением к сырью АСПО.

Ключевые слова: асфальто-смоло-парафиновые отложения, кинетика, присадка, висбрекинг, утилизация.

ABSTRACT

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THE PROBLEMS OF FORMATION OF ASPHALT-RESIN-PARAFFIN DEPOSITS. PREVENTION AND UTILIZATION

The formation and accumulation of asphalt-resin-paraffin deposits (ARPD) leads to pipelines capacity’s reduction, reduces the useful capacity of tanks, reduces the heat exchange equipment efficiency.

The actual task is to study the process of ARPD formation for further development of methods for reducing their quantity and ways of processing the organic part of ARPD.

The objects of the study are oil, additives of various types, tar and bottom accumulation deposits of the oil storage tank.

The purpose of this work is to determine the kinetic parameters of the ARPD formation process depending on the medium temperature and its chemical composition, to study the additives effect on oil’s disperse characteristics, to develop effective visbreaking technology using ARPD as a part of raw material.

Key words: asphalt-resin-paraffin deposits, kinetics, additive, visbreaking, utilization.

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1.2 THE BIOMASS USE TO OBTAIN HIGH-PURITY CARBONACEOUS MATERIALS

Lina Kieush[1], Serhii Fedorov[1], Andrii Koveria[2], Artem Sybyr[1]

Among the renewable sources, biomass is a promising resource since it is abundant and is the neutral nature of carbon. The term of “biomass” embraces the biodegradable component of products, wastes and residues from agricultural sources (including vegetable substances and animal substances), forestry and the products of related industries, including fish and aquaculture, as well as biodegrading fractions of wastes, including industrial and municipal wastes of biological origin [1].

The biomass resource can be considered as an organic substance, in which the energy of sunlight is stored in chemical bonds. When the bonds between the elements adjacent to carbon, namely, hydrogen and oxygen molecules are broken, for instance, via combustion, these substances release their stored chemical energy. With regard to the European Biomass Association, AEBIOM (currently Europe Bioenergy[1]), bioenergy will show stable growth rates by 2020 (Fig. 1). According to the forecasts, the consumption of biomass for heating will increase to 90 ktoe. It is expected that receiving heat for heating will remain the leading issue on bioenergy market. Moreover, the usage of biomass will grow to about 20 ktoe in the industry of electricity generation and 29 ktoe for biofuels for transport.

The main goal of Bioenergy Europe is to develop a sustainable bioenergy market based on fair business conditions. Bioenergy Europe is a non-profit international organisation founded in Brussels in 1990, which brings together about 40 associations and 90 companies, as well as academic and research institutes from all over Europe. Bioenergy Europe is the main organisation, which also includes the European Pellet Council (EPC), the European Industry of Pellet Suppliers (EIPS) and the International Biomass Torrefaction Council (IBTC).

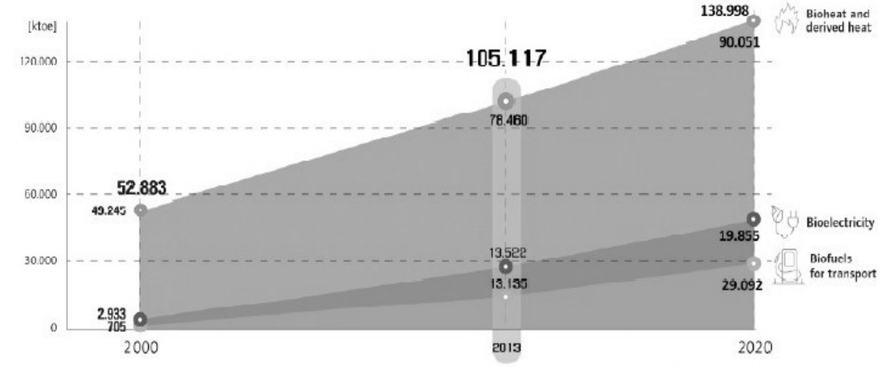

Fig. 1. Biomass Consumption for Bioenergy [5]

It is worth noting that from all European countries only the United Kingdom has adopted the most stringent requirements for the reduction of greenhouse gas emissions within governmental projects which employ solid and gaseous biofuels [4].

Solid biomass and biogas [6] requirements have been expanded and are mainly based on sustainability criteria for biofuels and biofuels liquids.

Thus, the biofuels shall not be made from the raw materials obtained from land with high carbon stock:

– wetlands, namely the lands that are permanently or during a significant part of the year covered or saturated with water;

– lands covering more than one hectare with trees above five meter high and a forest cover of more than 30 % or trees capable of reaching these thresholds in situ;

– lands covering more than one hectare with trees above five meters and a forest cover from 10 % to 30 % or trees capable of reaching these threshold areas in situ.

Further, there are several restrictions, for instance, no biofuels allowed to be made from the biomass which raw materials have been harvested from the lands as follows:

– peat lands used to be in January 2008, unless it is proven that the cultivation and collection of the dedicated raw material do not involve drainage of previously undiluted soils;

– the lands of the countries with national and/or subnational laws applicable in the harvesting area as well as the areas under monitoring and surveillance systems that ensure the observance of certain conditions: 1) harvesting should be carried out in accordance with the terms of the harvest permit within the limits of the officially certain boundaries; 2) there is a reforestation of areas where biomass collection takes place; 3) areas of high conservation value, including wetlands and peatlands; 4) the impact of the forest operation on the quality of the soil and biodiversity is minimized, and the harvest does not exceed the long-term production capacity of the forest.

The agricultural raw material has to be obtained in accordance with the requirements and standards with regard to the provisions of (EC) 73/2009 on the establishment of common rules for direct support of the farmers under the common agricultural policy and the establishment of certain support schemes for farmers and in accordance with the minimum requirements for good agricultural and environmental conditions [1].

Additionally, biofuels and biofuels liquids should not have been obtained from the raw materials derived from lands that are characterised by biodiversity, namely lands that have at least one of the following statuses:

- primary forests and others covered with forest vegetation of the earth, namely forests and other wooded local breeds where there are no clearly visible signs of human activity, and ecological processes are not significantly violated;
- designated areas (by law or by the competent authorities for the protection of nature, or for the protection of rare, extinct, endangered ecosystems, or species recognised by international agreements or included in the lists drawn up by intergovernmental organisations or by the International Union for Conservation of Nature);
- biodiversity grassing, that is natural, namely pasture, which would remain grassing in the absence of human intervention and maintain a natural species composition, ecological characteristics and processes; or unnatural, namely pasture that ceases to be pastures in the absence of human intervention and which are rich in species and are not degraded.

Cheaper and more environmentally friendly or even harmless as compared with non-renewable carbon, biomass is a real alternative to fossil fuels in the production of high-carbon materials. Thus, biomass is readily available raw materials with a low content of mineral components and sulphur. The significant advantage of biomass is its multivariability, both in terms of transformation technologies and end-use methods.

Biomass can be applied in various processes without complex preliminary technological operations. The application of biomass does not cause an increase in the CO_2 balance in the atmosphere during combustion; moreover, when biomass and its products are used in production instead of fossil fuels, there is a negative CO_2 balance for the life cycle of the final product. As a good instance can serve metallurgical final products contained biomass derived carbon, provide negative CO_2 impact.

By nowadays, the technologies to utilize biomass with the objective to obtain motor fuels, fuels for chemical industry and reducing agents for metallurgy have already been developed and they are currently being improved.

Biomass has been and remains to be of a great scientific interest as it is a raw material for the production of high-purity carbonaceous materials, which are widely used for manufacturing modern power sources, carbon-carbon products, products with special thermal, physical, physical and chemical, and sorption properties, etc. In their turn, high-purity carbonaceous materials can be obtained, mainly, by artificial ways as a result of thermal action on carbon-containing raw materials.

The purpose of the current publication is to consider the particularities of the processes that allow obtaining high-purity carbonaceous materials from the biomass, as well as the properties of the obtained materials.

Previous studies [7] of different types of biomass (brushwood, coniferous wood, sunflower husks, walnut shell, straw, corn stalks) allow the conclusion that the most promising raw material for obtaining high-purity carbonaceous materials is the walnut shell.

The main criteria acting in favour of this raw material is that after pyrolysis it shows relatively low residual ash content (3.7 %), almost complete absence of sulphur, the relatively high content of carbon and good mechanical properties that ensure the material's resistance to abrasion during fluidization.

Further, the original properties of the walnut shell are characterized by the following range of particle sizes: lengths of 1.9–29.4 mm, widths of 1.2–27.5 mm, and thicknesses of 0.5–2.8 mm; the surface area varies in the range of 3.4–1000 mm^2 while bulk density is 392.2–430.4 kg/m^3.

After conventional pyrolysis conducted at the different temperatures, the properties of the walnut shell have been studied again with the focus on the features of the oxidative pyrolysis process as the first stage of the two-stage technology for obtaining high-purity carbonaceous materials.

Biomass Pyrolysis. In order to assess whether the walnut shells are acceptable as carbonaceous raw materials, have been conducted the ultimate analyses for the original walnut shells and their residues after pyrolysis at the temperatures ranged 300 °C–1000 °C. These studies have shown that the unaffected raw walnut shells were characterized by the carbon content of 56.4 % and a relatively high hydrogen content of 6.5 % (refer to the Table1). The content of total sulphur was 0.2 %. After pyrolysis, the carbon content increased significantly and reached 93.20 % at the temperature of 1000 °C (Fig. 2). In its turn, the hydrogen content decreased to 0.63 %. Moreover, the pyrolysis effected the walnut shells and changed the content of nitrogen: for untreated residues it was 0.4 % and after pyrolysis at the temperature of 1000 °C it became 0.29 % while any sulphur compounds were not detected.

Table 1

Ultimate Analysis of the Walnut Shells (Original State and after Pyrolysis)

Pyrolysis Final Temperature, °C	H^d, %	C^d, %	H^{daf}, %	C^{daf}, %	S^d, %	N^d, %
Original State	6.5	56.4	6.52	56.57	0.2	0.4
300	4.46	75.38	4.55	76.81	not available	0.33
400	3.92	79.48	4.00	81.12	not available	0.39
500	2.93	81.57	3.01	83.91	not available	0.52
600	2.87	88.74	2.97	92.09	not available	0.35
700	1.86	89.74	1.90	91.93	not available	0.31
800	1.08	91.86	1.11	94.49	not available	0.28
900	0.98	92.96	1.01	94.81	not available	0.28
1000	0.63	93.20	0.65	96.12	not available	0.29

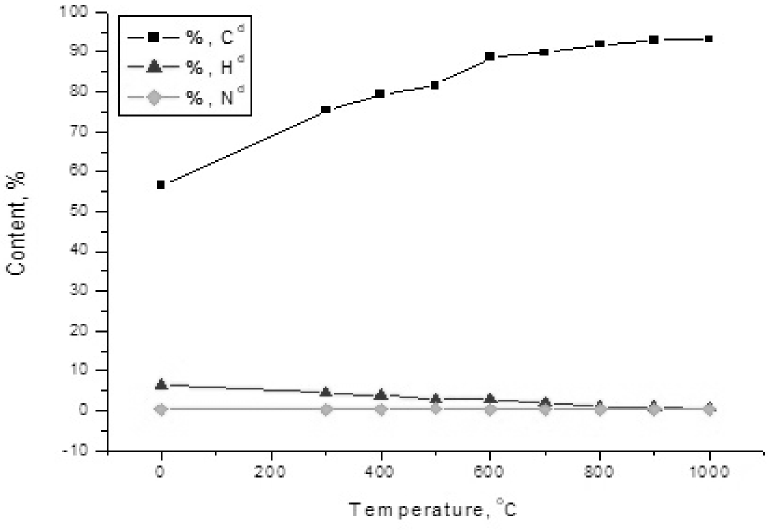

Fig. 2. Dependence of the Walnut Shell Composition in the Dry State (Carbon Content, Hydrogen Content and Nitrogen Content) on the Pyrolysis Final Temperature

With the purpose of the effective usage of pyrolysis products, it is also necessary to determine their technical properties, viz. moisture, ash content, volatile matter release, fixed carbon, and the chemical composition of the mineral part. The mineral components can play an important role in the processing of pyrolysed biomass.

The parameters of the proximate analysis of the solid residue walnut shell after pyrolysis are presented in the Table 2. It is worth noting that the ash content of the residues showed the dependence not only on the original amount of mineral components in the walnut shells, but also on the conditions of the obtained residue pushing and quenching. Due to the high reactivity of the hot-red residue, when it was pushed, there were cases of a slight ignition of the organic part and, as a result, an increase in the concentration of mineral components in the residue.

The results of the proximate analysis allow us to reveal the dependence of the changes in the volatile matter release and in the fixed carbon on the pyrolysis temperature (Fig. 3).

Table 2

Proximate Analysis of the Walnut Shells (Original State and after Pyrolysis)

Pyrolysis Final Temperature, °C	W^a, %	A^a, %	A^d, %	V^a, %	V^d, %	V^{daf}, %	FC^d, %
Original State	7.2	0.28	0.3	70.4	75.86	76.1	20.53
300	2.21	1.82	1.86	36.66	37.49	38.2	58.0
400	3.25	1.95	2.02	26.27	27.15	27.71	66.3
500	2.64	2.72	2.79	17.51	17.98	18.5	75.09
600	1.62	3.58	3.64	11.07	11.25	11.68	82.37
700	1.4	2.35	2.38	7.83	7.94	8.14	87.18
800	1.55	2.74	2.78	6.74	6.15	7.04	87.59
900	1.59	1.92	1.95	6.33	6.43	6.56	88.73
1000	1.76	2.98	3.03	5.98	6.09	6.28	87.71

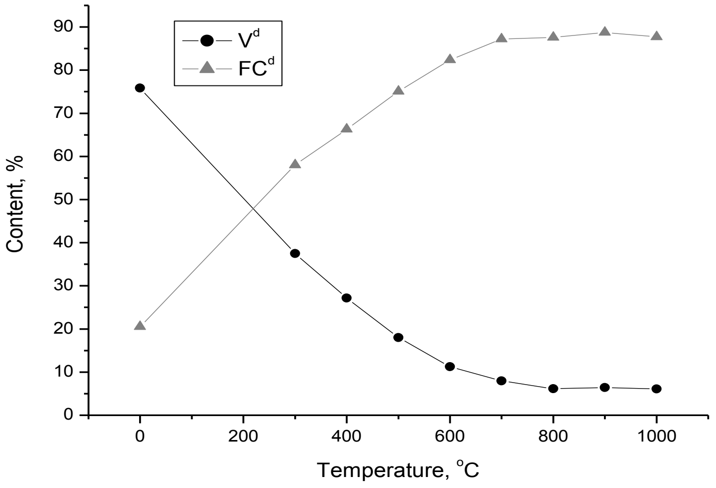

Fig. 3. Dependence of the Change in the Volatile Matter Release and in the Fixed Carbon on the Pyrolysis Temperature

Apparently, when the temperature reaches 700 °C, the value of the fixed carbon stabilises. This is explained primarily by to the stabilisation in volatile matter release when this temperature is reached. At the temperatures of 800–1000 °C, the volatile matter remains almost at the same level. Therefore, it brings the conclusion that when one applies the pyrolysis of the biomass as a preliminary stage of raw materials preparation for the further production of high-purity carbonaceous materials, the optimum final temperature of pyrolysis should be determined in order to reduce processing costs.

Further, the chemical composition of the walnut shells in the original state and their residues after pyrolysis at the temperature of 1000 ^{o}C have been carried out to supplement the dedicated characteristics. Thus, in Fig. 4 and in Fig. 5, there have been showed the spectra while Table 1 shows the quantitative composition of its certain elements.

The chemical composition of the studied samples was detected by X-ray fluorescence analysis using the EXPERT 3L precision analyser with the following features: the detection limit of the elements for 100s (from 12Mg to 92U) is ≤0.05 %; the detector (SDD) is with a nominal statistical loading of the spectroscopic tract 52000 1/s; the resolution of the detector (for KαMn) at a nominal loading does not exceed 149 eV.

Table 3 evidences that the highest content in a walnut shell is the following chemical elements of K, Ca, Si and Fe.

Table 3

. The Chemical Composition of the Walnut Shells Inorganic Part in the Original State and after Pyrolysis at 1000 °C.

Sample	Chemical Composition												
	O	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Mn	Fe	Zn
Original	32.74	1.74	1.99	4.99	4.34	1.83	3.42	21.18	18.55	0.70	0.30	7.62	0.33
After Pyrolysis	27.95	1.66	2.11	2.14	0.75	0.43	-	26.54	35.58	0.32	0.17	2.14	-

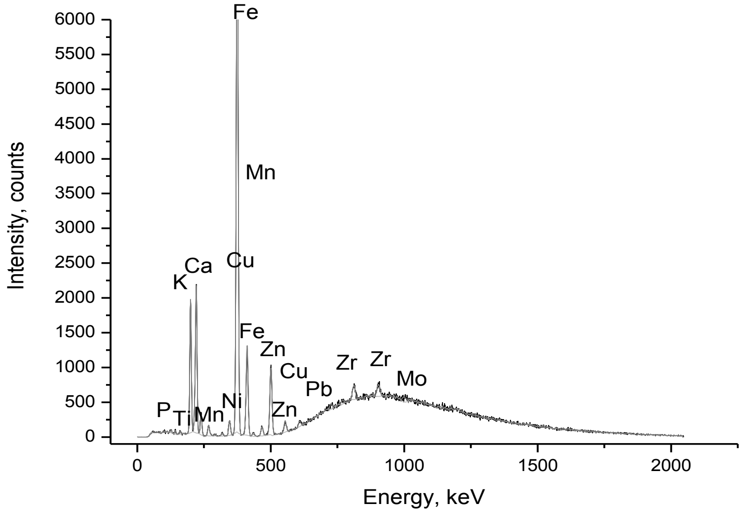

Fig. 4. XRF Spectra of the Walnut Shells in the Original State

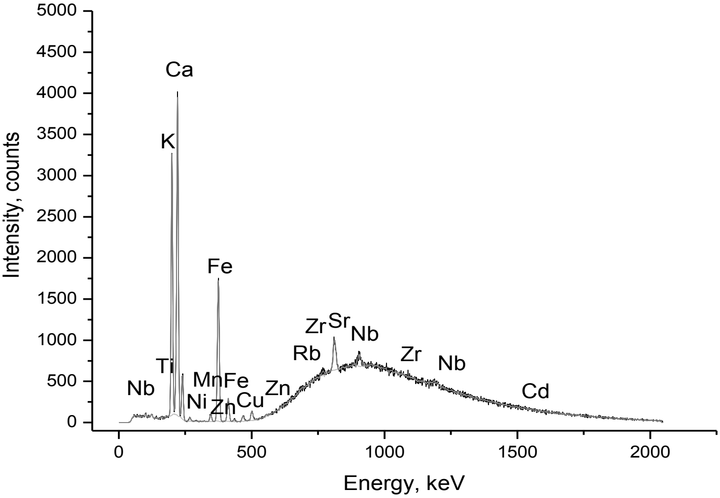

Fig. 5. XRF Spectra of the Walnut Shells after Pyrolysis at the Temperature of 1000 °C

As a result of pyrolysis influence, the increase in the contents of K, Ca, Al can be observed while the contents of Fe, P, Si and S are significantly reduced. Within walnut shell residues subjected to pyrolysis, Cl and Zn have not been detected though these elements were present in the original material.

Nanomaterials Obtaining from Biomass. One of the possible ways for biomass utilization is to prepare carbon nanomaterials from it. For this purposes, have been experimented with the original hazelnut shells to determine the presence of carbon nanoparticles in them. With TEM 125K, equipped with a digital output system for images SEO-SCAN, the images presented in Fig. 6 have been received. The presence of carbon nanoparticles has been determined, their sizes range from 15 nm to 70 nm.

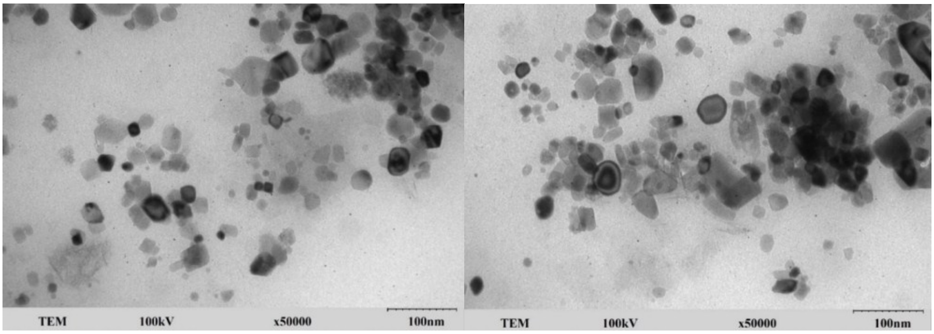

Fig. 6. Carbon Nanomaterials from Hazelnut Shells

The Oxidative Pyrolysis and the Graphitization of the Biomass. The earlier researching results allowed the development and improvement of the multi-stage technology[2], it enables not

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[2] The technology has been developed at the Department of Industrial Thermal Engineering (National Metallurgical Academy of Ukraine, NMAU) together with the engineers from Thermal & Material Engineering Center (Dnipro, Ukraine).

only obtaining a pure product with the carbon content of C > 99.95 %, but also its partial graphitizing [8, 9]. The technology is applicable with walnut shells.

The first stage of this technology involves oxidative pyrolysis of the biomass with the energy consumed from gaseous products. As a result, a semi-finished product has been formed like a coke residue. The second stage is its high-temperature treatment in an electro-thermal fluidized bed at the temperatures up to 3000 ^{o}C.

According to this technology, the process of oxidative pyrolysis has been carried out in the closed layer of the filtration combustion condition. The process scheme is shown in Fig. 7, the source of the heat is the partial oxidation reaction of the pyrolysis gases [10]. The released heat is used for drying, heating and the pyrolysis occurring below the underlying biomass layers. Air acts as the oxidant.

The biomass layer is ignited from the side opposite to the air supply. The resulting pyrolysis gases contain CO, CO_2, H_2, CH_4, N_2 and a significant amount of tar, these substances react with the oxygen of the air to form a combustion zone that is shifted towards the airflow. This effect is termed as “counter flow heat wave”.

The displacement of the temperature and concentration profiles occurs isomorphically. The reverse motion of the combustion zone is possible due to a sufficiently high thermal conductivity of the layer. The red-hot coke residue is formed behind the combustion zone. the layer due to the action of high temperatures in non-condensable gases (CO, CO_2, H_2, etc.).

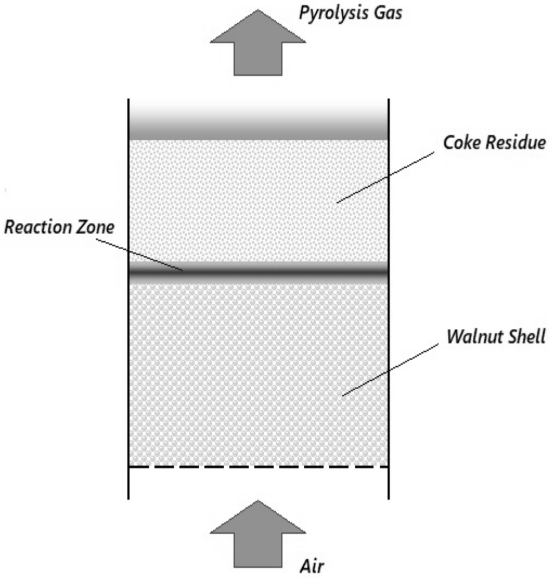

Fig. 7. The Scheme of the Oxidative Pyrolysis Process

Pyrolysis gases and products of their partial oxidation, moving in the same direction as the airflow, pass through the layer of the red-hot coke residue. The tar contained in pyrolysis gases decomposes as the gas moves through

This above introduced scheme allows the process to be conducted without any external source of heat, and also decreasing in the tar content within the pyrolysis gases. Additionally, by regulating the airflow it is possible to change the amount of heat released from the partial oxidation of pyrolysis gases and it is necessary for drying the biomass. This allows application of the biomass with considerable humidity.

The pilot reactor developed for oxidation pyrolysis possesses the capacity of about 100 kW per the original biomass and consists as follows: the reactor, the burner, the TG-0.25 blower, air supply piping system, and the dedicated instruments. The reactor is a vertical shaft-type apparatus with 0.6 m of a diameter and the height of 1 m. The fuel layer was placed on an air supply steel grid with a cell diameter of 10 mm. The sheets of fiber glass shielded with heat-resistant aluminum foil are applied as the thermal insulating means.

The experiments conducted with the purpose to study the process of oxidative pyrolysis have allow defining the optimal range of air flow as 6.5–13.1 m^3/h, which corresponds to a specific load on the firebed surface of 27.4–55.2 m^3/m^{2}h. The further studies carried out with the observance of the above-mentioned range of the airflow are capable of determining the parameters of different technological conditions of oxidative pyrolysis (Table 4). The qualitative data of the process are the shape of the combustion zone and the uniformity of its movement along the reactor volume. The released gaseous substances contain CO_2, H_2, H_2O, CH_4, CO, O_2, N_2 and tar, which by reacting with the oxygen of the air provide the temperature in the combustion zone of 500–750 °C. This temperature is determined by the processes of combustion and heat exchange between the biomass and the gases, which, in turn, depend on the intensity of the cold air intake and the removal of combustion products from the combustion zone.

Table 4

The Results of the Biomass Oxidative Pyrolysis in the Closed Layer

Parameters	Varieties of Technological Conditions		
	No 1	No 2	No 3
Specific Airflow Rate in the Pyrolysis, m^3/h	6.5	9.5	13.1
Specific Gas Flow Rate per Square Meter, m^3/m^{2}h	27.4	40.0	55.2
Process Time, min	230	180	150
The Average Temperature in the Zone, ºC	585	670	741
The Filtration Velocity, m/s	0.105	0.164	0.241
The Average Velocity of the Counter Flow Heat Wave, cm/h	11.4	15.2	18.2
The Sedimentation Velocity of the Fuel Layer, cm/h	6.52	9.67	12.40
The Average Temperature of the Pyrolysis Gases, ºC	350	390	425
Content of the Pyrolysis Gases			
CO	5.3	5.6	6.5
H_2	8.7	9.5	10.1
CH_4	7.2	6.3	6.2
CO_2	13.8	12.7	11
N_2	56.5	57.3	57.6
O_2	8.5	8.6	8.6
LCV, kJ/m^3	4185.0	3987.0	4129.4
Carbon Content in the Solid Residue, %	79.3	82.2	86.9

During the pyrolysis of the walnut shell, the deposition of the biomass layer has been registered under all technological conditions. At the same time, as the airflow rate increased, the average process temperature for the walnut shells increased as well from 585 °C to 740 °C, and the velocity of the thermal wave was changing within the range of 11.4 cm/h to 18.2 cm/h.

The repeatability of the process character allows the assumption that the process can be implemented on the industrial scale. The gas forming during the pyrolysis can be used for heat generation or for internal combustion engines to generate electricity.

The second stage of the technology is to produce a high-purity carbonaceous material. Preliminary, a number of technologies have been studied for making conclusions concerning the new technology, the materials analyzed embraced the chemical refining, heat treatment in layered electric furnaces of continuous action (calcination unite) and those of periodic action (Acheson furnace).

It has been established that the most reasonable is the treatment of the solid residue of the walnut shell in a high-temperature electro-thermal fluidized bed. The working space of the furnace has an expansion and is divided into two cylindrical parts: the lower one is the zone of the fluidized bed and the upper one is a super layer (separation) zone of the larger diameter. The diameters of these zones provide the ratio of the gas velocity in the lower part and the gas velocity in the upper part as 2:3. The advantage of the technology is in the continuous condition of operation; the material is loaded and unloaded with screw feeders.

The release of the finished product is provided from the bottom of the furnace to the cooling chamber, which is a heat exchanger in the form of four vertical stainless steel pipes lined inside with the graphite and allowing lowering the temperature of the material from 2500 °C to 1100 °C. The further cooling down to 200 °C is carried out in a water-cooled screw feeder.

The summary data of analysis on the existing technologies of graphitisation and refining are reported in Table 5. With regard to the characteristics of the raw materials and the requirements for the ash content in the battery graphite, the electro-thermal fluidized bed furnaces are concluded to be the main competitive method of processing carbon materials with respect to chemical cleaning. In the course of the on-line process implementation, this type of furnaces has better energy indices by 40–60 % than the Acheson furnaces, while at the same time they allow the recovery of thermal waste energy. Moreover, it is worth noting that due to the limited results of practical implementation, technologically these solutions leave issues to be studied, which retards the usage this method in industries.

Table 5

Technological Parameters of the Principle Graphite Refining Techniques

Technology	Content of C_g, %	Fractional Composition of Raw Materials, μm	Process Temperature	Energy Intensity, kW·h/kg
Chemical Refining	> 99.98	< 1000 μm	up to 900 °C	0.2–0.6
Electro-Calcinators	to 97.5	6–25 mm	up to 2500 °C	1.5–2.0
Acheson Furnace	> 99.97	no limits	up to 3000 °C	4.5–9.0
Chlorothermic Methods	> 99.9995	no limits	up to 2300 °C	3.5–7.0
Electro-Thermal Fluidized Bed Furnace	> 99.95	150–1250	up to 3000 °C	2.0–3.0

Taking into account the analysis carried out in the laboratory of the Thermal & Material Engineering Centre, several laboratory facilities related to the electro-thermal fluidized bed technology have been developed:

- high-temperature furnace (up to 3000 °C) for thermal cleaning of the carbonaceous material under conditions simulating the emulsion phase of the fluidized bed (Fig. 8a);
- low-temperature electro-thermal fluidized bed furnace (up to 1000 °C) for hydrodynamic and electrical regimes of the fluidized bed (Fig. 8b).


(*a*) (*b*)

Fig. 8. Electro-Thermal Furnaces by T&MEC Design: (*a*) fixed bed thermal treatment furnace (*t* = 3000 °C); (*b*) the fluidized bed furnace for studying hydrodynamic and electrical parameters

The carried out studies on the usage the above-mention technology allow determining that the carbon residue of the walnut shell after oxidative pyrolysis is a conductive material, which can be applied in electro-thermal heating.

Heat treatment of the residue at 3000 °C enabled us to obtain a high-purity carbonaceous material with impurities content kept within 0.01–0.05 %.

In the context of the increasing cost of the conventional carbon reducing agents and with regard to the impact of the combustible fossil fuels on the greenhouse gases emissions, the utilization of renewable CO_2-neutral substances, such as plant biomass has to be a solution for the issues of obtaining carbon materials of the required quality. Biomass has several advantages when applied for preparing high-purity carbonaceous materials, they are, for instance, availability, relative cheapness, environmental friendliness, low content of mineral components and sulphur. The significant advantage of biomass is its multivariability, both in terms of transformation technologies and end-use techniques. Biomass can be used in various processes without complex preliminary technological operations.

The elemental composition of the organic mass of the walnut shell after pyrolysis from 300 °C to 1000 °C has been analysed with an interval of 100 C. After pyrolysis conducted at the temperature up to 1000 °C, the carbon content reached 93.20 %. In its turn, the hydrogen content was 0.63 % and the nitrogen content was 0.29 %. The presence of sulphur compounds were not detected at all. The change in the chemical composition of the mineral part of the shell after pyrolysis has been shown in comparison with the original composition. After pyrolysis at 1000 °C, the contents of K, Ca increased and slightly increased Al content in the mineral part of the residue.

Since nanoobjects are high-purity carbonaceous materials, the utilization of biomass for their production seems to be a promising area. The presence of carbon nanoparticles obtained from hazelnut shell has been registered, the size of the particles ranges from 15 nm to 70 nm.

The multi-stage technology for producing high-purity carbonaceous materials (C > 99.95 %) based on biomass utilization has been developed and improved, including the stages of oxidative pyrolysis (700 °C) and heat treatment in an electro-thermal fluidized layer (3000 °C). The analysis on the potential materials has shown that the most suitable for the process is the walnut shell.

The carried out researches at the different intensities of airflow allows determining the parameters of technological conditions for oxidative pyrolysis, and the repeatability of the process permits its implementation on an industrial scale. The resulting pyrolysis gas can be used for heat generation or in internal combustion engines to generate electricity.

The laboratory facilities of the furnaces for oxidative pyrolysis and high-temperature treatment in an electro-thermal fluidized bed have been developed. According to the results of the conducted test runs on the technology, it has been defined that the ash content in the final product does not exceed 0.01–0.05 %.

Acknowledgments

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ВИКОРИСТАННЯ БІОМАСИ З МЕТОЮ ОТРИМАННЯ КАРБОНОВМІСНИХ МАТЕРІАЛІВ ВИСОКОГО СТУПЕНЯ ЧИСТОТИ

Розглянуто основні критерії використання біомаси замість горючих копалин з метою отримання біопалив. Показано переваги біомаси у порівнянні з традиційною непоновлювальною сировиною. Представлено результати досліджень властивостей шкаралупи волоського горіха після класичного піролізу за температур від 300 °C до 1000 °C та зроблено акцент на особливостях процесу окисного піролізу як першої стадії двостадійної технології отримання високочистих вуглецевих матеріалів із біомаси. Встановлено можливість отримання наноматеріалів з біомаси на прикладі шкарлупи ліщинного горіха. Отримані результати дозволяють говорити про можливість реалізації технології виробництва високочистих вуглецевих матеріалів у промислових масштабах.

Ключові слова: біомаса, піроліз, окисний піроліз, графітизація, високочисті вуглецеві матеріали, наноматеріали

РЕФЕРАТ

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ИСПОЛЬЗОВАНИЕ БИОМАССЫ С ЦЕЛЬЮ ПОЛУЧЕНИЯ КАРБОНОСОДЕРЖАЩИХ МАТЕРИАЛОВ ВЫСОКОЙ СТЕПЕНИ ЧИСТОТЫ

Рассмотрены основные критерии использования биомассы вместо горючих ископаемых с целью получения биотоплив. Показаны преимущества биомассы по сравнению с традиционным невозобновляемым сырьем. Представлены результаты исследований свойств скорлупы грецкого ореха после классического пиролиза при температурах от 300 °C до 1000 °C, показаны особенности процесса окислительного пиролиза как первой стадии двухстадийной технологии получения высокочистых углеродных материалов из биомассы, а также установлена возможность получения наноматериалов из биомассы на примере скорлупы лесного ореха. Полученные результаты позволяют говорить о возможности реализации технологии производства высокочистых углеродных материалов в промышленных масштабах.

Ключевые слова: биомасса, пиролиз, окислительный пиролиз, графитизация, высокочистые углеродные материалы, наноматериалы

ABSTRACT

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THE BIOMASS USE TO OBTAIN HIGH-PURITY CARBONACEOUS MATERIALS

The current publication considers the main criteria for biomass utilization instead of combustible fossils for the purpose of obtaining biofuels. The advantages of the biomass in comparison with the traditional non-renewable precursor materials have been shown. The results of the properties of walnut shell studies after conventional pyrolysis at the temperatures from 300 °C to 1000 °C are presented. Additionally, have been highlighted the peculiarities of the oxidative pyrolysis process as the first stage of a two stage technology for the production of high-purity carbonaceous materials from biomass. The possibility of obtaining nanomaterials from the biomass has been established, as instance can serve the hazelnut shell. The obtained results allow implementing the production technology for high-purity carbonaceous materials on an industrial scale.

Key words: biomass, pyrolysis, oxidative pyrolysis, graphitisation, high-purity carbonaceous materials, nanomaterials.

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1.3 METHODS VIRTUALIZATION IN CHEMMOTOLOGY RESEARCHES

Alexandr Moiseev, Alexandr Oreshencov, Nikolay Grishin

The usual purpose of mathematical modelling of technological processes is forecasting course of these processes in various conditions, including not covered by natural experiment. Two basic demands are usually made to similar model – universality and adequacy. Universality allows to use model in a wide range of external conditions, including in structure of models of higher level. Adequacy provides conformity of model to concrete conditions of carrying out of experiment. The specified requirements define typical structure of model. In a basis of last the base model describing process in general is pawned as a skeleton. Adequacy thus is provided during parametrization of model by results of comparison with calibration experiments. It causes the basic requirements to the interface of model – along with the inputs defining conditions of carrying out of numerical experiment, it includes preliminary adjusted calibration parameters. Completeness and consistency of system of these parameters define adequacy of model and are provided during its identification.

Being applied discipline, chemmotology assumes essential domination of experimental methods of the research sold including in the form of qualifying tests of object. At the same time, as it was specified above, construction of base model covering systems or process is carried out within the limits of theoretical, mainly physical and chemical, researches. In turn adequate adjustment of these models is carried out by results of qualifying tests. The main feature of the last is that their basic method is laboratory research of object which basically nothing will differ from maintained [1]. Laboratory installation in these conditions can be considered as physical model of the system covering object. In this sense qualifying tests are a special case of wider concept semi-scale experiment within the limits of which the covering model or its part can be realized as mathematical. In these conditions adequate mathematical model of the system covering object, it is possible to interpret as a certain virtual reality, and numerical experiment in structure of semi-natural – as virtual qualification. Thus the natural experiments spent within the limits of usual qualifying tests, can act as means of identification of created mathematical models [2, 3].

Statement of a question on mathematical modelling any object includes conditionally three stages: *model-algorithm-program* (Fig. 1) [4].

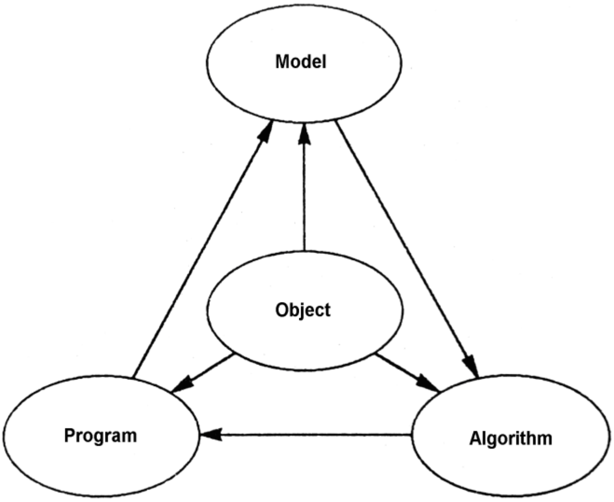


Fig. 1. Scheme of mathematical modeling

At the first stage the «equivalent» of object reflecting in the mathematical form, the major it properties-laws to which it submits, the communications inherent in parts making it, etc. Mathematical model (or its fragments) are researched by theoretical methods that allows to receive the important preliminary knowledge of object is under construction.

The Second stage – development of algorithm for realization of model on a computer. The model is represented in the form of, convenient for application of numerical methods, the sequence of computing and logic operations is defined, which need to be made to find required sizes with the set accuracy. Computing algorithms should not deform the basic properties of model and, hence, initial object to be economic and adapting to features of solved problems and used computers.

At the third stage the programs «translating» model and algorithm on language accessible to a computer are created. Demands of profitability and adaptibility also are made to them. They can be named a «electronic» equivalent of studied object, already suitable for direct test for «experimental installation» – a computer.

Having created a triad «model-algorithm-program», the researcher receives the universal, flexible and inexpensive tool which in the beginning is debugged, tested in «trial» computing experiments in hands. After adequacy of a triad to initial object is certified, with model the various and detailed «experiences», demanded qualitative demanded qualitative and quantitative properties and characteristics of object are spent. Process of modelling is accompanied by improvement and specification, as required, all parts of a triad.

The mathematical model of object is under construction on the basis of its description and can cooperate with the regular software in case of controllability of object. In turn, the mathematical model of covering system is under construction on the basis of its description and can realize the functions which are not sold by physical model. Virtual qualification is carried out during numerical experiment with mathematical models of object and system.

Thus two primary goals are solved: comparative identification of mathematical models in the conditions provided by physical model – laboratory installation; preliminary debugging of the regular software in case of controllability of object.

Example of application of such common approach is modeling internal combustion engine (ICE) displayed in works [5, 6].

First of them is devoted to creation of the simplified mathematical model ICE intended for modelling of influence chemmotology of processes on dynamics of the engine, its efficiency and lubricant ability of used oils. The model allows to spend the numerical experiments reproducing separate stages of bench tests. In the long term, as it is supposed, it will allow to replace carrying out of the same natural experiments by their numerical analogues that will provide economy of time and means.

For identification of model results of qualifying tests on installation IM-1, spent according to GOST 20303 were used. Therefore it is considered, that the virtual engine in structure of model is loaded on the simulator of the asynchronous machine, and losses on friction in the engine are described depending on deterioration cylinder-piston group (CPG) and a degree of its pollution within the limits of Hersey-Stribeck curve. These factors influence factor of friction of pair the piston – the cylinder, and also on size of a backlash between the piston and a wall of the cylinder and, hence, on size of the mixed friction.

The simplified model is based on the ratio of balance and engine load, loaded onto asynchronous machine in generating mode. In the normalized form the equation of balance (1) looks like:

$$T\frac{du}{td} = \pi\sqrt{u} - \pi_{fr}\sqrt{u} - n_0\left(\sqrt{u} - 1\right)\max(1, \sqrt{u}) \tag{1}$$

where $u = \left(\frac{\omega}{\omega_0}\right)^2$ – normalized a square of frequency; $\pi = \frac{p}{p_0}$ – normalized pressure in the cylinder; $\pi_{fr} = \frac{p_{fr}}{p_0}$ – normalized a pressure of friction; $T = \frac{J\omega_0^2}{2N_0}$ – characteristic time of dispersal, where J – the moment of inertia of a crank; ω_0 – current and nominal cyclic frequency accordingly; p – pressure in the cylinder, Pa; p_{fr} – a pressure of friction, Pa.

The General scheme of the model is shown in Fig. 2. In essence, it is the scheme of realization of the equation solution (1) with an opportunity of a variation of power of the engine and synchronous frequency.

The basic feature of model is that for the description of dynamics of pressure in the cylinder the display diagram of the engine is used. Last represents dependence of pressure in the engine from displacement of the piston on various steps of the engine. To these steps there correspond various ranges of a corner of turn of a crank (a cranked shaft) which is an additional input of the display diagram. In model the display diagram is realized in the form of linear interpolators pressure depending on position of the piston, corresponding various steps of the engine and chosen on size of a corner of turn of a crank. As a rule, the display diagram corresponds to rated power of the engine.

To account for possible nenominalizate used adjustable multiplicative factor g, making sense degrees of opening of a virtual throttle of submission is used. This factor is formed by the simulator of submission which basis is PID a regulator of power.

The rated load n_l of the engine is related to the nominal n_0 ratio $n_l = n_0 max(1, \sqrt{u})(\sqrt{u} - 1)$. In turn, the rated load is formed by the simulator of a dynamic brake which basis is the regulator of synchronous frequency. Normalized power of losses is defined normalized by the moment of frictionπ_{fr}.

The further development of the simplified model was carried out in a direction of perfection of imitation of processes in the engine. In work [6] the multipurpose model of an internal combustion engine uniting submodels of the basic subsystems of the engine. These include: model of the internal mixture formation, defining characteristics of a gas mixture; models of a thermal emission and gas exchange in the cylinder, simulating clock processes in the engine; model of crank mechanism model, connecting processes in the engine with external influences.

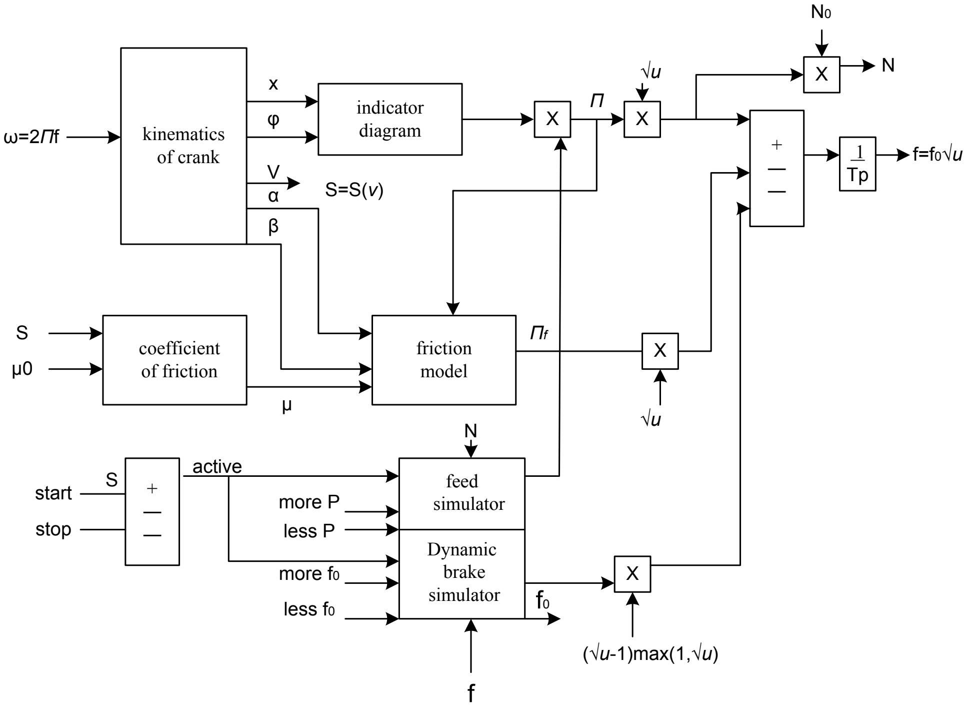
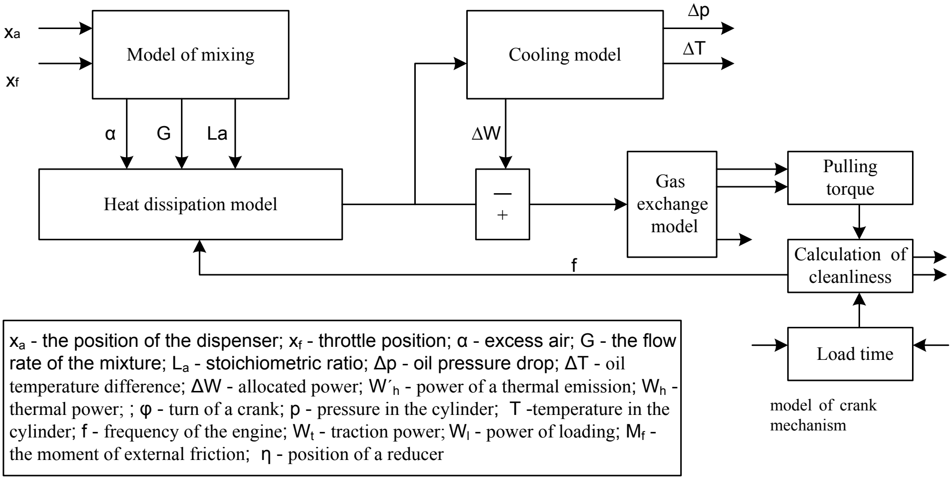


Fig. 2. General control scheme of the engine model

The General scheme of the model is shown on Fig 3. Its inputs are positions of an air throttle, fuel dispenser, and also transfer number of the reducer connecting a running axis with cranked shaft. These inputs naturally interpret controls the engine.

The model also can include the auxiliary submodels intended, in particular, for imitation of structure of an exhaust and cooling of the engine. First of them is based on simplification of system of the kinetic equations of chain process in the quasi-stationary approximation. It allows to simulate dynamics of structure of an exhaust in the form of time dependences of molar fractions its components. The developed technique can be used at forecasting structure of an exhaust for different chain processes with a specified sequence of paired reactions.



x_a - the position of the dispenser; x_f - throttle position; α - excess air; G - the flow rate of the mixture; L_a - stoichiometric ratio; Δp - oil pressure drop; ΔT - oil temperature difference; ΔW - allocated power; W'_h - power of a thermal emission; W_h - thermal power; ; φ - turn of a crank; p - pressure in the cylinder; T -temperature in the cylinder; f - frequency of the engine; W_t - traction power; W_l - power of loading; M_f - the moment of external friction; η - position of a reducer

Fig. 3. Scheme of the multi-function models

The model of cooling is based on the developed design procedure of hydraulic circuits. In this calculation linear regulators are used as numerical nonlinear equations Kirchhoff for balance of charges and pressure differences. The given technique is less labour-consuming, than traditionally used, and применима at квазистационарных changes of parameters of a hydraulic circuit. The engine in this model is interpreted as a heat exchanger.

Simulated dynamics of pressure and temperatures of gas in the cylinder according to phases of gas exchange is displayed on Fig. 4.

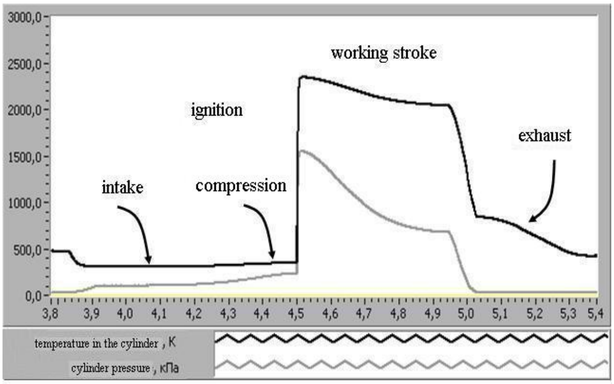


Fig. 4. Cycle without self-ignition

The cycle with spontaneous ignition is presented on Fig. 5. The constructed model was used also for imitation of the basic processes in the engine.

The results of simulation of step loading of the engine are shown in Fig. 6 and 7. Relative loading thus increased with some temporary delay concerning submission.

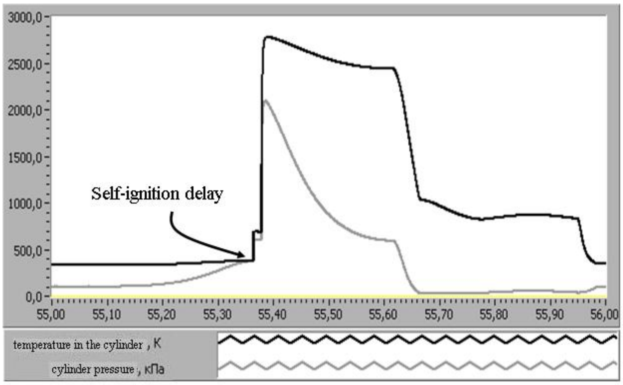


Fig. 5. Self-ignition cycle

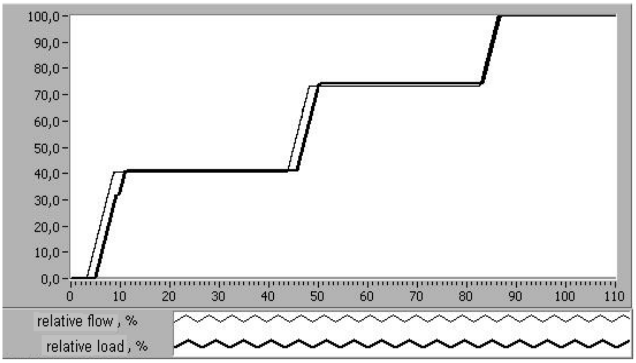


Fig. 6. Stepwise engine loading (feed, load)

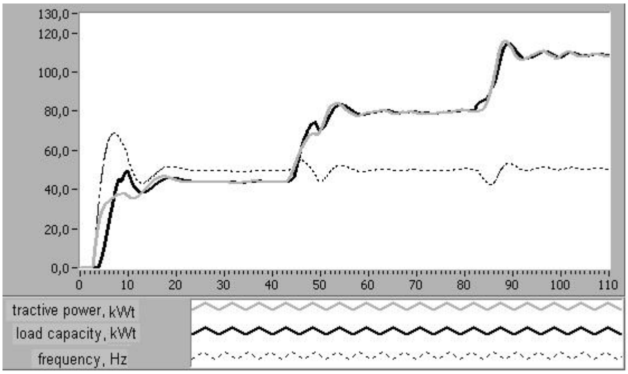


Fig. 7. Stepwise loading of the engine (traction and load power)

During regulation simulated frequency of the engine was stabilized at a nominal level, and traction and loading powers were leveled. Thus, the effect self-regulation of frequency of the engine has been shown at change of loading. Results of compulsory regulation of frequency of the engine are displayed on Fig. 8 and 9.

Installation of regulation was nominal frequency of the engine, and an output – size of relative submission. In an initial condition the size of relative loading was zero. After inclusion of a regulator the size of installation on frequency increased up to nominal frequency. The additional increase in loading led to corresponding increase in submission under action of a regulator. Current frequency thus was stabilized at a nominal level, and traction and loading powers were leveled. The qualitative analysis of simulated dynamics shows, that as a whole the model adequately displays processes in the engine and can be used to study the influence of petroleum products characteristics on the processes in the cylinder.

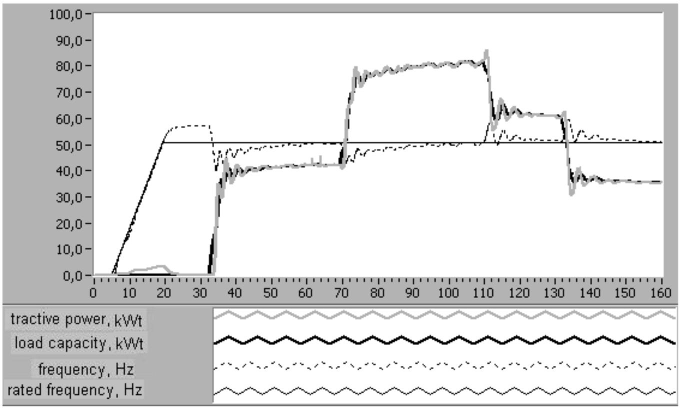


Fig. 8. Frequency control of motor (tractive and load power)

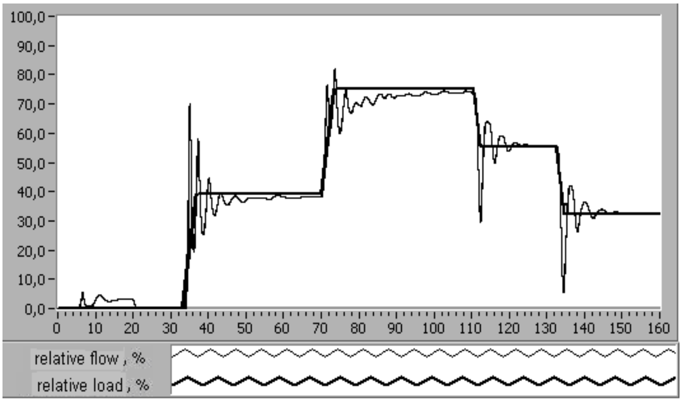


Fig. 9. Engine frequency control (feed, load)

Prominent aspect of application of virtual qualification is extrapolation of laboratory results on regular conditions of operation of researched object. As an example of such extrapolation is the prediction of volumetric wear of the pump plunger head taking into account the anti-wear properties of the lubricating fuel [7–10].

As criterion of similarity between laboratory installation and researched plunger the criterion of volumetric deterioration displayed on Fig. 10 has been chosen. Its physical sense – the relation of an impulse износного a material to an impulse of force of friction.

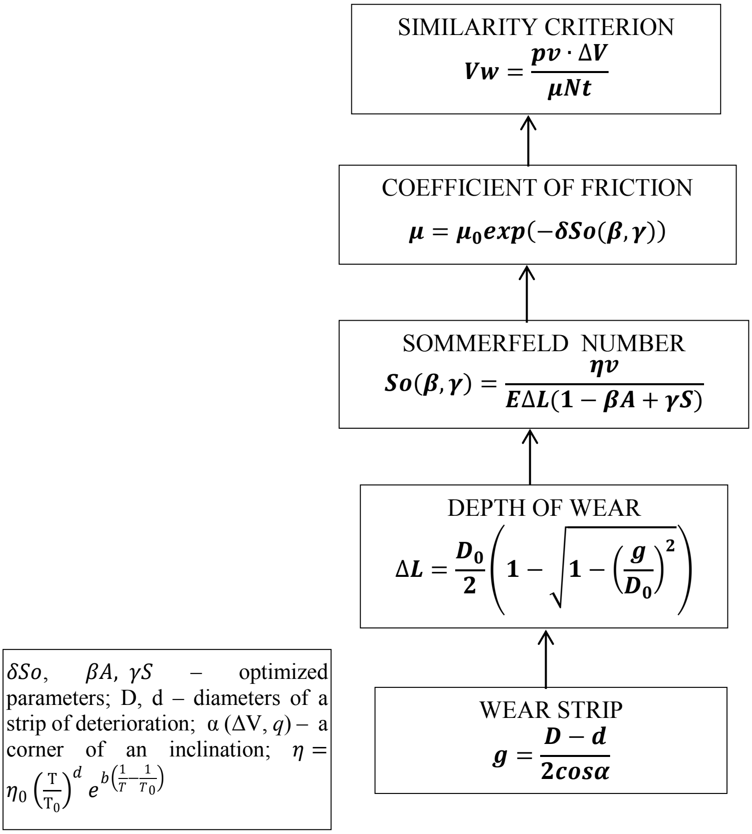


Fig. 10. Criterion of volume of wear

The criterion includes density wear material, speed of sliding and normal pressure in frictional contact, and also the duration of wear. The factor of boundary friction is defined by factor of dry friction and Sommerfeld number. It was assumed that the Sommerfeld number in addition to viscosity, speeds of sliding and hardness depends also from A the greasing environment and percentage of sulfur S in it's.

The size of a backlash in frictional contact was accepted to equal depth of deterioration and was defined by diameter of a spherical measuring element and size of a strip of deterioration. Temperature dependence of viscosity according accordance with the modified Andrade's formula.

The volumetric wear and the wear strip were determined by the maximum and minimum diameters of the wear strip of the measuring element, observable in experiment, and also a corner of an inclination of an axis of this element to a plane of frictional contact. Parameters of model were factor at Sommerfeld number in expression for factor of boundary friction, and also factors at acidity and percentage of sulfur.

The scheme of optimal parameterization of this model is shown on Fig. 11.

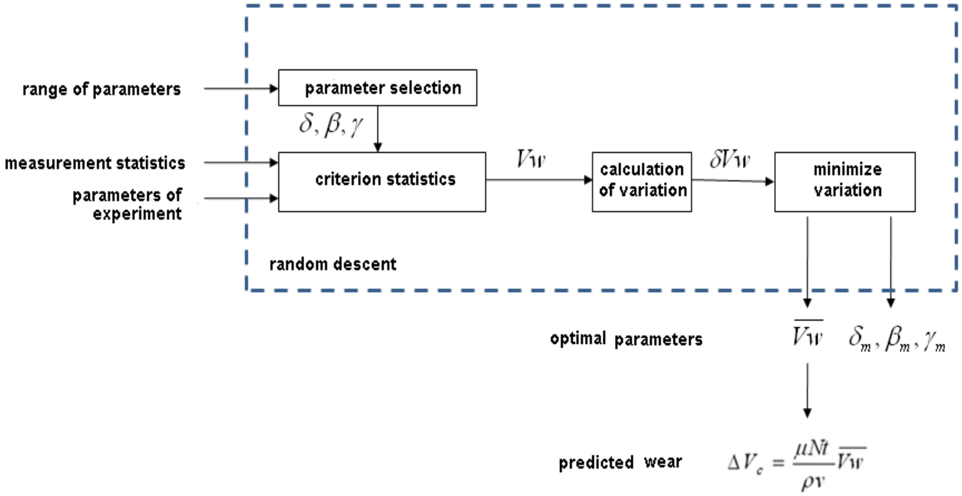


Fig. 11. Optimal parameterization

The first stage of parametrization included formation of statistics of criterion of similarity according to measurements and to the chosen values of parameters. On measurements and the chosen parameters the criterion of volumetric deterioration paid off. Thus the received statistics was used for calculation of a variation of criterion δVw for the chosen values of parameters. Optimum parameters got out a method of casual descent of a condition of a minimality of the specified variation. The size of the average criterion of similarity $\overline{Vw}$ on which predicted wear.

By parameterized model forecasting deterioration on the basis of equality of predicted and settlement deterioration was carried out. This equality was interpreted as the equation concerning depth and strips of deterioration. It was solved by minimization of the module of a mismatch between settlement and predicted deterioration for various duration according to Fig. 12.

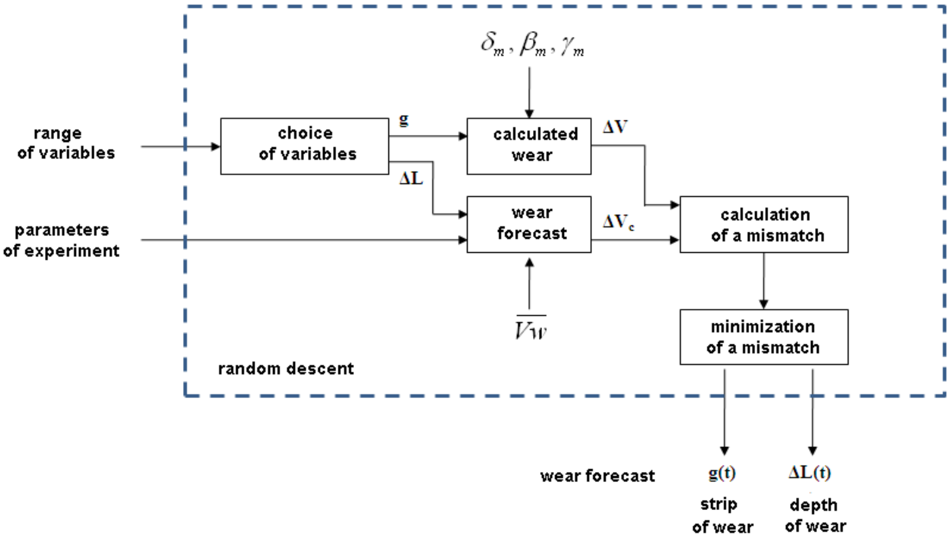


Fig. 12. Wear prediction

Result of this minimization which are carried out by a method of casual descent, temporary dependences of depth and the strips of deterioration interpreted as forecasts of deterioration are. Thus, the developed model of deterioration can be used for formation of qualifying norms on the basis of operational restrictions on the depth wear, corresponding specified duration of last.

Carrying out of tests is preceded with a preliminary choice of their extreme conditions. Parametrization criteria model models by results of qualifying tests in the given conditions allows to lead forecasting of frictional deterioration which results can be interpreted as the guaranteed norms of deterioration.

Traditional qualifying tests are interpreted as a special case semi-scale experiment in which laboratory installation plays a role of physical model of the system including researched object. Virtualization represents transition from physical to mathematical models of system and object and supposes virtual qualification, that is realization of qualifying tests in the form of numerical experiment. Obvious advantage of virtual qualification is restriction of quantity of the natural experiments used only for calibration of mathematical models, and, hence, reduction in expenses for their carrying out.

Virtualization allows to carry out extrapolation of results of qualifying tests for regular conditions of operation. Efficiency virtualization is shown on examples of optimization of mathematical models, perfection of qualifying experiments and forecasting of their results.

Simplified model internal combustion engine is intended for modelling influence chemmotology and tribological factors on dynamics of the engine and its efficiency. It was based on a ratio for balance of power of the engine and its loading created by asynchronous machine in a generating mode. Its feature is that for imitation of dynamics of pressure in the cylinder the display diagram of the engine was used. The account of friction within the limits of model was based on approximation of Hersey-Stribeck curve and its use for calculation of factor of the mixed friction depending on Sommerfeld number. Input in structure of this number of the factors considering deterioration and pollution of pair the piston – the cylinder, has allowed to carry out modelling of these processes and qualitatively to estimate their influence on dynamics of lubricant ability and efficiency of the engine.

On the basis of the analysis anti-wear properties of greasing fuel the model of the volumetric deterioration intended for forecasting of size of last under set conditions. Optimum parametrization criterion model was based on interpretation of criterion of wear as an invariant with the minimal variation. Thus the ratio, connecting criterion of volumetric wear with its average value, was interpreted as the equation of communication between size of wear and factors influencing it. It has allowed to use the given equation for forecasting size of deterioration in the set conditions and for various terms of operation. Synthesized thus criterion model was offered for using for forecasting wear in extreme conditions and formations of corresponding qualifying specifications.

РЕФЕРАТ

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МЕТОДИ ВІРТУАЛІЗАЦІЇ У ХІММОТОЛОГІЧНИХ ДОСЛІДЖЕННЯХ

Віртуалізація в хіммотології дозволяє здійснити екстраполяцію лабораторних результатів на штатні умови експлуатації, а також зворотний перерахунок цих умов в адекватні параметри кваліфікаційного експерименту. Ефективність віртуалізації продемонстрована на прикладах оптимізації математичних моделей, вдосконалення кваліфікаційних експериментів і прогнозування їх результатів.

Ключові слова: кваліфікаційні випробування, напівнатурний експеримент, чисельний експеримент, фізична модель, віртуалізація, віртуальна кваліфікація, критеріальна модель, крива Герсі-Штрібека, число Зоммерфельда, протизносні властивості, ідентифікація.

РЕФЕРАТ

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МЕТОДЫ ВИРТУАЛИЗАЦИИ В ХИММОТОЛОГИЧЕСКИХ ИССЛЕДОВАНИЯХ

Виртуализация в химмотологи позволяет осуществить экстраполяцию лабораторных результатов на штатные условия эксплуатации, а также обратный пересчет этих условий в адекватные параметры квалификационного эксперимента. Эффективность виртуализации продемонстрирована на примерах оптимизации математических моделей, совершенствования квалификационных экспериментов и прогнозирования их результатов.

Ключевые слова: квалификационные испытания, полунатурный эксперимент, численный эксперимент, физическая модель, виртуализация, виртуальная квалификация, критериальная модель, кривая Герси–Штрибека, число Зоммерфельда, противоизносные свойства, идентификация.

ABSTRACT

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METHODS VIRTUALIZATION IN CHEMMOTOLOGY RESEARCHES

Virtualization in chemmotology allows to carry out extrapolation of laboratory results on regular conditions of operation, and also return recalculation of these conditions in adequate parameters of qualifying experiment. Efficiency virtualization is shown on examples of optimization of mathematical models, perfection of qualifying experiments and forecasting of their results.

Key words: qualifying tests, semi-scale experiment, numerical experiment, physical model, virtualization, virtual qualification, criterion model, Hersey-Stribeck curve, Sommerfeld number, anti-wear properties, identification.

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1.4 POLYMER MODIFIED BITUMEN

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According to [1] in 2013 ten major bitumen producers are: USA – 19.365 mln.tons (18.9 %); China – 17.938 (17.5); Russia – 6.193 (6.0); India – 6.193 (4.7); Canada – 4.335 (4.2); Iran – 3.896 (3.8); Japan – 3.659 (3.6); South Korea – 3.614 (3.5); Germany – 3.410 (3.3); Italy – 3.104 (3.0). These countries account for 68.5 % of world bitumen production. Ukraine occupies only 53 place – 0.123 mln.tons (0.1 %).

The largest exporters of bitumen are [2]: South Korea – 2.264 mln.tons (11.5 %); Iran – 2.179 (11.1); Singapore – 2.178 (11.1); Canada – 1.778 (9.0); USA – 1.539 (7.8). Due to the deficit Ukraine actualy does not export bitumen.

The largest importers of bitumen are [3]: China – 3.225 mln.tons (19.8 %); USA – 1.641 (9.8); France – 1.193 (7.1); Saudi Arabia – 0.996 (5.9); Algeria – 0.729 (4.3). Ukraine imports 0.165 mln.tons (1.0 %; 21st place in the world).

World consumption of bitumen is on the average 87 mln.tons per year. The structure of consumption by world regions is shown in Fig. 1.

About 85 % of petroleum bitumen are used as a binder in various types of asphalt laying: sidewalks, highways, airports, etc. (Fig. 1).

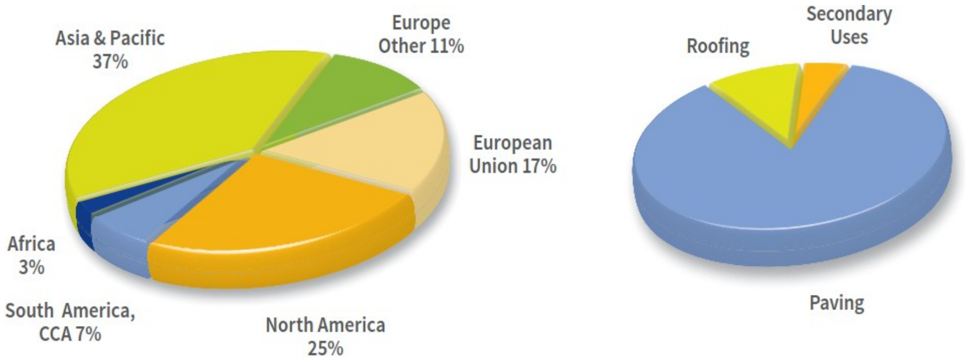

Fig. 1. World consumption of bitumen

To date bitumen-mineral mixtures for pavement are prepared by two ways: (i) as a result of bitumen heating to the temperatures exceeding their dropping points; (ii) by obtaining aqueous bituminous emulsions. Table 1 represents the composition of petroleum bitumen consumption by the road industry in Europe according to EAPA (European Asphalt Pavement Association).

When using bitumen for the production of asphalt mixtures it is not always possible to create a material that fully satisfied consumers by their performance properties. In particular, bitumen is generally characterized by poor adhesion, low temperature and plastic properties, leading to poor strength of the roadway. One of the ways of solving this problem is modification of commercial bitumen. Modified bitumen is characterized by improved flexibility and longer service life, it also has a lower brittleness temperature and higher softening temperature [4–7].

The share of modified bitumen, relative to its total use in road construction, is irregularly distributed between European countries, but as a rule, this share is above 10 %. The leaders are (%): Romania – 75; Slovakia – 29.1; Belgium – 26.5; Hungary – 25; Czech – 21.5 (Table 1).

Table 1

Consumption of bitumen in the road industry

Country	Tonnage in 2014, mln. t	Percent of modified bitumen (of total)				Emulsions in 2014, mln. t
		in 2011	in 2012	in 2013	in 2014	
Austria	0.37	25.0	25.0	30.0	18.9	0.005
Belgium	0.21	25.5	27.0	25.4	26.5	No data
Croatia	0.13	No data	No data	No data	10.00	No data
Czech Republic	0.33	18.0	22.4	22.1	21.5	0.008
Denmark	0.19	5.0	5.0	5.0	5.0	0.020
Estonia	0.08	No data	No data	4.0	3.3	0.016
Finland	0.27	0	No data	0	0	0.001
France	2.47	<10	13.0	13.0	6.9	0.792
Germany	1.60	No data	No data	No data	No data	No data
Great Britain	1.28	8.0	8.0	8.0	8.0	0.100
Greece	No data	2.0	1.5	2.2	No data	No data
Hungary	0.19	11.0	15.4	30.0	25.0	0
Iceland	No data	No data	No data	No data	0	0
Ireland	0.13	No data	No data	No data	No data	0
Italy	No data	14.0	13.0	14.0	No data	No data
Lithuania	No data	14.0	11.0	No data	No data	No data
Luxembourg	0.05	20.0	30.0	No data	15.0	No data
Netherland	0.30	No data	No data	5.0	No data	No data
Norway	0.35	15.0	No data	No data	No data	No data
Poland	No data	21.0	22.0	25.0	No data	No data
Romania	0.20	74.0	45.0	76.0	75.0	0
Serbia	0.26	14.7	6.0	4.2	4.4	No data
Slovakia	0.08	60.0	37.0	31.0	29.1	0
Slovenia	0.07	10.0	11.0	9.0	10.0	No data
Spain	0.56	13.1	19.6	10.0	15.0	0
Sweden	0.45	6.0	5.0	No data	7.0	0
Switzerland	0.28	10.0	11.0	2.0	12.0	0
Turkey	2.39	8.0	7.5	4.4	3.2	0.026

As mentioned above, due to its natural properties petroleum bitumen is not able to create the conditions for long-term operation of pavement under modern heavy duty traffic and adverse weather factors.

Therefore, in addition to providing the required quality and durability it is necessary to radically improve the physical and mechanical characteristics of these materials by complex modification with additives.

From a technical point of view, to create a bitumen-based composite materials with a given set of properties only those substances may be applied, which meet the following requirements [14]:

– they are not destroyed at the temperature of asphalt-concrete mixture preparation;

– they are compatible with bitumen during the mixing process on conventional equipment at the temperatures usual for preparation of asphalt-concrete mixtures;

– in summer they increase the stability of bitumen (which is a part of the roadway) to the deformation impact loads without increasing its viscosity at the temperatures of mixing and laying and do not impart brittleness to bitumen at low temperatures;

– they are chemically and physically stable and do not change their properties during transport, storage, processing and operating conditions of pavement.

According to their action the modifiers can be divided into adhesion, plasticizing, structuring and complex ones.

Adhesion additives significantly improve bitumen adhesion to stone materials and, as a rule, bitumen particles with each other, provide high water resistance of asphalt-concrete and prevent damage of the pavement. Adhesion additives also retard the bitumen aging [8, 9].

Plasticizing additives provide modified bitumen with necessary consistency due to which they withstand deformation load and temperature changes [10].

Structuring additives can become cross-link binders and thereby provide the required strength of the roadway coating.

Complex additives are widely used in the road-building. They significantly improve the rheological properties of modified bitumen and their adhesion to mineral materials surface [11–14].

Additives for improving roadway quality are introduced into bitumen or directly into asphalt-concrete mixtures.

Additives which are introduced directly into bitumen can be divided into: polymer compounds, adhesive agents and specific components (*e.g.* sulfur). Additives introduced into asphalt-concrete mixtures are divided into: stabilizing (based on fibers), structuring (mineral powder, cement), structuring and stabilizing (natural bitumen, polymers, waxes).

Modification by polymer materials is one of the most perspective ways to improve the quality of binders to produce road surfaces with improved characteristics. The compounds used to produce polymer modified bitumen (PMB) are described below.

Polymer compounds, used as modifiers, may be assigned to one of four groups according to their nature, which implies a way to influence the properties of bitumen and method of introduction into PMB [4, 6, 13–14].

1) elastomers – natural and synthetic rubber, rubber crumb;

2) thermoplastic elastomers – block copolymers of butadiene and styrene type SBS;

3) thermosetting plastics – various copolymers and kooligomers (further – resins), which are usually have a large number of functional groups: epoxy, furfurol- and phenol-formaldehyde, carbamide, silicone, *etc*.

4) thermoplastics – polyvinyl acetate, polystyrene, polyisobutylene, polyethylene, polypropylene, atactic polypropylene, polyvinyl chloride, thermoplastics Elvaloy-4170 (copolymer of ethylene with butyl acrylate and glycidyl methacrylate), latexes of ButonalNS type, Viskoplast-S, ethylene methyl acrylate (EVA), petroleum resins.

By volumes of using the polymers are placed in the following order: thermoplastic elastomers of SBS type; thermoplastics of ethylene vinyl acetate type (EVA), polyisobutylene, polypropylene, a variety of block copolymers; polymer latexes and thermopolymers of ethylene glycidyl acrylate type [6, 7].

This type of modifiers includes polymers, rubbers and rubber polymers [6, 7, 15–21]. For the bitumen-polymer composition rubber imparts a new property – flexibility, which is typical of natural rubber in a wide temperature range. The new rheological state provides composition deformation at low temperatures, despite the lack of plastic properties of bitumen. In other words, this additive in bitumen improves its extensibility and elasticity at low temperatures, improves thermal and crack resistance, strength, deformation resistance, water resistance, frost resistance, durability, resistance to aging.

Rubber can be introduced into bitumen by direct fusion, or in the presence of a solvent.

The example of most suitable for bitumen modification elastomers is synthetic rubbers of general purpose (isoprene, divinyl, divinyl styrene, ethylene propylene). These rubbers are produced as a briquetted solid elastic product which is used for gum production *via* rubber vulcanization.

The main disadvantage of elastomers is their poor dispersion in bitumen, so special measures are needed to obtain homogeneous modified bitumen (fusing, special solvents, *etc*.). Moreover, phase separation between polymer and bitumen in a liquid phase takes place, especially during storage. To avoid this phenomenon complicated devices that can support high temperatures and PMB continuous mixing are needed.

According to the published data [20, 21] rubber crumb is a promising product to be used for the modification. The main advantages are low cost and possibility of tires and other waste rubber products recycling. Despite the obvious advantages over other modifiers, using crumb rubber in road building is also limited because of the technological difficulties that arise when they are mixed with bitumen.

There are three types of styrene block copolymers: styrene-butadiene-styrene (SBS), styrene-isoprene-styrene (SIS), styrene-ethylene / butylene-styrene (SEBS). The content of polymers in PMB can reach 3–10 wt %. Thermoplastic elastomers (TE), compared to thermoplastics, are characterized by higher elasticity, *i.e.* TE combine the strength of thermoplastics and elasticity of elastomers [4, 6, 7, 15–17, 22–24].

Styrene block copolymers of SBS type are mostly used for bitumen modification due to their ability to increase the strength of bitumen, and to provide polymer-bitumen compositions with elasticity, including that at low temperatures. Thermoplastic elastomer of SBS type is a linear polymer, which provides elasticity (ability to initial distortion) for bitumen-polymer system due to its structure (styrene units are linked by butadiene "flexible" blocks). TE retain the ability to highly elastic deformations within the temperature range of 193–353 K. The temperature of TE destruction is 463–483 K.

Block copolymers of butadiene and styrene of SBS type are well combine with bitumen because polystyrene and polybutadiene are swelled in paraffin-naphthenic and aromatic hydrocarbons of bitumen and partially dissolved in them at 423 K.

To improve polymer dissolution in bitumen the plasticizers are used (usually a mixture of aromatic based hydrocarbons). Plasticizer significantly improves the polymer solubility in bitumen, but slightly decreases the adhesive properties of the resulting binder compared to the original bitumen [4, 7].

Due to their properties TE are produced in a variety of trademarks [25–28]: Kraton D1101, Kraton D1184, Kraton D1186 (Kraton Polimers, USA); Finaprene 411 (Total, France); Europrene Sol T 161B (Eni, Italy); Calprene 411 (Dynasol, Spain); DST 30–01 and DST-30R-01 (Voronezh factory, Russia).

The main disadvantage, restraining the growth of modified bitumen production is its high cost. Bitumen modified by TE is 1.5–2.5 times more expensive than unmodified bitumen [5].

Thermosetting plastics (TP) are polymers, which turn into solid state while heating or introducing hardener. Before hardening TP molecules have a linear structure, the same as thermoplastics molecules, but the size of their molecules is significantly smaller. TP molecules are chemically active. They contain either double (unsaturated) bonds or chemically active groups. Therefore, under certain conditions (at heating, irradiation or adding hardeners) thermosetting molecules react with each other and form a continuous network. Epoxy, phenol-formaldehyde, carbamide, polyester, silicone and other resins belong to TP [4, 6, 7, 29–33].

Bitumen-polymer binders with thermosetting plastics have relatively high adhesion to the mineral particles and high strength.

The use of TP for bitumen-polymer mixtures create a number of disadvantages [4]:

– when entering hardener the technological properties of PMB are almost immediately deteriorated;

– rigidity is increased at low temperatures;

– the use of special hardeners complicates the system and raises its price;

– the effectiveness of thermosetting plastics appears usually at their large quantities in bitumen – more than 10 wt %.

These polymer additives improve strength and deformation characteristics of bitumen and asphalt: the resistance to rutting at elevated temperatures increases, risk of cracking at low temperatures and fatigue cracking of asphalt under prolonged stress is reduced. Polymers which are quite often used now: polyvinyl acetate, polystyrene, polyisobutylene, polyethylene, polypropylene, atactic polypropylene, polypropylene, polyvinyl chloride, Viskoplast-S, EVA, ethylene methyl acrylate [4, 6, 7, 15, 27, 34–37]. However, the use of "traditional" polymers (polyethylene, polypropylene, *etc.*) is accompanied by a number of problems because rigidity and brittleness of resulting PMB increase after modification. As a result, a pavement using such binders, is disposed to increased cracking at low temperatures.

Synthetic latex of ButonalNS type (BASF, Germany) [38–41] and thermopolymers of Elvaloy series (DuPont, USA) [4, 15, 42] are widely used. These polymers not only reduce bitumen sensitivity to temperature changes, but also enhance the cohesive and adhesive strength resulting in the increase of strength and crack resistance of asphalt concrete pavement.

Petroleum resins obtained from by-products of fossil fuels thermodestruction occupy a special position among thermoplastics. They can be used to improve bitumen properties, namely they increase the viscosity, hardness, durability and adhesion to mineral materials [43–45]. The additives containing polar groups in their molecules, contribute to improved wettability of the mineral materials with bitumen, creating an adsorption and hemosorption monomolecular layers providing strong adhesion of bitumen-mineral mixture.

Petroleum resins with functional groups are of special attention. These compounds may belong both to thermoplastics and thermosetting plastics. The presence of functional groups in petroleum resin structure significantly improves the adhesion properties of bituminous materials, resulting in increased durability of the products based on them. The use of petroleum resins for bitumen modification is limited due to their considerable cost. Moreover, under high temperatures these compounds can form three-dimensional cross-linked structure with petroleum bitumen that reduces its plasticity. As a result cracking of asphalt pavement occurs. Under long-term exposure to high temperatures during preparation, transportation and laying of road surfaces thermal degradation of polymers is also possible, so they can lose modifying properties.

Resin modifiers may also be produced from coal processing secondary products. The investigations concerning using coumarone-indene resin (CIR) as a modifier were carried out at the Department of Oil and Gas Processing of Lviv Polytechnic National University [46–48]. CIR is a polymerization product of a mixture of compounds (mainly indene, coumarone and styrene), which are by-products of the coking process («heavy» benzene, coal tar light fractions).

Phenol-cresol-formaldehyderesinsare also high-effective modifiers of bitumen, the road bitumen first of all. Resins are producedviapolycondensationmethodfromphenolicfractionwhich is obtained from coal tar [49, 50].

Taking into account the high efficiency of above-mentioned modifiers, their relatively simple methods of production and low cost, the Section 3 is devoted to the application of resins in polymer modified bitumen production.

Other types of modifiers (non-polymer modifiers) should be mentioned here, as well. Sulfur is considered to be the most promising among them. Technical sulfur is inexpensive and small-scale product. While producing sulphur asphalt the part of expensive bitumen is substituted for relatively cheap sulfur (50 wt %). The result is reduction of the finished product price and improvement of asphalt properties. Sulfur asphalt has several unique properties such as high compressive and flexural strength, adhesion, chemical resistance, frost resistance, low water absorption and waterproofness. A major disadvantage of sulfur compositions is their low thermal stability. In addition, there is a significant change in volume during sulfur solidification due to phase transition of sulfur from a liquid to a solid state.

Mineral materials are often added to bitumen but they should be rather fillers than modifiers. For example, the wastes obtained during haydite and soda production are added to bitumen. The use of haydite dust improves crack resistance and strength characteristics of the bituminous binder. When using wastes of soda production the asphalt strength is quite high but water resistance after long-term water saturation is below limit. This problem may be solved by using silica powder. However, mineral fillers do not usually improve adhesion and/or plasticity of bitumen.

To obtain PMB, commercial bitumen of BND 60/90 for road constructions, which was produced by Lviv asphalt-bitumen storehouse, was used. Bitumen characteristics are represented in Table 2.

CIR was used as a modifier. CIR is obtained from a chemical product of coal charge coking, the characteristic of which depends on composition and quality of coal [53, 54]. The synthesis procedure of coumarone-indene resins are given in [47, 51, 52]. Depending on synthesis conditions and the composition of initial raw material different CIRs were obtained. Some main properties of CIR are given in Table 2.

A range of compounds with a relatively high content of aromatic-naphthenic based oil were used as plasticizers for the modified bitumen (Table 2), in particular:

– tars produced from West-Ukrainian and Orkhovitska oils taken at West-Ukrainian refineries;

– distillation extract of selective treatment by furfurol and residual extract of selective treatment manufactured by Ukrtatnafta, JSC;

– resin after lignitethermodestruction;

– SAE-140 transmission oil.

Resin derived from thermodestruction of lignite is one of the products obtained in the process of oxidative desulphurization [55–57].

The laboratory unit intended to obtain PMB is shown in Fig. 2. PMB has been prepared in the following way. A necessary amount of bitumen was heated to 110 °C. Then the modifier and plasticizer were added in a required amount and stirred for 1 h at Re = 1200.

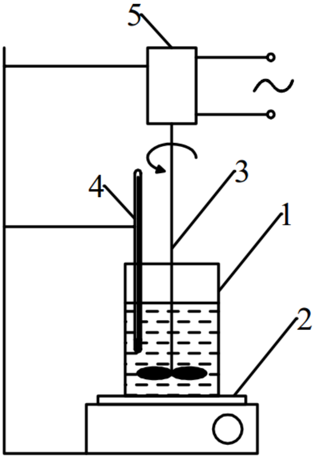

Fig. 2. The laboratory unit for obtaining PMB.
1– vessel; *2*– electric heater; *3*– stirrer; *4*– thermometer; *5*– electric motor

Table 2

Characteristics of initial compounds

Index	BND 60/90	Modifier (CIR)	Plastisizers				
			TarproducedfromWest-Ukrainian oils	Tar produced from Orkhovitska oil	Residual extract of oil selective treatment	Distillation extract of oil selective treatment	Resin of lignite thermodestruction
Penetration at 25 °C ($m\times10^{-4}$)	62	–	98	112	–	–	–
Softening point (ball & ring method) (°C)	47	97–186	43	38	–	–	–
Ductility($m\times10^{-2}$)							
at 25 °C	75	–	15	>100	–	–	–
at 0 °C	6	–	–	–	–	–	–
Change of properties after heating:							
Brittleness temperature(°C)	-15	–	–	–	–	–	–
Flash point determined in open firepot(°C)	235	–	–	–	–	–	–
Change of weight after heating (%)	0.2	–	–	–	–	–	–
Residualpenetration (%)	50	–	–	–	–	–	–
Change of softening point (°C)	4	–	–	–	–	–	–
Adhesion to glass (%)	46	–	–	–	–	–	–
Low-temperature adhesion (%)	38	–	–	–	–	–	–
Mass partof paraffins (wt. %)	5.1	–	–	–	–	–	–
Solubility in organic solvents (%)	99.9	–	–	–	–	–	–
Penetration index	-1.0	–	–	–	–	–	–
Density (kg/m^3)	–	–	–	–	987.3	985.7	1048.0
Viscosity (mm^2/s)							
at 50 °C	–	–	–	–	128.4	115.4	–
at 80 °C	–	–	–	–	–	–	33.08
at 100°C	–	–	–	–	11.8	10.3	–
Freezing point, ºC	–	–	–	–	–	–	42
Molecular weight	–	820**	–	–	–	–	–
Bromine number, g Br_2/100 g CIR	–	27.5**	–	–	–	–	–

*DSTU – Ukrainian National standards

**Determined for CIR with the softening temperature of 135 °C.

Chemical group composition of the bitumen was analyzed by the Marcusson method. The type of the structure of the bitumen sampled was determined according to this procedure (Table 3).

Table 3

Group analysis and type of the initial bitumen structure

Type of structure	Group composition, wt %				Ratio	
	Carbenes, carboids and mechanical impurities	Asphaltenes (A)	Resins (R)	Oils (O)	A/(A+R)	A/(O+R)
I type – gel	–	>25	<24	>50	>0.50	>0.35
II type – zol	–	<18	>35	≤47	<0.34	<0.22
III type – zol-gel	–	21–23	30–34	45–49	0.39–0.49	0.25–0.30

Technical parameters of the raw material and products were determined according to standard procedures (see tables 1, 2). The value of low-temperature adhesion which characterizes the dependence of bitumen adhesion on great temperature difference was determined according to the devised procedure. Differential-thermal analysis (DTA) of the initial and modified bitumen was done on a Q-1500D derivatograph (system F. Paulik, J. Paulik and L. Erdey) in a dynamic mode at the heating rate of 10 °C/min under atmosphere of air. The weight of the sample was equal to 200 mg. An analytical signal of mass loss and thermal effects were registrated via the computer. Aluminium oxide was used as a standard.

To determine the adequacy of mathematical model the mean relative error of approximation was calculated according to the formula.

$$\varepsilon_j = \frac{1}{n}\sum_{j=1}^{n}\left|\frac{Y_{ij}-Y_{ij}^{reg}}{Y_{ij}}\right| \qquad (1)$$

where Y_{ij} – experimental values; Y_{ij}^{reg} – values of response function calculated according to regression equations; n – number of experiments.

To evaluate the effect of resin indices (softening temperature, in particular) on the properties of road bitumen we prepared a series of PMB samples with the softening temperature of 52 °C. The results are represented in Table 4.

Table 4

Dependence of PMBs properties on CIR softening temperature

Index	Value						
Conditions of PMB obtaining							
Bitumen content (wt. %)	100.0	88.0	91.9	92.7	93.3	93.6	95.0
CIR content (wt. %)	0.0	12.0	8.1	7.3	6.7	6.4	5.0
Softening point of CIR (ball & ring method) (°C)	–	97	120	128	135	140	186
Molecular weight of CIR	–	680	760	765	810	830	–
Characteristics of PMB							
Softening point of PMB (ball & ring method) (°C)	47	52	52	52	52	52	52
Ductility at 25 °C (m×10^{-2})	75	45	46	38	36	33	21
Penetration at 25 °C (m×10^{-4})	62	53	51	37	38	37	25
Adhesion to glass (%)	46	77	85	100	100	100	100
Low-temperature	38	70	74	97	98	100	100

The obtained results allow to assert that the increase in polymerization degree (softening temperature) of the resins increases PMB adhesion including that at low temperatures. To prepare PMB with good adhesive properties it is necessary to use CIR with the softening temperature no lessthan 128–140 °C. On the other hand, it is complicated (from the technological point of view) to obtain CIR with such softening temperature. Moreover, with the increase in softening temperature

PMB plastic properties are deteriorated (penetration and ductility are decreased). Therefore, for the further investigations we used CIR with the softening temperature of 135 °C.

The results of the studies are given in Table 5 in terms of how plasticizers affect the properties of PMBs obtained.The quantity of plasticizer (see Table 5), obtained from oil stock (samples 3–7) was equalto 8 wt %. To compare the plasticizer obtained from brown coal (sample 2) and the best plasticizer from oil stock (sample 3) we fitted the composition of the sample 2 in such a way, that its softening point was the same as that for the sample 3 (52 ^{o}C).

The Table 5 shows that PMB with no plasticizer added (Sample 1) was obtained using CIR and does not conform to the requirements [47] (Table 1) by penetration index. Adding the plasticizer to PMB in most cases (Table 5):

- decreases softening points;
- makes adhesion worse;
- increases penetration.

Table 5 demonstrates that resin of thermodestruction of lignite and tar from West-Ukrainian oil most effectively increase penetration and least of all enhance a decrease in softening points and ductility. The properties of Samples 2 and 3 actually meet the requirements suggested [47].

Considering that resin derived from the lignite thermodestruction is a product being currently produced only in laboratory, it was decided to use the tar from West-Ukrainian oil (TWUO) as a plastisizer in further researches.

To establish the optimal composition of bitumen-CIR-TWUO mixture, the empiric mathematical models were developed on the basis of full-factorial experiments (Table 6). The models describe the dependence of PMB properties on its composition. The mathematical dependence of response function (Y) on individual components content (X) was developed as a linear function:

$$Y_i = B_0 + B_1 \cdot X_1 + B_2 \cdot X_2 \tag{2}$$

For response function and main parameters of obtaining PMB, the following symbols were used: Y_1 – PMB softening point, °C; Y_2–depth of needle penetration at 25 °C, 0.1 mm; X_1–CIR amount, wt %; X_2–plasticizer amount, wt %.

Table 5

Effect of plasticizer nature on PMB properties

Sample number	Plasticizer	Blend composition,wt. %			Main characteristics of obtained PMB			
		bitumen	ICR	plasticizer	Softening point (ball & ring method) (°C)	Ductility at 25°C ($m\cdot10^{-2}$)	Penetration at 25 °C ($m\times10^{-4}$)	Adhesion to glass (%)
1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
1	–	93.0	7.0	0	52	36	38	100
2	Resin of lignite thermodestruction	84.0	7.0	9.0	52	28	62	100
3	Tarproduced from West-Ukrainianoils	85.0	7.0	8.0	52	26	60	93

Table 5 continue

Sample number	Plasticizer	Blend composition, wt. %			Main characteristics of obtained PMB			
		bitumen	ICR	plasticizer	Softening point (ball & ring method) (°C)	Ductility at 25°C ($m\cdot10^{-2}$)	Penetration at 25 °C ($m\times10^{-4}$)	Adhesion to glass (%)
4	Residual extract of selective treatment	85.0	7.0	8.0	49	55	55	84
5	Tar produced from Orkhovitska oil (Ukraine)	85.0	7.0	8.0	52	21	40	78
6	SAE 140 transmission oil	85.0	7.0	8.0	46	41	65	51
7	Distillation extract of selective treatment	85.0	7.0	8.0	47	51	61	48

The following regression equations were obtained:

$$Y_1 = 48.49 + 0.75 \cdot X_1 + 0.13 \cdot X_2 \tag{3}$$

$$Y_2 = 70.12 + 3.02 \cdot X_1 + 1.38 \cdot X_2 \tag{4}$$

Substituting the values of X_1 and X_2 into Eqs. (3) and (4), the values of response function (Y_{ij}^{reg}) and relative errors of experimental statistical model for every experiment were found. These values are represented in Table 6.

Table 6

Experimental data, calculated values of response functions, and relative errors

№	X_1 (wt. %)	X_2 (wt. %)	Y_1 (°C)	Y_1^{reg} (°C)	Y_2 ($m\cdot10^{-4}$)	Y_2^{reg} ($m\cdot10^{-4}$)	Relative errors	
							ε_1	ε_2
1	7	3	50	52.95	43	53.26	0.0590	0.2386
2	13	3	54	57.45	35	35.26	0.0639	0.0074
3	7	11	49	51.91	65	64.30	0.0594	0.0108
4	13	11	53	56.41	35	46.30	0.0643	0.3229
Mean relative error of approximation (ε)							0.0617	0.1449

Mean relative errors of approximation are: $\varepsilon_1 = 0.0617$ (6.17 %), $\varepsilon_2 = 0.1449$ (14.49 %). It is assumed that at $\varepsilon = 0–10$ % the accuracy of prediction is high, at $\varepsilon = 10–20$ % – good and at $\varepsilon = 20–50$ % – fair. Thus, the models developed correlate well with experimental data.

Graphical interpretation of Eqs. (3) and (4) is given in Figs. 3 and 4.

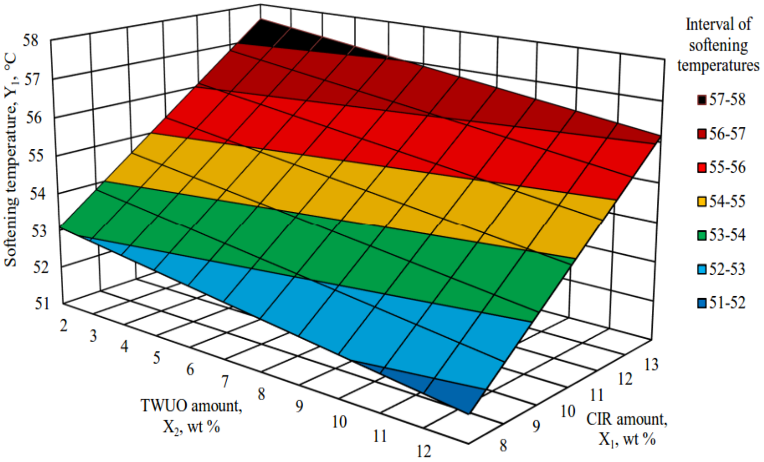

Fig. 3. Effect of CIR and TWUO amount on PMB softening point

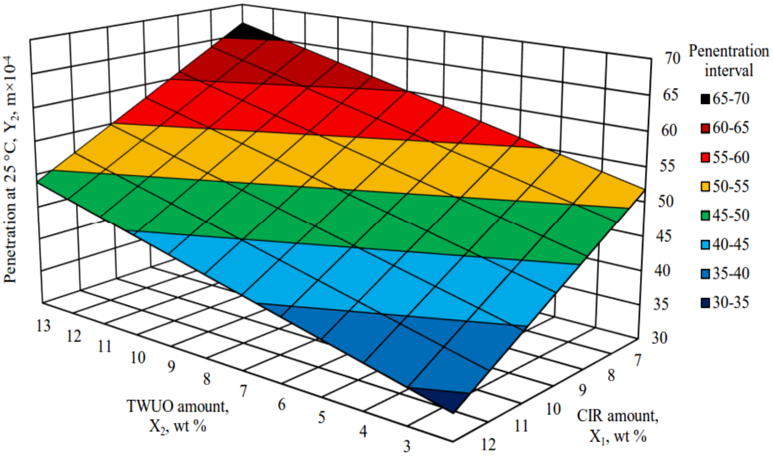

Fig. 4. Effect of CIR and TWUO amount on PMB penetration

Fig. 3 shows that an increase in the CIR amount and a decrease in the plasticizer amount (tar produced from West-Ukrainian oils) give rise to the softening point. The increasing penetration (Fig. 4) is accompanied by an opposite tendency: the CIR amount decreases while the amount of plasticizer increases. Therefore, the amount CIR and plasticizer in the blend should be optimum.

On the basis of regression equations using the method of uniform search of response functions, optimal amounts of components were found, which would provide the necessary values of main parameters (response functions) of the process effectiveness, namely: softening point – above 52 °C and the depth of needle penetration at 25 °C – above 61 °C. PMB I was obtained at optimal amount of CIR 7 wt % and tar amount of 8 wt %. PMB II was obtained for the comparison. It consists of bitumen (91.5 wt %), Kraton D 1192 commercial modifier (1.5 wt %) and tar produced from West-Ukrainian oil as the plasticizer (7 wt %). PMB II composition was fitted in such a way that its softening temperature was equal to the softening point of PMB I. PMB characteristics are presented in Table 7.

Table 7

PMB characteristics

Index	Standard for BMP 60/90-52 according to DSTUBV.2.7-135:2007*	Actual values	
		PMB I	PMB II
Homogeneity	Homogeneous	Homogeneous	Homogeneous
Penetration at 25 °C (m·10^{-4})	61–90	62	61
Softening point (ball & ring method) (°C)	≥52	52	52
Ductility (m·10^{-2})			
at 25 °C	≥25	26	36
at 0 °C	≥5,0	6	5
Elasticity at 25 °C (%)	≥50	52	54
Brittleness temperature (°C)	≤-15	-16	-15
Flash point determined in open firepot (°C)	≥230	236	236
Change of properties after heating:			
Change of softening point (°C)	≤6	5	5
Residual penetration (%)	≥60	61	62
Adhesion to glass (%)	≥ 75	93	90
Low-temperature adhesion (%)	-	82	74
Destruction while storage:			
Difference between softening points (°C)	≤ 8	8	8
Difference between penetrations at 25 °C (m·10^{-4})	≤ 30	22	25

*DSTU is Ukrainian National standards

Both samples with CIR used and PMB based on a commercial additive meet the requirements DSTU B V.2.7-135:2007, and PMB Imay be used to produceSlurry Seal [47]. Both types of bitumen have satisfactory aging properties (change of properties after heating, destruction while storage).Theplasticityproperties (ductilityandelasticityat 25 °C) aresomewhatbetterforPMBII butPMBIhasbetteroperationalcharacteristicsat low temperatures (ductilityat 0 °C, brittlenesstemperature). It should be noted that adhesion, including low-temperature adhesion, is higher for PMB I. It means that CIR is an effective modifier of petroleum bitumen.

Group compositions of the binders are given in Table 8. When comparing the structure of the initial bitumen with the modified one, it may be asserted that bitumens upon their modification are converted from gel-structure into zol-structure. This explains why rheological and plastic properties are improved. The zol-gel structure is considered to be optimal for binders used in road constructions.

Table 8

Group analysis of the modified bitumen

Component	Oxidated bitumen (non-modified)	PMB I	PMB II
1	*2*	*3*	*4*
Carbenes, carboids and mechanical impurities	0.6	0.4	0.5

Table 8 continue

Component	Oxidated bitumen (non-modified)	PMB I	PMB II
1	*2*	*3*	*4*
Asphaltene	25.3	22.0	23.4
Resins	24.2	35.8	33.1
Oils	49.9	41.8	43.0
Structure	Gel	Zol-gel	Zol-gel
A/(O+R)	0.34	0.30	0.28
A/(A+R)	0.51	0.41	0.37

The results of TG and DTA for the initial bitumen, PMB I and PMB II are represented in figs. 5 and 6, respectively.

The smallest mass loss is observed for PMB II (Fig. 5), that is why this type of binder may be used at high temperatures.Using PMB I at high temperatures (above 100–150 °C) is undesirable because a considerable mass loss is observed in such a case (0.13 %).

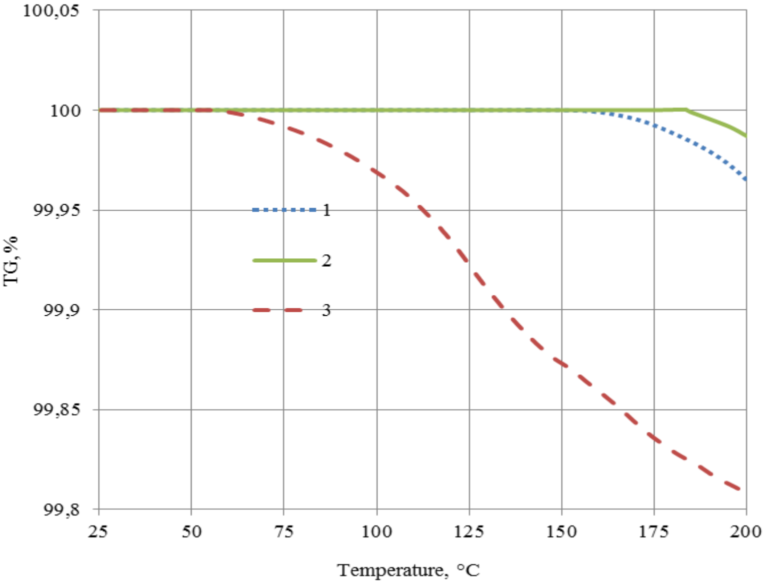

Fig. 5. Mass losses vs. temperature. *1* – initial bitumen; *2* – PMB II; *3* – PMB I

So, the modification of bitumen by CIR is recommended to be used under low temperatures, for example for emulsion technology.

DTA indicates that the deepest endothermal effect is observed for PMB I within 20–100 °C (Fig. 6) indicating its higher thermal stability as compared with PMB II and the initial bitumen. The bitumen-based asphalt modified by CIR will be less strained during the hot season.

The wide phenolic fraction (WPhF) was sampled at Zaporizhkoks PJSC for investigations. The WPhF characteristic is given in Table 1. For the purpose of concentration (separation) of phenol and cresols, the WPhF was divided into two fractions, an initial boiling point (IBP – ~92 °C) – 185 and 185 an end boiling point (EBP ~211 °C) °C (the boiling point of phenol is 182 °C, of cresols – 191–202 °C). Table 1 lists the characteristic of fractions derived. The mass balance of distillation is shown in Table 9.

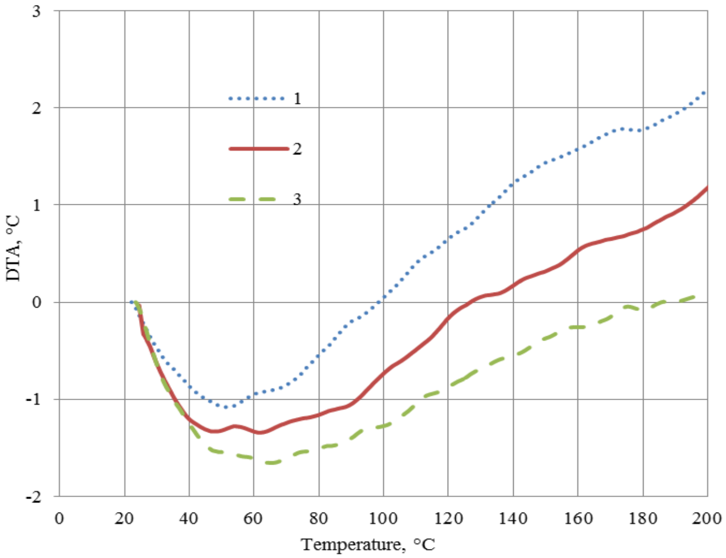

Fig. 6. DTA in the air flow (*1* initial bitumen; *2* PMB II; *3* PMB I)

Table 9

Characteristics of a starting material

Indexes	Values			Procedure
	wide phenolic fraction (WPhF)	Fraction IBP – 185 °C	Fraction 185 – EBP °C	
Distillation (°C):				
Initial boiling point	105	92	172	GOST 2177
10 % distilled at the temperature	164	147	177	
20 % distilled at the temperature	172	156	179	
30 % distilled at the temperature	174	161	181	
40 % distilled at the temperature	177	166	183	
50 % distilled at the temperature	179	169	184	
60 % distilled at the temperature	182	172	187	
70 % distilled at the temperature	185	174	190	
80 % distilled at the temperature	197	181	200	
90 % distilled at the temperature	202	184	206	
95 % distilled at the temperature	208	189	211	
Molecular weight	136	108	167	–
Bromine number (g Br_2/100 g product)	81.64	81.28	75.84	GOST 8997–89

Table 10

Mass balance of the WPhF distillation.

Article	Yield by weight, %
Fraction IBP – 185 °C (phenol concentrate)	50.60
Fraction 185 – EBP °C (cresols concentrate)	46.77
Distillation residue	2.63
Total	100.00

Phenol and its derivatives hereinafter called raw (technical) phenols – RPh1, RPh2 and RPh3 – were separated from the WPhF, the fraction IBP – 185 and the fraction 185 – EBP °C by using a 20 % NaOH solution. The removal of phenols with the solution of NaOH was based on the fact that phenol and its derivatives form water-soluble phenolates. The latter were made into phenols by using the concentrated hydrochloric acid. The yield of raw phenols with the WPhF, the fraction IBP – 185 and the fraction 185 – EBP °C accounted for 32.3, 32.0 and 35.1 % wt, respectively.

The resins were derived from initial fractions and those raw phenols that were obtained from them by the method of formaldehyde condensation polymerization.

The scheme of the research is given in Fig. 7.

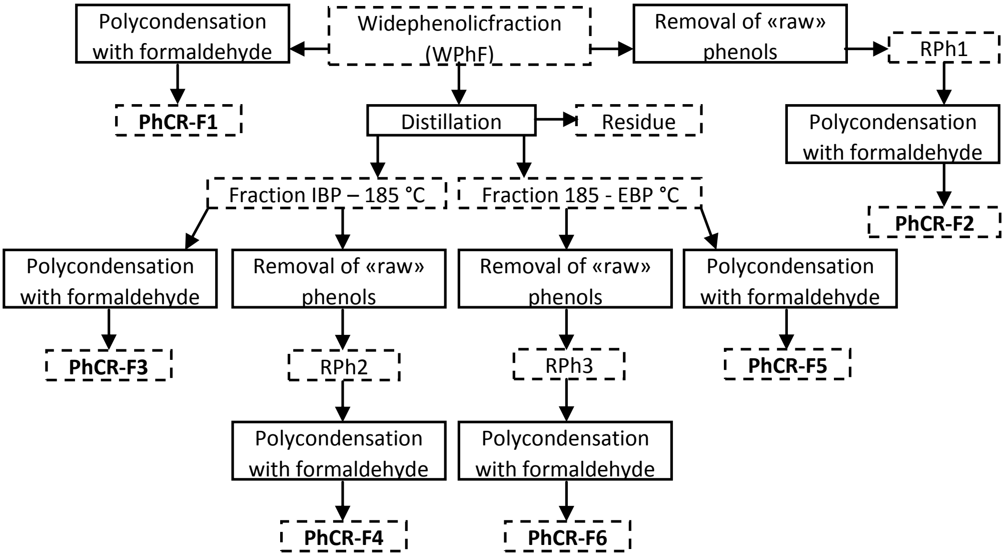

Fig. 7. Scheme ofthe research: PhCR-F – phenol-cresol-formaldehyde resin; RPh – raw (technical) phenols

The process of formaldehyde condensation polymerization of phenols was carried out on the laboratory setup depicted in Fig. 2. The raw material was placed in a three-pipe reactor and heated while stirring at 100 °C in a thermostat. Then, a necessary amount of formalin (a weight content of formaldehyde in formalin equaled 37 %) was added along with a concentrated hydrochloric acid (catalyst), followed by recording the start of the process that was done for 60 s. As the synthesis is over, a hot reaction mixture, obtained from raw phenols, was poured into a glass. After cooling the mixture, an aqueous phase was drained and the resin was exposed to the 3-hour drying in a vacuum dryer at 100 °C. When the WPhF was used as the starting material, the fraction IBP – 185 and the fraction 185 – EBP °C, at first there was the distillation of water and unreacted constituents carried out under vacuum. After that the resulting resin was dried some more in the vacuum dryer for 3 hours at 100 °C. The yield of the resins obtained was determined by the weighing of the starting material and the phenol-cresol-formaldehyde resins (PhCR-F).

In order to obtain PMBs, the distillate (residual) petroleum-derived bitumen for roads of the BD 60/90 grade and the BND 60/90 oxidized petroleum-derived bitumen for roads were utilized.

The BD 60/90 distillate (residual) petroleum road bitumen was selected at the road maintenance department of Frankivsk region (Lviv city). The oxidized petroleum-derived road bitumen of the BND 60/90 grade was sampled at *Ukrtatnafta* PJSC (the city of Kremechuk).

The PMB has been prepared by virtue of mixing in the following sequence: a necessary amount of bitumen was heated while stirring (Re = 1200) to the temperature of modification. Then with a required amount of the modifier added, it was sustained for 1 hour.

Novolac phenol-cresol-formaldehyde resins were obtained according to the scheme given in Figure 1 by the method of formaldehyde condensation polymerization with the WPhF, the fraction IBP – 185 and the fraction 185 – EBP °C and from the raw phenols extracted from these fractions. Synthesis conditions for the resins were set out on the basis of [58] and are shown in Table 11. As recommended by [58], the obtaining of novolac phenol-formaldehyde resins requires maintaining the mole ratio of phenol to formaldehyde at 1.12–1.42, while for novolac cresol-formaldehyde resins it should equal 2.27. Considering that the raw phenols that were derived from the phenolic fraction of coal tar contain both phenols and cresols at various ratios, the syntheses were done at the mole ratio of raw phenols to formaldehydes at the value of 1.42. For calculations of reactor loading, it was assumed that the molar mass of the resulting raw phenols was 94.1 g/mole, which is equal to the molecular weight of pure phenol. The effect of the ratio of reaction constituents on the production of resin will be looked into in further studies.

Table 11

Synthesis conditions for PhCR-F

Parameter	Value
*Mole ratio of raw phenols to formaldehyde	1.42
Weight ratio of raw phenols to formalin (formaldehyde content in formalin – 37 % wt)	1.78
Catalyst weight content (concentrated HCl), % by raw phenols	1.0
Temperature, °C	100
Process duration, min	60

*The molar mass of raw phenols was proposed to be 94.1 g/mol.

The mass balance for the obtaining of phenol-cresol-formaldehyde resins is given in Table12.

Table 12

Mass balances involved in syntheses for the obtaining of PhCR-F.

Article	PhCR-F1	PhCR-F2	PhCR-F3	PhCR-F4	PhCR-F5	PhCR-F6
1	*2*	*3*	*4*	*5*	*6*	*7*
Loaded						
1. Starting material	WPhF	RPh1	fr. IBP-185 °C	RPh2	fr. 185-EBP °C	RPh3
g	100.00	32.30	50.60	16.19	46.80	16. 43
% wt to be loaded	84.42	63.64	84.54	63.64	83.30	63.64
wt for a frond-end fraction	10.00[1]	32.30[1]	100.00[2]	32.00[2]	100.00[3]	35.10[3]
% wt for WPhF	100.00	32.30	50.60	16.19	46.80	16.43

Table 12 continue

1	*2*	*3*	*4*	*5*	*6*	*7*
Loaded						
2. Formalin	WPhF	RPh1	fr. IBP-185 °C	RPh2	fr. 185-EBP °C	RPh3
% wt for a frond-end fraction	18.13[1]	18.13[1]	17.96[2]	17.96[2]	19.70[3]	19.70[3]
% wt for WPhF	18.13	18.13	9.09	9.09	9.22	9.22
3. Concentrated HCl						
g	0.32	0.32	0.16	0.16	0.16	0.16
% wt to be loaded	0.27	0.64	0.27	0.64	0.29	0.64
% wt for a frond-end fraction	0.32[1]	0.32[1]	0.32[2]	0.32[2]	0.35[3]	0.35[3]
% wt for WPhF	0.32	0.32	0.16	0.16	0.16	0.16
Total, g	118.45	50.75	59.85	25.44	56.18	25.81
Results						
1. Tar						
g	18.20	29.65	8.20	13.20	9,03	14.39
% wt to be loaded	15.36	58.42	13.70	51.87	16,08	55.75
% wt for a front-end fraction	18.20[1]	29.65[1]	16.20[2]	26.08[2]	19.30[3]	30.75[3]
% wt for WPhF	18.20	29.65	8.20	13.20	9.03	14.39
2. Water and unreacted components G	100.25	21.10	51.65	12.25	47,15	11,42
% wt to be loaded	84.64	41.58	86.30	48.13	83.92	44.25
% wt for a front-end fraction	100.25[1]	2.10[1]	102.08[2]	24.20[2]	100.75[3]	24.40[3]
% wt for WPhF	100.25	21.10	51.65	12.25	47.15	11.42
Total, g	118.45	50.75	59.85	25.44	56.18	25.81

[1] for the wide phenolic fraction (WPhF)
[2] for the fraction IBP – 185 °C
[3] for the fraction 185 – EBP °C

When the concentrated phenols (raw phenols) are used in the act of synthesis, the yield is observed to be higher while loading the reactor (almost fourfold increase: 51.9–58.4 % wt against 13.7–16.1 % wt) and for the initial fraction (nearly 2 times higher: 26.1–30.8 % wt against 16.2–18.2 % wt). So, for the obtaining of effective modifiers of petroleum bitumens, it is mostly appropriate to carry out the synthesis not with the use of the coal tar phenolic fraction but with the raw phenols being separated from this tar.

Additionally, it is counterproductive to break up the WPhF with two narrower factions. This is explained by that using RPh1 as the starting material produces 29.65 % of the resin yield (calculated per WPhF) whereas the total resin yield if two raw phenols – RPh2 and RPh3 – are used appears to be lower: 13.20 + 14.39 = 27.59 %.

From then on, in order to specify a temperature for bitumen modification, the BD 60/90 residual bitumen was modified with PhCR-F3 and PhCR-F4 resins derived directly from IBP – 185 °C and RPh2 raw phenol, respectively, at 110 °C and 190 °C temperatures. It can be stated that mechanical mixing of bitumen components occurs at 110 °C while at 190 °C physical and chemical interactions between them are likely to be. Characteristics of bitumen-polymer blends obtained are given in Table 13.

Table 13

Preparation conditions and main characteristics of obtained PMBs

Index	BD 60/90	Modification temperature, °C (modifier content in PMB – 2.4 % wt)			
		PhCR-F3		PhCR-F4	
		110	190	110	190
Penetration at 25 °C(m×10^{-4})	80	78	75	–	62
Penetration decline, %	–	2.5	6.3	–	22.5
Softening point (ball & ring method) (°C)	43	44	46	–	47
Softening point increase, %	–	2.3	7.0	–	9.3
Ductility at 25 °C (m×10^{-2})	>100	>100	>100	–	>100
Adhesion to glass (%)	60	83	82	–	88
Increase in adhesion to glass, %	–	38.3	36.7	–	46.7
Homogeneity	non standardized	homogeneous	homogeneous	not homogeneous	homogeneous

Based on the data of Table 13, it can be suggested that the addition of synthesized PhCR-F3 and PhCR-F4 (except for the case of 110 °C and PhCR-F4) into bitumen leads to an increase in the softening point and, especially, in the adhesion of residual petroleum bitumen. The modification of petroleum bitumen with PhCR-F3 can be done at both 110 °C and 190 °C. In comparison, with PhCR-F4 – at 190 °C as 110 °C produces modified bitumen that does not meet requirements of homogeneity. Mixing at 190 °C makes it possible to increase the softening point to a greater extent. It follows from mentioned above that further modification of petroleum-based bitumens with phenol-cresol-formaldehyde resins that were obtained from the coal tar phenolic fraction was decided to be made at 190 °C.

A comparison of main characteristics of obtained bitumen-polymer blends is shown in Table 14.

*Table*14

Preparation conditions and main characteristics of obtained PMBs

Index	BD 60/90	Modified bitumen at 190 °C (modifier content in PMB – 2.4 % wt)					
		PhCR-F1	PhCR-F2	PhCR-F3	PhCR-F4	PhCR-F5	PhCR-F6
1	*2*	*3*	*4*	*5*	*6*	*7*	*8*
Penetration at 25 °C (m×10^{-4})	80	75	65	75	62	74	70
Penetration decline, %	–	6.3	18.8	6.3	22.5	7.5	12.5
Softening point (ball & ring method) (°C)	43	44	46	46	47	45	46
Softening point increase, %	–	2.3	7.0	7.0	9.3	4.7	7.0
Ductility at 25 °C (m×10-2)	>100	>100	>100	>100	>100	>100	>100
Adhesion to glass (%)	60	87	94	82	88	95	96

Table 14 continue

Index	BD 60/90	Modified bitumen at 190 °C (modifier content in PMB – 2.4 % wt)					
		PhCR-F1	PhCR-F2	PhCR-F3	PhCR-F4	PhCR-F5	PhCR-F6
1	*2*	*3*	*4*	*5*	*6*	*7*	*8*
Increase in adhesion to glass, %	–	45.0	56.7	36.7	46.7	58.3	60.0
Homogeneity	non standardized	homogeneous	homogeneous	homogeneous	homogeneous	homogeneous	homogeneous

Table 14 shows that adding all the obtained resins essentially improves the adhesive properties of bitumen. The data outlined in Table 14 indicate that the addition of the BD 60/90 resins synthesized from raw phenol (PhCR-F2, PhCR-F4 and PhCR-F6) gives rise to a larger increase in the softening point and adhesion compared to the ones synthesized from the WPhF, fraction IBP – 185, 185 – EBP °C (PhCR-F1, PhCR-F3 and PhCR-F5), but more increasingly reduces the plasticity (penetration) of the BD 60/90 residual bitumen.

With an increased content of cresols in the starting material (PhCR-F5 and PhCR-F6) compared to PhCR-F3 and PhCR-F4, the obtained modified bitumen possesses better adhesive properties (95–96 % against 82– 88 %, see Table 14). Nevertheless, the use of raw phenols produced from the WPhF allows almost the same adhesive properties to be obtained and the softening point to be raised as when PhCR-F5 and PhCR-F6 are used.

Consequently, this results in:

– higher yield of resin if raw phenols are used for its synthesis;

– slightly better characteristics of resin-modified bitumens, which contain more cresols (PhCR-F2, PhCR-F5 and PhCR-F6);

– lack of appropriateness to break up the WPhF with two narrow fractions.

– distilled road bitumens should be preferably modified with PhCR-F2.

To confirm the possibility of modifying the resulting resins as well as the oxidized bitumens coupled with the ability to compare the effectiveness of modifying the oxidized and residual bitumens, Table 15 shows the main characteristics of these PhCR-F2 modified bitumens.

Table 15

Comparison of main characteristics between residual and oxidized PhCR-F2 modified bitumens

Index	BD 60/90	BD 60/90 + PhCR-F2 (2,4 % wt)	BND 60/90	BND 60/90 + PhCR-F2 (2,4 % wt)
Penetration at 25 °C ($m \times 10^{-4}$)	80	65	70	60
Penetration decline, %	–	18.8	–	14.3
Softening point (ball & ring method) (°C)	43	46	46	49
Softening point increase, %	–	7.0	–	6.5
Ductility at 25 °C ($m \times 10^{-2}$)	>100	>100	63	25
Adhesion to glass (%)	60	94	47	97
Increase in adhesion to glass, %	–	56.7	–	106.4
Homogeneity	non standardized	homogeneous	non standardized	homogeneous

Supported by data given in Table 9, it may be argued that the modification with PhCR-F2 resin raises the softening point of both distilled and oxidized road bitumens by 3 °C. For the distilled bitumen, the adhesive properties of PMBs are increased by 56.7 % (from 60 to 94 %), while the oxidized one exhibits an increase of 106.4 % (from 47 to 97 %). This indicates that the resin obtained can also be utilized as adhesive additives in particular for the oxidized bitumens.

Conclusions. 85 % of bitumen production (on the average about 90 mln.tons of bitumen per year) is used as a binder in road construction. However oxidized and residual bitumen does not have the necessary properties to meet modern requirements to the pavement.The most common way to increase the performance properties of oil bitumen (primarily, oxidized bitumen) is the use of various polymers as modifiers. Polymer modified bitumen compared to conventional bitumen has a number of significant advantages. They are more elastic, flexible and durable, less sensitive to the temperature changes and aging, have better adhesive and cohesive properties.But the main reason that restrains thermoplastic elastomers prevalence is their high cost. An effective solution of this problem is their partial or complete replacement by cheaper polymers.

A promising direction is the production of modifiers from by-products of fossil fuels thermodestruction, which contain a sufficiently large amount of unsaturated compounds. The latter one can be used to produce modified bitumen, which meets regulatory requirements and has extremely high adhesion (till 100 %).

Using coumarone-indene resin as the modifier of road bitumen increases the softeningpoints from 47 to 52 °C and improves adhesive properties (adhesion to glass increases from 38 to 93%) but degrades plastic properties (especially penetration). Therefore to solve this problem it is necessary to use the plasticizer together with the modifier. It is recommended to use tar as the plasticizer. The commercial polymers modified bitumen 60/90-52 bitumen was obtained as a result of mixing road bitumen of BND 60/90 brand (85 wt. %), CIR (7 wt. %) and tar from West-Ukrainian oils (8 wt. %) at 110 °C.

Novolac phenol-cresol-formaldehyde resins were produced by the method of formaldehyde condensation polymerization and from the wide phenolic fraction, fraction IBP – 185 and 185 – EBP °C and from the raw phenols extracted from these fractions. The results achieved show that the use of raw phenols as the starting material is the most advisable for the synthesis of resins as this allows the resin yield to be increased nearly fourfold while loading the reactor (from 13.7–16.1 % wt to 51.9–58.4 % wt, respectively).

Modification of petroleum-derived road bitumens should be performed with phenol-cresol-formaldehyde resin that was obtained from raw phenols, extracted from the wide phenolic fraction of coal tar. It is counterproductive for the obtaining of resin to break up the wide phenolic fraction with phenol concentrate (fraction IBP – 185 °C) and concentrate of cresols (185 – EBP °C). It has been observed that with a content of 2.4 % by weight of phenol-cresol-formaldehyde resins in distilled (residual) and oxidized petroleum-derived road bitumens, there is an increase of 3 °C in the softening point and adhesive properties for the distilled bitumenby 56.7 % (from 60 to 94 %), for the oxidized one – by 106, 4 % (from 47 to 97 %).

РЕФЕРАТ

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БІТУМИ, МОДИФІКОВАНІ ПОЛІМЕРАМИ

У статті розглянуто основні способи модифікації бітумів полімерами. Встановлено, що використання полімерних модифікаторів дає змогу покращити експлуатаційні властивості бітумів. Проаналізовано позитивні і негативні аспекти використання різних груп полімерних модифікаторів (еластомери, термоеластопласти, реактопласти, термопласти). Показано досягнення кафедри хімічної технології переробки нафти та газу Національного університету «Львівська політехніка» в галузі модифікації бітумів полімерами: інден-кумароновою, нафтополімерними, фенол формальдегідними і епоксидними смолами.

Ключові слова: бітуми, модифіковані полімерами, еластомери, термоеластопласти, реактопласти, термопласти, інден-кумаронові смоли, фенолформальдегідні смоли.

РЕФЕРАТ

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БИТУМЫ, МОДИФИЦИРОВАННЫЕ ПОЛИМЕРАМИ

В статье рассмотрены основные способы модификации битумов полимерами. Установлено, что использование полимерных модификаторов позволяет улучшить эксплуатационные свойства битумов. Проанализированы положительные и отрицательные аспектыиспользования различных групп полимерных модификаторов (эластомеры, термоэластопласты, реактопласты, термопласты). Показано достижения кафедры химической технологии переработки нефти и газа Национального университета «Львовская политехника» в области модификации битумов полимерами: инден-кумароновой, нефтеполимерной, фенолформальдегидной и эпоксидной смолами.

Ключевые слова: битумы, модифицированные полимерами, эластомеры, термоэластопласты, реактопласты, термопласты, инден-кумароновые смолы, фенолформальдегидные смолы.

ABSTRACT

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POLYMER MODIFIED BITUMEN

The reasons for bitumen modification were analysed since bitumen is a main binder used at road coatings construction, including airports and airdromes. The main ways of bitumen modification by polymers were examined. Positive and negative aspects of the usage of different polymer modifiers (elastomers, thermoplastic elastomers, reactive polymers, thermoplastics) were analysed. Author's main achievements are described in the sphere of bitumen modification by polymeric compounds produced at by-product-coke plants: coumarone-indene and phenol-cresol-formaldehyde resins.

Key words: polymer modified bitumen, elastomer, thermoplastic elastomer, reactive polymer, thermoplastic, coumarone-indene resin, phenol formaldehyde resin.

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1.5 STATISTICAL METHODS IN VIRTUALIZATION

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The basis for virtualization is virtualization tools, including families of base functional means and base mathematical models [1]. Functional means usually use for synthesis or simulation of the software of various purpose, including processing of results of qualifying tests [2]. Base models use for testing the software, synthesis of identification models for is modelling – the focused control systems, and also algorithms of processing of results of qualifying tests.

An important component of the virtualization toolkit (see Fig. 1) is a statistical component to solve the following problems: identifications of statistical models by results of qualifying tests, parametrization criteria models for carrying out of forecasting within the limits of virtual qualification, synthesis regression models, the statistical analysis of their adequacy and consecutive optimization during factorial planning. Regression model in structure of the toolkit, calibrated by results of qualifying tests, use for planning qualifying experiments. As a rule, this planning is based on use of the sated plans and gives following opportunities to:

- research the importance and completeness of system of the entered factors;
- carry out consecutive optimization of the parameters corresponding significant factors, during qualifying tests;
- carry out forecasting qualifying tests with use calibrated regression models.

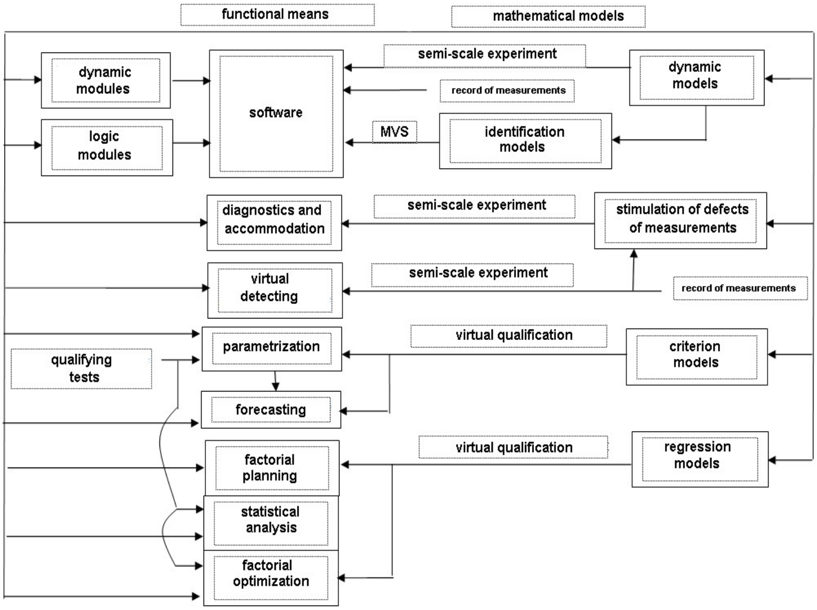


Fig. 1. Virtualization tools

Thus linearity used regression models allows to carry out the control of the importance of factors and completeness of their system over use of traditional statistical methods, and optimization of parameters by means of methods of linear programming.

The statistical analysis of adequacy regression models assumes use of some statistical criteria. In work [3] improvement of methods Cochran and Grubbs methods, providing them robustness and based on preliminary normalization of researched sample by means of corresponding Smirnov's transformation. It is shown, that the developed a process to ensure robustness reduces probability of error of the first sort at decision-making on reproducibility of results of qualifying experiment.

Distribution of Cochran's statistics on the basis of *F*–Fisher's distribution and Grubbs statistics on the basis of *T*–Student's distribution are constructed of following reasons. On the normalized samples of Student relations dispersions which then are analyzed by Cochran's criterion [3].

The decisive statistic of the Cochrane represents relation of the maximal private dispersion $\max\limits_{i=1\ldots l} S_i^2$ and the sum of private dispersions $S_1^2 + \cdots + S_l^2$ of Student relations. Here l is the number of measurement samples by which partial variances for student fractions are calculated. Each of them represents not displaced selective estimation of a kind:

,
$$S_{i1}^2 = \frac{S_{i1}^2 + \cdots + S_{il}^2}{l-1} \qquad (1)$$

$$S_{ij}^2 = \left(\xi_{ij} - \frac{1}{l}\sum_{k=1}^{l} \xi_{ik}\right)^2 \qquad (2)$$

Which can be transformed as follows:

$$C = \frac{\max\limits_{i=1\ldots l} S_i^2}{S_1^2 + \cdots + S_l^2} = \max_{i=1\ldots l} C_i \qquad (3)$$

$$C_i = \frac{S_i^2}{S_1^2 + \cdots + S_l^2} \qquad (4)$$

Under the assumption of the normality of the distribution of the numerator in C_i distributed on χ^2 with a degree of freedom *np-1,* and the denominator represents the sum *l* sizes with such distribution and therefore, it is distributed on χ^2 with a degree of freedom *l (np-1*). From here follows, that statistics $F_i = lC_i = \dfrac{\dfrac{S_i^2}{np-1}}{\dfrac{S_1^2 + \cdots + S_l^2}{l(np-1)}}$ has an f-Fisher distribution with degrees of freedom *np-1* and *l(np-1).* Statistics Kohren takes, thus, the form $C = \dfrac{F_M}{l}$, where $F_M = \max\limits_{i=1\ldots l} F_i$.

Similarly, the Grubbs criterion for normalized student relations is constructed. These relations form a variational series $\xi_1, \ldots, \xi_p$, the decisive statistics in which are the minimum and maximum Student ratios: $G_{\min}=\xi_1$, $G_{\max}=\xi_p$. In the case of normality of the sample student relations are distributed by Student, and serial statistics $G_{\min}$ and $G_{\max}$ have distributions of a kind $T_{n-1}^{p}(-G_{\min})$ and $T_{n-1}^{p}(-G_{\max})$, where T_{n-1} Student distribution with *n*–1 a degree of freedom. The decision on absence of reproducibility is accepted, if the condition

$T^{p}_{n-1}(-G_{\min}) > P$ or $T^{p}_{n-1}(-G_{\max}) > P$, where *P*– the set confidential probability is satisfied. Otherwise it is considered, that measurements are reproduced.

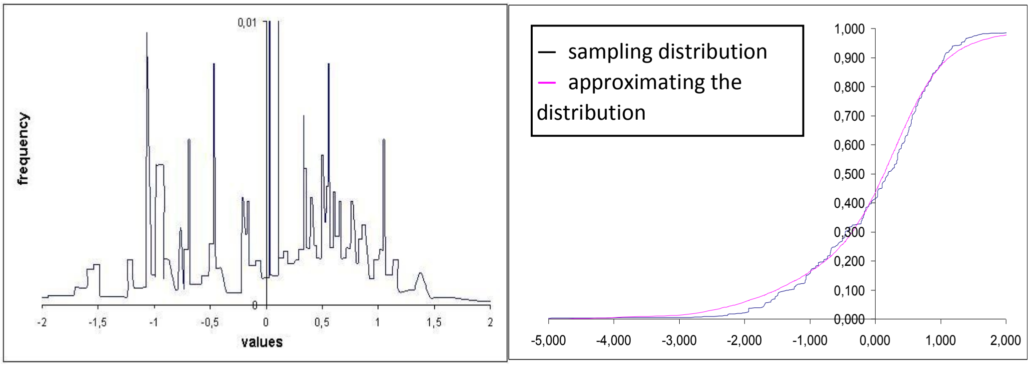
Is equivalent to the Grubbs criterion is the criterion Hawkins, crucial statistics which H is associated with statisticians $G_{\max}$, $G_{\min}$ ratio:

$$H = \max(|G_{\max}|, |G_{\min}|). \tag{5}$$

In view of that *H* is an ordinal statistic, its distribution under the assumption of normality of the General set of measurements has the form $(2T_{n-1}(H) - 1)^{p}$. The relevant decision rule is as follows: the decision on the absence of reproducibility of measurements, if $(2T_{n-1}(H) - 1)^{p} > P$, and about their reproducibility otherwise.

The important component of interlaboratory measurements of characteristics of mineral oil is identification of distribution of their error defining a technique of the further processing of measurements. The article [4] presents an analysis of the distribution of these errors, including measurements of density and viscosity is lead at temperatures 20 ^{o}C and 100 ^{o}C, and also temperatures distillate and flashes. The analysis of errors of measurements of these characteristics, lead by a method χ^2, has shown, that the assumption used usually about normality this distribution is represented superficial. In these conditions there is a necessity to lead identification of the specified law of distribution and on this basis to develop algorithm of rational processing of measurements.

Below some methods of construction of approximating distributions and their parametrization are considered. A starting point of construction of approximating distribution of an error of measurement of density, construction of the frequency histogram of the specified error displayed on Fig. 2.



Frequency histogram of density error

Fig. 2. Approximation of distribution of an error of measurement of density

It obviously specifies on bimodal character of distribution of an error of corresponding measurements. For approximation of this distribution it is offered to use distribution of a kind:

$$f(x) = \frac{exp\left(-\dfrac{(x-m_1)^2}{2\sigma_1^2}\right)}{2\sigma_1\sqrt{2\pi}} + \frac{exp\left(-\dfrac{(x-m_2)^2}{2\sigma_2^2}\right)}{2\sigma_2\sqrt{2\pi}}. \tag{6}$$

Corresponding integrated distribution is represented thus in the form of:

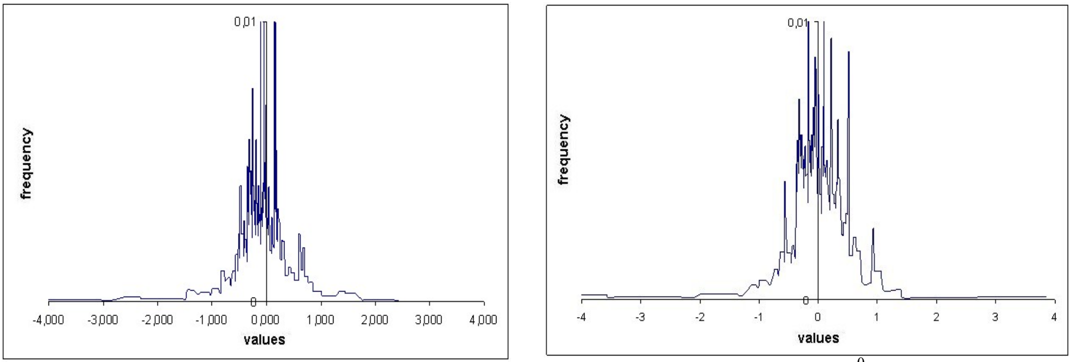
$$F = \frac{1}{2}\Phi\left(\frac{x-m_1}{\sigma_1}\right) + \frac{1}{2}\Phi\left(\frac{x-m_2}{\sigma_2}\right). \tag{7}$$

From expressions 6 and 7 it is visible, that approximating distribution includes following parameters:m_1, m_2 – population means of components of distribution;σ_1, σ_2 – root-mean-square errors of a deviation components of distribution.

For an estimation of these parameters it is offered to use a method of the moments which allows to receive for them system of the algebraic equations:

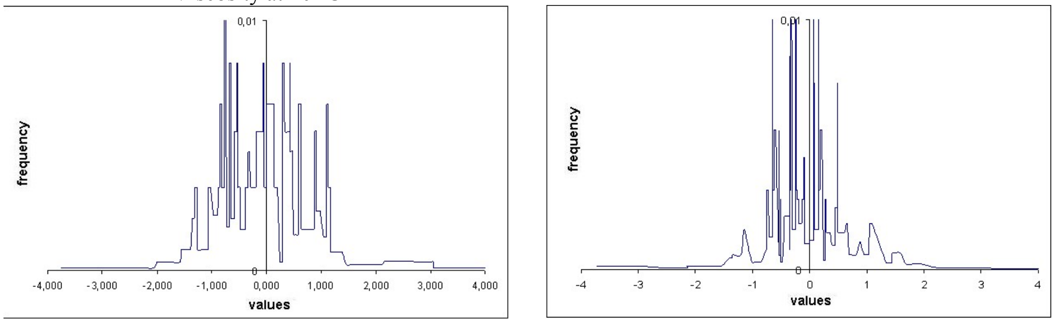
$$\begin{cases} \dfrac{m_1+m_2}{2}=m \\ \sigma_1^2=\sigma^2-\dfrac{m_2-m_1}{2}-\dfrac{A}{3\left(\dfrac{m_2-m_1}{2}\right)} \\ 3\left(\dfrac{m_2-m_1}{2}\right)\dfrac{\sigma_2^2-\sigma_1^2}{2}=A \\ 3\dfrac{\sigma_1^4-\sigma_2^4}{2}+\left(\dfrac{m_2-m_1}{2}\right)^4+6\left(\dfrac{m_2-m_1}{2}\right)^2\dfrac{\sigma_1^2-\sigma_2^2}{2}=E \end{cases} \tag{8}$$

Here A and E – selective asymmetry and an excess for sample of errors of measurements. The decision of the constructed system of the equations was carried out by a method of search on parameter m_1 in a range (0, m). Valuem_2 was for datam_1 from the first equation of system (8), σ_1^2 – from the second on setm_1 and calculate dm_2, and σ_2^2 – from the fourth equation which at setm_1 and calculated m_2,σ_1^2represents a quadratic rather σ_2^2. During a variation the parameterm_1 stole up so what to provide the minimal deviations of the calculated parameters from selective. Result of the calculation lead thus were following values of parameters: m_1 = -0.353; m_2 = 0.314; σ_1 = 1.384; σ_2 = 0.519.



Viscosity at 20 ^{0}C

Viscosity at 100 ^{0}C



Temperature distillate

Flash point

Fig. 3. Frequency histograms of an error of measurements

Substituting these values in expressions (6) and (7), we receive approximating distributions of an error of measurements of density. The result of comparison of integrated approximating distribution with selective is resulted on Fig. 2 and specifies qualitatively satisfactory approximation of distribution of the specified error.

Frequency histograms for the standardized error of measurements of other characteristics of mineral oil – viscosity at temperatures 20 °C and 100 °C, and also temperatures distillate and flashes – are resulted on Fig. 3 and specify unimodal character of distributions of an error of their measurements. As possible approximations of these distributions in work [4] were considered alongside with normal Pearson and Weibull approximation, and also lognormal. Parametrization of these distributions also was carried out by a method of the moments. The lead comparative analysis of the constructed approximations of unimodal distributions of an error shows, that the best on accuracy is approximation by the Weibull. Comparison of the received distributions of an error with bimodal approximation for an error of measurement of density, and Weibull approximation for an error of measurement of other characteristics specifies sufficiency of used approximations.

The modified algorithm of the control of reproducibility of interlaboratory measurements is based on alignment of the last by transition to Student fractions that allows to carry out the control of reproducibility over measurements of changing sizes. However in case of normal sample of measurements distribution of Student fractions appears standard and cannot be used for the control of reproducibility. Therefore Student's relation is expedient for defining in the form of $\xi = \frac{x - m}{s(m)}$, where $s(m)$ – approximation of dependence standard deviation from a population mean. Thus transformation of measurements in Student's relation provides precomputation mathematical expectations and standard deviation, corresponding different levels. They are used to construct the function $s(m)$ of linear regression which together with settlement population means is used for construction of fractions of Student's relation.

The further statistical conclusions base on the analysis of constructed Student fractions which are analyzed by Grubb's criterion. In case of non-reproducibility measurements by Grubb's criterion, a series corresponding extreme statistics, is rejected. The defective series leaves from sample of measurements, and solving statistics recalculate for the remained levels in the assumption, that approximation $s(m)$ remains constant. It can be interpreted as replacement of the defective series such which does not change approximation, i.e. we neglect influence of an abnormal series on last. If and in the truncated sample it appears possible to allocate an abnormal series, the assumption of weak influence of the rejected series on approximation is considered insolvent and it is necessary to carry out recalculation of approximation without taking into account the defective series.

On the samples of Student's relation generated thus dispersions, which then are analyzed by Cochran's criterion. It is serial and has distribution $F^l\big(F_m, np - 1, l(np - 1)\big) = F^l\big(lC, np - 1, l(np - 1)\big)$, where F – Fisher's distribution. The condition of heterogeneity in these conditions looks like $F^l\big(lC, np - 1, l(np - 1)\big) > P$, where P– confidential probability of the decision about non-reproducibility. At default of this condition the decision on uniformity of sample, and, hence, makes of reproducibility. Thus, the modified algorithm of the control of reproducibility is applied in conditions of possible change of measured sizes. In this sense it differs universality from a usual technique of the classification focused on an invariance of measured values. Use of alignment of measurements by transition to Student fractions allows to apply this technique without any restrictions.

According to [5] criteria model allows to carry out forecasting by results of the qualifying tests spent in set conditions. There is, however, a question on a choice of such conditions which would provide the guaranteed forecast – for example, its top border. The problem of a preliminary choice of extreme conditions of qualifying tests for which decision it is offered to use a method of factorial planning of experiment from here follows. The statistical processing of these measurements displayed on Fig. 4, includes: an estimation of reproducibility of multiple measurements by the analysis of their disorder; construction linear-regression models and an estimation of the importance of the entered factors; the analysis of adequacy of model and an estimation of completeness of system of the entered factors.

For an estimation of reproducibility of measurements Cochran's criterion is used. It provides calculation of dispersions of multiple measurements, formation on them Cochran's statistics and calculation of probability of its realization. This probability is compared to confidential probability non-reproducibility measurements. If the calculated probability appears below confidential, the hypothesis about reproducibility of measurements is accepted. Their dispersions thus are averaged, forming a dispersion of reproducibility. Otherwise a series of measurements is considered abnormal and should be repeated.

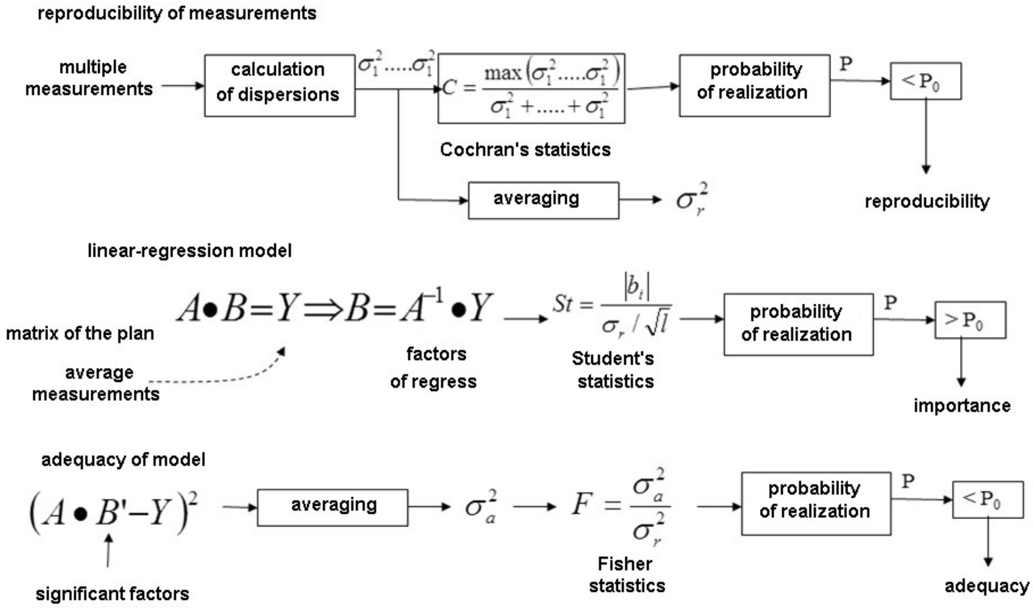


Fig. 4. Statistical processing of measurements

Calculation of factors of regress is carried out from following reasons. The matrix of the plan for not fictitious factors is nondegenerate matrix of system of the linear equations which right part is the vector of the average measurements. The vector of the factors interpreted as loading of factors, represents the decision of the specified system.

For an estimation of the importance of factors are used Student relations, the decision on which is accepted by Student criterion. For this purpose, student statistics are calculated for factors of regress and probability of their realization. Significant factors are considered, probabilities of realization of statistics Стьюдента for which exceed confidential. Other factors of regress are considered insignificant and in model should be nulled.

The control of adequacy linearly-regression models (completeness of system of the entered factors) is carried out by Fisher's criterion with use of the relation of a dispersion of adequacy to a dispersion of reproducibility. For this purpose the average square of a deviation of the average measurements from regression models, in which significant factors of regress. This size is interpreted as a dispersion of adequacy. After it and a dispersion of reproducibility Fisher's statistics is under construction and the probability of its realization. The decision on adequacy is accepted, if the specified probability below confidential. Otherwise the model is considered inadequate, that, as a rule, means loss of essential factors at its construction.

Two-level factorial planning can be used for consecutive optimization of parameters of researched object or qualifying experiment. As local optimum thus are reached in tops multidimensional simplices, corresponding lines of the two-level plan, search of a global extremum is offered to be carried out a method of successive approximation. Consecutive optimization provides use of points of the reached local extremum as the centers of new areas in parametrical space.

When using a linear regression models search of an extremum represents a problem of linear programming for the closed area of factorial values in the form of a multivariate simplex. The local extremum of linear regress is reached thus in one of tops of area and, hence, is equal to the extreme average measurement corresponding one lines of the plan of experiment. The simplex-planning provides inclusion in factorial area also the simplex symmetric considered.

It corresponds to the plan of the experiment with the inverted matrix of factors, and the common area of search of an extremum according to Fig. 5 is formed initial, symmetric and additional simplices, adjoining to the beginning of coordinates.

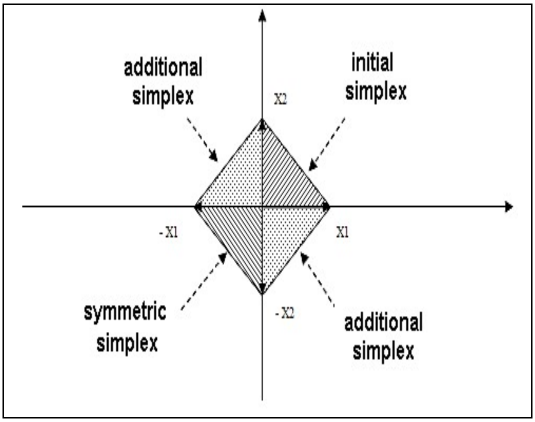


Fig. 5. Expansion of factorial area

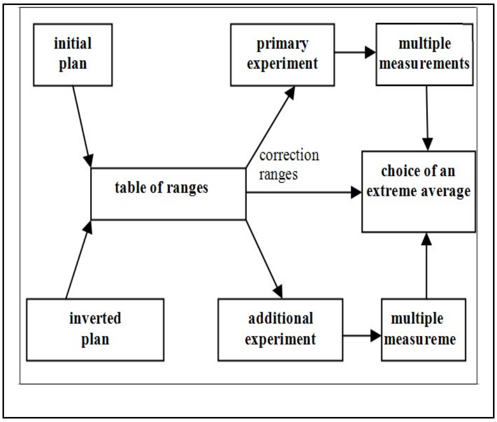


Fig. 6. Statistical processing of measurements

At the expanded planning displayed on Fig. 6, for formation of tables of parameters the initial and inverted plans are used. According to these tables qualifying tests during which multiple measurements are carried out are spent. Processing of these measurements is carried out in two stages. During primary processing search of the extreme average measurement which parameters are compared with the new center of ranges is carried out. To this center there corresponds the corrected range of parameters used for realization of following approach of procedure of search. If the extremum reached in following approach is more extreme" previous, procedure proceeds. Otherwise it stops also to a global extremum value previous local is compared. Parameterization of the criterion mode by results of qualifying tests in extreme conditions allows to lead forecasting of frictional deterioration in these conditions and to generate on this basis the guaranteed norms of deterioration.

Interesting example of application of statistical methods in problems virtualization is factorial planning in the analysis of criteria of similarity [6.] Criterial models are natural base for virtualization qualifying tests as the last are based on physical model of researched object or process in the form of laboratory installation [7]. The experiments spent on it, allow to carry out parameterization of the criterion model that then to use it for recalculation of laboratory results in operational characteristics, and also for return recalculation of operational conditions in parameters of qualifying tests.

The important problem at a substantiation of invariancy of used criteria of similarity is their representation in the form of functions from standard numbers of similarity as their invariancy provides invariancy of the constructed criterion. Often this function is multiplicative-power, i.e. it is represented in the form of:

$$K = K_0 N_1^{\beta_1} \ldots . N_l^{\beta_l} , \tag{9}$$

where $N_{1,}$.... N_l – used numbers of similarity, and $\beta_{1,}$.... β_l – their degrees in structure of criterion.

The logarithm of criterion (3) transforms the multiplicative-power function into a linear combination $\ln K_0 + \beta_1 \ln N_1 + \ldots + \beta_l \ln N_l = \ln K.$ Logarithms of numbers of similarity are interpreted as natural parameters, standard image converted in two-level factors, and the linear combination constructed above for natural parameters with a priori uncertain factors is transformed to linear regress for these factors. Its factors are a subject to definition according to the results of calibration experiments. For the decision of this problem two-level factorial planning is traditionally used. The factors defined on the basis of natural parameters, are not fictitious, but can be added by fictitious factors as part of the linear regression model.

The matrix of two-level planning is a matrix of factors in linear system of the equations for factors of regress, including fictitious. The right part of this system are «measurements» – values of the logarithm of criterion the similarity corresponding borders of natural parameters in structure of a linear combination. The analysis of the importance of counted factors of regress and adequacy of the linear regression model as a whole are carried out by standard statistical methods.

As an example of the offered approach the analysis of criterion of frictional deterioration in a greasing liquid is considered. The given criterion looks like [8]:

$$Vw = \frac{pv\Delta V}{\mu N t} \tag{10}$$

where p – density of a wearing out material, v – speed of sliding, ΔV – size of volumetric deterioration, μ – factor of friction, N – normal loading on a rubbing surface, t – duration of deterioration. Physical sense of this criterion – the ratio of the wear material pulse to the friction force pulse.

Let's present the given criterion in the form of linear function of numbers of similarity:

$$\ln(Vw) = \beta_0 + \beta_1(\ln St) + \beta_2(\ln So) + \beta_3(\ln Re) + \beta_4(\ln De) \tag{11}$$

where – factor of proportionality; $St = \frac{vt}{D}$ Strouhal number (homochronity); D – maximum diameter of the wear band of the ball; $S_0 = \frac{\eta v}{\mu \frac{N}{D^2} \Delta L}$ – number of Sommerfeld; η – dynamic viscosity of the liquid; ΔL – depth of wear of the ball; $Re = \frac{p_f v \Delta L}{\eta}$ – Reynolds number, ρ_f – liquid density; $De = Re\sqrt{\frac{d}{D}}$ – Dean's number; d – minimum diameter of the wear band of the ball.

For recalculation of natural parameters in corresponding factors we use ratio:

$$\begin{aligned} x_1 &= 2\frac{\ln St - (\ln St)_{min}}{(\ln St)_{max} - (\ln St)_{min}} - 1 \\ x_2 &= 2\frac{\ln So - (\ln So)_{min}}{(\ln So)_{max} - (\ln So)_{min}} - 1 \\ x_3 &= 2\frac{\ln Re - (\ln Re)_{min}}{(\ln Re)_{max} - (\ln Re)_{min}} - 1 \\ x_4 &= 2\frac{\ln De - (\ln De)_{min}}{(\ln De)_{max} - (\ln De)_{min}} - 1 \end{aligned} \tag{12}$$

The borders of the natural parameters calculated by results of mentioned above experiments, are resulted in [6]. Thus to boundary values of natural parameters there correspond values of factors -1 and 1. Return recalculation of factors in natural parameters is carried out according to ratio:

$$\begin{aligned} \ln St &= (\ln St)_{min} + ((\ln St)_{max} - (\ln St)_{min})\frac{x_1 + 1}{2} \\ \ln So &= (\ln So)_{min} + ((\ln So)_{max} - (\ln So)_{min})\frac{x_2 + 1}{2} \\ \ln Re &= (\ln Re)_{min} + ((\ln Re)_{max} - (\ln Re)_{min})\frac{x_3 + 1}{2} \\ \ln De &= (\ln De)_{min} + ((\ln De)_{max} - (\ln De)_{min})\frac{x_4 + 1}{2} \end{aligned}$$

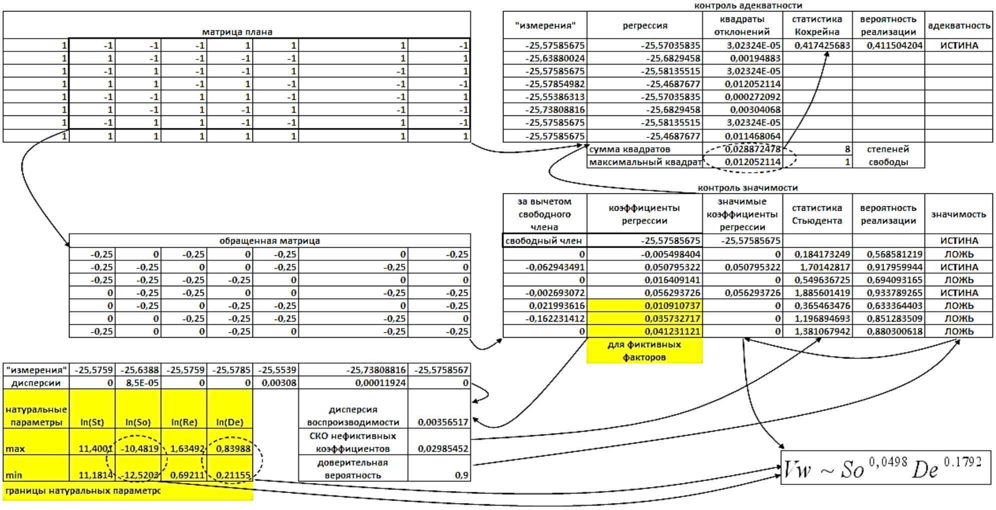
Substituting them in (12), we receive for regress of criterion concerning not fictitious factors $\ln(Vw) = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4$, where:

$$\begin{aligned} b_0 = \beta_0 &+ \frac{(\ln St)_{max} + (\ln St)_{min}}{2} + \frac{(\ln So)_{max} + (\ln So)_{min}}{2} + \frac{(\ln Re)_{max} + (\ln Re)_{min}}{2} \\ &+ \frac{(\ln De)_{max} + (\ln De)_{min}}{2} \\ b_1 &= \beta_1 \frac{(\ln St)_{max} - (\ln St)_{min}}{2} \\ b_2 &= \beta_2 \frac{(\ln So)_{max} - (\ln So)_{min}}{2} \\ b_3 &= \beta_3 \frac{(\ln Re)_{max} - (\ln Re)_{min}}{2} \\ b_4 &= \beta_4 \frac{(\ln De)_{max} - (\ln De)_{min}}{2} \end{aligned} \tag{13}$$

Construction of the regular plan for the analysis of influence of the entered factors is carried out on the basis of a fractional retort of full factorial experiment. Thus the number m factors in structure of this experiment should satisfy the condition $2^{m-1} < l + 1 \leq N = 2^m$, where l – the number of not fictitious factors certain above, and N– the common number of factors equal nearest dominating to the degree of the two. Considering this circumstance, it is necessary to enter into a ratio for regress additional fictitious factorsx$_5$, x$_6$, x$_7$. As a result it gets a kind:

$$\ln(Vw) = b_0 + b_1 x_1 + b_2 x_2 + b_3 x_3 + b_4 x_4 + b_5 x_5 + b_6 x_6 + b_7 x_7 \tag{14}$$

The matrix of planning thus corresponds to a fractional retort 2^{7-4} full factorial plans which is resulted on Fig. 7. Characteristic property of this matrix is centeredness its columns, except for the first. From here follows, that the free memberb$_0$ in expression for regress is equal to an average of the right parts of the equations of linear system. Proceeding from it, we shall accept it in the further equal to result of averaging ln(Vw) on all lead experiments. The truncated matrix of the plan concerning factors of regress for the remained factors is allocated on Fig. 7.



матрица плана							
1	-1	-1	-1	1	1	1	-1
1	1	-1	-1	-1	-1	1	1
1	-1	1	-1	-1	1	-1	1
1	1	1	-1	1	-1	-1	-1
1	-1	-1	1	1	-1	-1	1
1	1	-1	1	-1	1	-1	-1
1	-1	1	1	-1	-1	1	-1
1	1	1	1	1	1	1	1

контроль адекватности

"измерения"	регрессия	квадраты отклонений	статистика Кохрейна	вероятность реализации	адекватность
-25,57585675	-25,57035835	3,02324E-05	0,417425683	0,411504204	ИСТИНА
-25,63880024	-25,6829458	0,00194883			
-25,57585675	-25,58135515	3,02324E-05			
-25,57854982	-25,4687677	0,012052114			
-25,55386313	-25,57035835	0,000272092			
-25,73808816	-25,6829458	0,00304068			
-25,57585675	-25,58135515	3,02324E-05			
-25,57585675	-25,4687677	0,011468064			
	сумма квадратов	0,028872478	8	степеней свободы	
	максимальный квадрат	0,012052114	1		

контроль значимости

за вычетом свободного члена	коэффициенты регрессии	значимые коэффициенты регрессии	статистика Стьюдента	вероятность реализации	значимость
свободный член	-25,57585675	-25,57585675			ИСТИНА
0	-0,005498404	0	0,184173249	0,568581219	ЛОЖЬ
-0,062943491	0,050795322	0,050795322	1,70142817	0,917959944	ИСТИНА
0	0,016409141	0	0,549636725	0,694093165	ЛОЖЬ
-0,002693072	0,056293726	0,056293726	1,885601419	0,933789265	ИСТИНА
0,021993616	0,010910737	0	0,365463476	0,633364403	ЛОЖЬ
-0,162231412	0,035732717	0	1,196894693	0,851283509	ЛОЖЬ
0	0,041231121	0	1,381067942	0,880300618	ЛОЖЬ
	для фиктивных факторов				

обращенная матрица						
-0,25	0	-0,25	0	-0,25	0	-0,25
-0,25	-0,25	0	0	-0,25	-0,25	0
-0,25	-0,25	-0,25	-0,25	0	0	0
0	-0,25	-0,25	0	0	-0,25	-0,25
0	-0,25	0	-0,25	-0,25	0	-0,25
0	0	-0,25	-0,25	-0,25	-0,25	0
-0,25	0	0	-0,25	0	-0,25	-0,25

"измерения"	-25,5759	-25,6388	-25,5759	-25,5785	-25,5539	-25,73808816	-25,5758567
дисперсии	0	8,5E-05	0	0	0,00308	0,00011924	0
натуральные параметры	ln(St)	ln(So)	ln(Re)	ln(De)		дисперсия воспроизводимости	0,00356517
max	11,4001	-10,4819	1,63492	0,83988		СКО нефиктивных коэффициентов	0,02985452
min	11,1814	-12,5203	0,69211	0,21155		доверительная вероятность	0,9
границы натуральных параметрс							

$Vw \sim So^{0,0498} De^{0.1792}$

Fig. 7. Statistical analysis of criterion of similarity

Thus, for calculation of factors of regress b_1, …., b_7 the truncated matrix of the plan is used, and the right part of linear system represents average "measurements" minus a free member. The vector of factors of regress represents the decision of this linear system calculated by multiplication of the turned matrix of the plan to the vector of the right parts certain above. Thus it is necessary to consider, that factors x_5, x_6, x_7 are fictitious and the sum of squares of factors corresponding them is summarized with the average dispersion calculated on repeating «measurements», giving a dispersion of reproducibility σ^2. Carrying it to quantity of not fictitious factors $l = 4$, we receive a dispersion of an estimation of corresponding factors of regress and its root-mean-square deviation $s_b = \dfrac{\sigma}{\sqrt{l}}$.

For an estimation of the importance of factors of regress at not fictitious factors $b_1 ... b_4$are used the statistics $\dfrac{|b_1|}{s_b} ... \dfrac{|b_4|}{s_b}$, distributed over the Student with the number of degrees of freedom l .

The probabilities of implementing these statistics are $T_l\left(\dfrac{|b_1|}{s_b}\right) ... T_l\left(\dfrac{|b_4|}{s_b}\right)$, where $T_l$is the Student distribution with l degrees of freedom. The decisive rule for confirming the significance of the i-th coefficient is as follows $\mathrm{T_l}\left(\dfrac{|\mathrm{b_1}|}{\mathrm{s_b}}\right) > \mathrm{P} = 0{,}9$, where P is the confidence probability of making a decision on significance. Factors of regress for which these conditions are not carried out, considered insignificant and are equated to zero. The results of calculations displayed on Fig. 4, show, that significant, i.e. nonzero, factors b_2 andb_4, corresponding to the similarity numbers of Sommerfeld and Dean. Other factors are insignificant and consequently dependence on the Strouhal and Reynolds criteria is ignored.

For the control of adequacy of the received regress the mismatch between average «measurements» and values of regress in each line of the plan. For calculation of these values the line of the plan is multiplied by a vector of significant factors of the regress, displayed on Fig. 7.

The decision on the adequacy of the linear-regression model is taken by the Cochran criterion. The decisive statistic is Cochrane C – the ratio of the maximum square of deviation to the sum of the squares of deviations. The probability of realization of this statistics makes $F^N(C,1,N)$, where F – Fisher's distribution. The decisive rule in this case is as follows: a decision is made on the adequacy if the probability of realization is lower than the confidence value 0.9, and on the lack of adequacy otherwise. Results of calculation of statistics C and probabilities of its realization also are resulted on Fig. 7. As the received probability below confidential value, is accepted a hypothesis about adequacy constructed linear-regression model.

For formation of a final kind of criterion of similarity it is necessary to transform preliminary significant factorsb_2 andb_4 to factors β_2 and β_4, entering in (9). It is carried out by the reference of corresponding expressions in (13):

$$\begin{gathered} Vw \sim So^{\beta_2} De^{\beta_4} \\ \beta_2 = \frac{2b_2}{(\ln So)_{max} - (\ln So)_{min}} = 0.0498 \\ \beta_4 = \frac{2b_4}{(\ln De)_{max} - (\ln De)_{min}} = 0.1792 \end{gathered} \tag{15}$$

The lead consideration shows, that factorial planning can be used for a substantiation of invariancy of a wide class of entered criteria of similarity, and also for the proof of adequacy of their representation depending on standard numbers of similarity. Advantage of the offered approach is that it can be used practically without restrictions of a generality and is based on well developed methods of the factorial and statistical analysis.

The usual technique estimation precisions corresponds to the standard approach to processing complex experiment. It differs possible distinction of the sizes measured in consecutive series. The basic in these conditions is the research problem of influence of considered factors on the measured size. Research of reproducibility is auxiliary in these conditions and is intended for branch of influence of an error of measurements from influence of considered factors. Other situation arises at the analysis precisions interlaboratory researches. Research of influence of factors thus becomes secondary, and the main thing becomes research of interlaboratory reproducibility [9]. A problem of interlaboratory comparative tests is the analysis of competence of laboratories, and also them rejection on the basis of incompetence. Below the statistical analysis algorithm of competence of the laboratories participating in specified tests is developed. The algorithm is based on preliminary standardization of spent measurements by their transformation to corresponding Student. Conditions of incompetence of laboratory are formulated in case of is abnormal the big error of measurements and in case of the several moderate errors.

In a basis of the given analysis lays the approach providing comparative measurements of polytypic standard samples of substances and materials, and also their rational processing with use of methods of the dispersive analysis. The purpose of the last is decomposition of a total dispersion on two sizes: a dispersion caused by technics of experiment, and a dispersion caused by action of the researched factor. In case of multifactorial experiment the dispersions corresponding various factors and their interactions are defined, and also the statistical importance of these sizes in view of an error of reproducibility is estimated.

Competence of laboratory is defined by reproducibility of results of comparative tests which is provided in turn with statistical uniformity of sample of the lead measurements. Traditional methods of the analysis of this uniformity are the comparative analysis of serial dispersions of researched sample or serial Student relations.

Quite often, the following parametric criteria are used to solve this problem: Cochrane, based on the comparison of the maximum of serial variances with their sum, and Grubbs (or Hawkins), based on the analysis of anomalies of extreme values in serial samples of student relations for measurements.

Preliminary stage of processing is standardization of made measurements. For the given standard sample it is carried out by transition from measurements of the characteristic of this sample to Student fractions, constructed according to these measurements. The last are formed according to ratio:

$$\xi_i = \frac{x_i - m}{s}$$
$$m = \frac{\sum_{k=1}^{L} x_k}{L} \qquad (16)$$
$$s = \sqrt{\frac{\sum_{k=1}^{L}(x_k - m)^2}{L-1}}$$

wherex_i– interlaboratory measurements of the standard sample; m, s– sizes of an average and standard deviation measurements; L – quantity of laboratories-participants.

In these conditions for the decision of a problem of processing of the standardized measurements it is natural to use criterion Hawkins with selective averages and standard deviation, counted on serial samples. Crucial statistics in this case are $Y = \max_{i=1\ldots n} \xi_i$ and $= \min_{i=1\ldots n} \xi_i$, and conditions of anomaly of extreme measurements in a series become:

$$(2T_{L-1}(H) - 1)^L > P$$
$$H = \max(|Y|, |y|) \qquad (17)$$

This condition can be interpreted as the first condition of incompetence: the laboratory in which corresponding measurement is lead, is considered incompetent.

One more condition of incompetence is connected with calculation of unsatisfactory measurements from all lead in given laboratories. Satisfactory the measurements close to an average m, and unsatisfactory – strongly deviating from it are considered. As these measurements concern to various samples, they also are preliminary standardized by transformation to Student relations. At transition to them satisfactory the values of fractions located in a vicinity *0*, and unsatisfactory-laying outside of this vicinity are considered.

We shall be set by probability p insufficiency of measurement. Considering, that Student fractions have T – distribution c L-1 a degree of freedom, we find for threshold H of decision-making on the specified insufficiency:

$$2T_{L-1}(H) - 1 = 1 - p \qquad (18)$$

Satisfactory it is considered value Student fraction smaller H, and unsatisfactory – greater H. Distribution of probabilities of quantity of unsatisfactory measurements n from N lead in given laboratories is binomial with parameters p and N. Being set by confidential probabilityP_{II} rejectionson number of unsatisfactory measurements, we receive solving rule for specified rejections:

$$\sum_{k=0}^{n} C_N^k p^k (1-p)^{N-k} > P_{II} \qquad (19)$$

The condition (19) is interpreted as the second condition of incompetence. The laboratory in which from N the lead measurements n are unsatisfactory, is considered incompetent at performance of this condition and competent otherwise.

Let's consider sense of the deduced conditions of incompetence. For this purpose we shall compare conditions (17) and (18) in the assumption, that $P_I = 1$-p. Assuming also, that in (17) equality takes place, we find from this comparison, that $\xi > H$. Thus, the first condition of incompetence is carried out in case of an abnormal error even one of the lead measurements. The second condition means, that the laboratory is considered incompetent in case of the several moderate errors in the lead measurements.

The modified algorithm of the control of interlaboratory reproducibility is applied in conditions of possible change of measured sizes. Use of alignment of measurements by transition Student fractions allows to apply it without any restrictions. All this enables to simplify algorithm of the control of reproducibility and to use it as a basis for correction of standard techniques of the specified control.

Efficiency of application of fractional retorts of the full factorial plan increases with growth of number of not fictitious factors. It also depends on a successful choice of system of mixing of linear effects with effects of interaction of factors, and also rationality of the plan of factorial experiments in case of the importance of separate interactions. Thus aprioristic data on the specified interactions frequently appear not only desirable, but also necessary. Below it is considered some other, intuitive method of ranging of factors in linearly-regression models with use of the sated plans and the subsequent elimination of the least loaded factors [10]. Its basic advantage, alongside with simplicity of realization, use is at the analysis only not fictitious factors.

Preliminary stage of the considered approach is ranging of factors on the importance with use of the sated plans. To these plans corresponds linear regression model of a kind $\hat{y} = b_0 + b_1 x_1 + \cdots + b_k x_k$, which factors are defined from system of the equations

$$\begin{cases} b_0 + b_1 x_{11} + \cdots + b_k x_{k1} = y_1 \\ \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \\ b_0 + b_1 x_{1k} + \cdots + b_k x_{kk} = y_N \end{cases} \tag{20}$$

The matrix of this system is nondegenerate matrix of the sated plan and thereof the specified system is authorized unequivocally. The importance of factors$x_1 \dots . x_k$ in linear-regression model we shall define relative loadings $L_i = \frac{|b_i|}{\Delta}$, where $\Delta = y_{max} - y_{min}$ – a range of measurements in a series, $i = 1 \ \dots \ .k$. We shall consider a situation when the number k researched factors satisfies to a condition $2n\text{-}1 = l < k < 2^{n+1}\text{-}1$, where n– number of factors of the full factorial experiment corresponding the regular sated plan. To this situation there corresponds a set of the regular sated plans for l the factors chosen from the common number of factors k. Number of these plans and, hence, necessary number of series of experiments equally $p = C_k^l$.

Let's take advantage for construction of the specified plans by a method of making functions. The last represent formal sedate numbers, final or Taylor for analytical function. In case of the combinatory analysis of combinations that fact is used, that at formation of a combination independent selection of elements is carried out. The rule of multiplication of probabilities allows to use representation of making function in the form of product of linear binomial from an independent variable. Factors of decomposition of this product correspond to factors at various combinations. We shall assume as an example that influence of five factors by means of the plans covering three factors is researched. Making function in this case looks like $\Pi(t) = (1 + x_1 t) \dots (1 + x_5 t)$. After carrying out of multiplication it is found for factors at degrees t:

$$\begin{aligned} &t^0: 1 \\ &t^1: x_1 + \cdots + x_5 \\ &t^2: x_1x_2 + x_1x_3 + x_2x_3 + x_1x_4 + x_2x_4 + x_3x_4 + x_1x_5 + x_2x_5 + x_3x_5 + x_4x_5 \\ &t^3: x_1x_2x_3 + x_1x_2x_4 + x_1x_3x_4 + x_2x_3x_4 + x_1x_2x_5 + x_1x_3x_5 + x_1x_4x_5 + x_2x_3x_5 \\ &t^4: x_1x_2x_3x_4 + x_1x_2x_3x_5 + x_1x_2x_4x_5 + x_1x_3x_4x_5 + x_2x_3x_4x_5 \\ &t^5: x_1x_2x_3x_4x_5 \end{aligned} \tag{21}$$

These factors are interpreted as sets of the sated plans corresponding samples of certain number of factors from five. To the samples including three factors from five, there corresponds factor at t^3, i.e. a set of plans of the kind $x_1x_2x_3 + x_1x_2x_4 + x_1x_3x_4 + x_2x_3x_4 + x_1x_2x_5 + x_1x_3x_5 + x_1x_4x_5 + x_2x_3x_5$ corresponding replicas 2^{5-3}. For each of the plans chosen by such principle a series of three times repeating experiments is spent. Factors of regress for each of these plans unequivocally according to (20), where $y_1 ..... y_N$ are interpreted as a median of repeating measurements. In turn, on the found factors loadings for the factors covered by a given series. As each factor is covered *P-1* by a series of experiments, for it the same number of relative loadings $L_{i1} ..... L_{iP-1}$, counted in view of change of a range of measurements from a series to a series turns out. The maximal loadings from received $L_{imax} = max(L_{i1} ..... L_{iP})$, $i = 1...k$, are considered as characteristics of the importance of factors... k on which ranging is carried out.

Relative maximal loadings $L_{1max} ..... L_{kmax}$ can be used also for rational elimination of insignificant factors. We shall assume without restriction of a generality, that number $L_{1max} ..... L_{kmax}$ represents result of ranging of loadings on decrease, and we form an equivalent number $\frac{L_{1max}}{L} \cdots \frac{L_{1max}}{L}$, where $L = L_{1max}$. We shall expose a threshold on the importance, for example, $h=0,05$, and all the factors, satisfying to a condition $\frac{L_{1max}}{L} < h$, we shall consider insignificant. This intuitive method of elimination is more simple in comparison with traditional statistical elimination. Its basic advantage, alongside with simplicity of realization, use is at the analysis only not fictitious factors. The basic lack, alongside with intuitivism, absence of a regular technique of a choice of a threshold of the importance which should be chosen intuitively is.

The lead consideration shows, that the statistical component of virtual toolkit covers the broad audience of problems of processing of results of qualification. Procedures used at it are led to an analytical kind and provide sufficient severity of the analysis. At the same time, they are based on standard approaches and are rather simple in circulation.

The Important component virtualization toolkit is the statistical component for the decision of following problems: identifications of statistical models by results of qualifying tests, parametrization criteria models for carrying out of forecasting within the limits of virtual qualification, synthesis regression models, the statistical analysis of their adequacy and consecutive optimization during factorial planning. Thus linearity regression models allows to carry out the control of the importance of factors and completeness of their system over use of traditional statistical methods, and also optimization of parameters by means of methods of linear programming.

Identification of distributions of measurements of various parameters of mineral oil specifies their abnormality. As alternative approximation bimodal the multipleparameter distribution representing the sum differing normal was offered to use distributions of density. Unimodular distributions of other characteristics are approximated are approximated by the Weibull. Parametrization of the constructed distributions was carried out by a method of the moments that provides sufficiency of used approximations.

For an estimation of reproducibility of results of qualifying experiments have been constructed analytical distribution of Cochran's statistics on the basis of *F*–Fisher's distribution and Grubbs statistic on the basis of *T*–Student's distribution. It is shown, that preliminary normalization allows to avoid the unreasonable conclusion about heterogeneities of the studied sample. That the probability of an error of the first sort decreases at decision-making on reproducibility of results of qualifying experiment.

Parametrization criteria model by results of qualifying tests is offered for spending models by results of forecasting effect in extreme conditions that allows to generate the guaranteed qualifying specifications. The preliminary choice of extreme test specifications at qualifying normalization is offered for carrying out a method consecutive approximations with use of factorial planning.

The approach for a substantiation of invariancy of a wide class of criteria of similarity Is offered.. The Approach is based on interpretation of the logarithm of criterion as linear form from the logarithms of numbers of similarity treated as independent factors. The estimation of factors of the specified form – loadings of factors – is carried out with use of the factorial analysis and includes also the proof of adequacy of the specified representation. Advantage of the offered approach is the opportunity of its application without restrictions of a generality.

The intuitive method of ranging of factors in the linear-regression model with use of the sated plans and the subsequent elimination of the least loaded factors Is developed. Its basic advantage, alongside with simplicity of realization, use is at the analysis only not fictitious factors, and the basic lack – absence of a regular technique of an establishment of thresholds of the importance which should be chosen intuitively.

РЕФЕРАТ

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СТАТИСТИЧНІ МЕТОДИ В ЗАДАЧАХ ВІРТУАЛІЗАЦІЇ

Показана важливість віртуалізаційного інструментарію вирішення завдань ідентифікації статистичних моделей за результатами кваліфікаційних випробувань.

В ході ідентифікації встановлена ненормальність розподілів похибки вимірювань характеристик нафтопродуктів. Для побудови алгоритмів обробки вимірювань синтезовано ряд альтернативних аппроксимаций. Для оцінки відтворюваності результатів віртуальної кваліфікації побудовані розподіли статистики Кохрейна і статистики Граббса. Параметризацію критеріальної моделі запропоновано проводити за результатами прогнозування ефекту в екстремальних умовах. Вибір умов запропоновано здійснювати методом послідовних наближень в рамках факторного аналізу.

Ключові слова: інструментарій, ідентифікація, параметризація, критеріальна модель, прогнозування, регресійна модель, факторне планування, лінійне програмування, бімодальний розподіл, апроксимація, статистика Кохрейна, статистика Граббса, кваліфікаційні нормативи, критерій подібності, число подібності, фіктивний фактор, значущість, ранжування.

РЕФЕРАТ

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СТАТИСТИЧЕСКИЕ МЕТОДЫ В ЗАДАЧАХ ВИРТУАЛИЗАЦИИ

Показана важность виртуализационного инструментария решения задач идентификации статистических моделей по результатам квалификационных испытаний.

В ходе идентификации установлена ненормальность распределений погрешности измерений характеристик нефтепродуктов. Для построения алгоритмов обработки измерений синтезирован ряд альтернативных аппроксимаций. Для оценки воспроизводимости результатов виртуальной квалификации построены распределения статистики Кохрейна и статистики Граббса. Параметризацию критериальной модели предложено проводить по результатам прогнозирования эффекта в экстремальных условиях. Выбор условий предложено осуществлять методом последовательных приближений в рамках факторного анализа.

Ключевые слова: инструментарий, идентификация, параметризация, критериальная модель, прогнозирование, регрессионная модель, факторное планирование, линейное программирование, бимодальное распределение, аппроксимация, статистика Кохрейна, статистика Граббса, квалификационные нормативы, критерий подобия, число подобия, фиктивный фактор, значимость, ранжирование.

ABSTRACT

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STATISTICAL METHODS IN VIRTUALIZATION

The importance of virtualization tools for solving the problems of identification of statistical models based by the results of qualification tests is shown.

During identification abnormality of distributions of measurements error of mineral oil characteristics was established. For construction of algorithms of processing of measurements a number of alternative approximations is synthesized. To assess the reproducibility of the virtual qualification results, the distribution of Cochrane statistics and Grubbs statistics is constructed. Parameterization of the criterion model is proposed based on the results of predicting the effect in extreme conditions. The choice of conditions is proposed to be carried out by the method of successive approximations in the framework of factor analysis.

Key words: toolkit, identification, parametrization, criteria model, forecasting, regression model, factorial planning, linear programming, bimodal distribution, approximation, Cochran's statistics, Grubbs statistics, qualifying specifications, criterion of similarity, number of similarity, fictitious factor, importance, ranging.

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Chapter 2

THE RELATIONSHIP BETWEEN THE PROPERTIES OF FUELS AND LUBRICANTS, CHEMMOTOLOGICAL RELIABILITY, OPERATIONAL TECHNOLOGY AND ECONOMICS OF ROAD AND AIR TRANSPORT

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2.1 CHEMMOTOLOGICAL, TRIBOTECHNICAL AND RHEOLOGICAL PROPERTIES OF BOUNDARY LUBRICATING LAYERS USED IN EVALUATION OF OPERATION RELIABILITY OF TRIBOSYSTEMS

Oksana Mikosianchyk, Rudolf Mnatsakanov, Nataliia Kichata

One of the directions in increasing the reliability of modern machines and mechanisms is the development and creation of such modes of their operation that provide a dominant manifestation of external friction conditions. A comprehensive approach to the solution of these problems should include an accurate system analysis with taking into account many factors whose kinetics of change affects the anti-friction and anti-wear properties of contact. External friction is primarily determined by the structure and properties of the surface layers of metal [1], stress-strain state of contact surfaces [2, 3], structure of boundary lubricating layers [4], modes of tribocoupling operation, *etc*. An integral component of a tribotechnical system is a lubricant, the self-organization of which at various load-speed modes is an important condition for the manifestation of external friction in contact and improvement of its operation reliability.

The development of tools and methods for control of oil lubricity directly during the operation process is an urgent trend in the study of processes of tribosystem self-organization, which makes it possible to predict the operation reliability. Under a boundary lubrication mode, the interaction between two surfaces occurs in areas of meeting surface irregularities in the friction contact. Such contacts manifest themselves *via* a wide range of thermal-mechanical-chemical transformations, from elastic deformation to plastic one up to the destruction of material; increase in the frictionand heat release intensity in contact, and growth of the rate of chemical reactions. As a result of these processes, organic and inorganic films are formed on friction surfaces.

Mechanisms of formation and structure of boundary lubricating layers have been investigated by U. B. Hardy, A.S. Akhmatov, F. Bowden, D. Teybor, G.V. Vinogradov, B.V. Deryagin, R.M. Matviyevskyi, I.A. Buyanovskyi, V.A. Godlevskyi, M.V. Raiko, *et al*. [5, 6, 7].

The investigation of a wide range of tribological boundary layers has shown that some of them are characterized by high wear-resistant and protective properties and some exhibit a destruction action [8]. Although the processes of physical and chemical interaction of lubricant components with the surface metal layers activated under friction are manifold, difficult to describe and still incomprehensible, there have been many models that take into account processes of contact mechanics, lubricant chemistry, molecular dynamics and thus contribute to the understanding of mechanisms of forming boundary lubricating films in the tribological contact [9, 10].

Contamination, lubricant and doping elements diffuse to the surface, which leads to a higher concentration of secondary elements near the surface than that in the bulk material. As known, solid body atoms are interconnected by various forces such as covalent, ionic, metallic, and Van der Waals'. Accordingly, the existence of these forces between the components of the boundary lubricating layers and secondary structures formed in the process of friction causes the need for different quantities of energy to break them. For some crystalline solids, different crystalline planes often exhibit different physical, mechanical, and chemical properties. In particular, friction studies have shown that different crystalline phases are characterized by different resistance to sliding friction under the same friction conditions, which indicates their anisotropic properties [11].

In [12], tribological properties of dry, liquid, and boundary modes of lubrication were analyzed. For dry friction, it was shown that with increase in the frequency of external periodic effects, the number of harmonics decreases up to the achievement of certain frequency, upon which the surfaces completely stick together and further behave as a single whole. For a hydrodynamic mode of lubrication, there were analyzed the characteristics of friction pair with a lubricant material having properties of the Newtonian fluid as well as of pseudoplastic and dilatant non-Newtonian fluids. It was established that pseudoplastic liquids and a boundary film of lubricant material in a wide range of parameters result in realizing a stick-slip i friction, which is one of the main causes of fracture of parts.

Modern lubricants consist of mineral or synthetic basic fractions and a number of multifunctional additives. The petroleum basic components generally consist of molecules containing from 18 to 40 carbon atoms and belong to three main types of hydrocarbons, namely paraffins, aromatic hydrocarbons, and naphthenes (cycloparaffins) [13]. Most of the molecules are of mixed types and contain two or more main hydrocarbon structures. These basic components also contain a small percent of heteroatoms, such as sulfur, nitrogen, and oxygen, and may transform into various stereochemical hydrocarbon structures. This is one of the reasons for the complexity in identifying the structure of formed boundary films. Generally, in typical basic components, the mass fraction of aromatic hydrocarbons ranges from 5 to 40 % (average content 20 %), straight chain paraffins fall in the range of 10 to 20 %, and cycloparaffins form the remainder. Molecules containing heteroatoms (N, S, O) are generally found in the base in the range of 0.5 to 4 % depending on oil type, processing technology, and viscosity class.

There have been many studies of physical and chemical properties of boundary lubricating films. Their findings indicate that the chemical composition of the films (predominantly micron and submicron particles of iron and iron oxides) interlace with a high molecular weight of organometallic compounds from 3000 to 100,000 [14]. The film appearance and morphology can be heterogeneous, continuous or discrete and can have various colors, from green to brown or black.

Over the last decades, many researchers have tried to measure the film strength. In studying shear strength of thin films under various high pressures (MPa to GPa), it was found that the shear strength increases with increasing pressure in films of calcium stearate, copper, and polyethylene [15]. As a rule, the film strength increases with increasing loads for basic fluids, zinc dithiophosphates, and calcium sulphonates, but it decreases with loading in the case of using friction modifiers. An increase in temperature reduces the shear strength of lubricating layers.

As shown in papers [16, 17], there is an optimal range of high lubricating properties thanks to the formation of a lubricating film on contact surfaces, which depends on external factors and the strength of its adhesion to the surface. Investigation into the structuring of boundary films has shown that the surface of triboelements, which is an integral part of reacting system, significantly influences the rates of oxidation and polymerization processes.

Improvement of test instruments and rapid development of computer technology provide a real opportunity to investigate, for the first time, tribological processes of the formation of dissipative structures under friction at the atomic and molecular levels. For example, the SFA complex allows one to measure film thickness to 0.1 nm and to detect extremely small surface forces, which gives it significant advantage over other devices and allows one to use it as a main tool for studying rheological, lubricating, and antifriction properties of tribocontact at the nanoscale [18, 19].

In calculating friction forces, the dependence of the oil viscosity on the pressure is taken into account. A lubricant in the boundary layer is characterized by anisotropic properties: in the tangential direction toward the surface, the molecular layers easily bend and, at a certain layer thickness, slide one on another, whereas in the normal direction, the film is characterized by high compression resistance. Herein the tensile stresses on the outlying surface under rolling-with-sliding conditions are determined by the formula [20]:

$$\tau = \mu_0 \exp^{\alpha p} \frac{U\sum}{h} \left(3 \frac{h - h_0}{h} + \frac{V_S}{U\sum} \right), \tag{1}$$

where μ_0 is the lubricant dynamic viscosity at contact input, $\alpha$is the piezoviscosity coefficient, p is the contact pressure, U_Σ is the total rolling speed, V_S is the sliding velocity, $h$is the thickness of lubricating film, h_0 is the minimum film thickness in contact, ($h_0 = 0{,}8h$).

However, at high pressure in contact, tangential stresses determined by this formula become overestimated. To eliminate this, the following assumptions should be used: the hypothesis of limit tangential stresses ($\tau \le \tau_{\text{пред}}$); the hypothesis of oil solidification for calculation of lubricant viscosity ($\mu \le \mu_0 \exp(\alpha p_{\text{затв}})$; models of non-Newtonian liquid behavior; and semiempirical dependences for calculation of the friction coefficient [20].

The properties of boundary lubricating layers markedly differ from their bulk characteristics because ofsupermolecular self-organization of boundary films. Such layers play a significant role in the processes of energy dissipation in friction pairs operating in mixed and limited modes of lubrication. In addition to the type and material of surface, which determine the nature and intensity of interaction on the solid-liquid boundary, the process of fluid structuring is facilitated by the introduction of additives that increase the wear-resistant properties of lubricant due to the formation of polymolecular mesomorphic epitropic liquid-crystal structures [21, 22].

The techniques for measuring viscosity of quasi-crystalline layers of motor oils using a rotary viscometer allowed simulation of the processes occurring in the friction pair "shaft – insert of diesel engine S6A2", in particular the shear rate and thickness of the lubricating layer [23]. In such a way, the dependence of viscosity on the shear rate was established, which confirmed the "non-Newtonian" properties of the lubricant in the narrow gap of the friction pair shaft – bearing insert. In addition, the results confirmed the assertion that boundary lubricating layers adjacent to the metal surface of the friction pair are more viscous and characterized by the orientational ordering of molecules [24]. In order to describe a lubricant state, a parameter of excess volume (which arises due to the structure disordering in solids during melting) was introduced [23]. It increases with increasing the total internal energy during the boundary film melting.

As shown in [25], there is a correlation dependence between the rheological (in particular, viscosity v) and liquid crystal characteristics (boundary layer thickness and degree of orientation ordering of molecules, $d_s \Delta n_{cp}$) of motor oil, which is determined experimentally. The dependence $v = f(d_s \Delta n_{cp})$ is linear in the range of shear rateγ (100, 150 s^{-1}).At higher shear rates it becomes exponential. Increase in the shear rate leads to a decrease in the liquid crystal characteristics of lubricant and, consequently, to a decrease in the oil viscosity in the boundary lubricating layer. This is due to the "cutting" of structured molecular layers with increasing the crankshaft rotation speed, which leads to a decrease in the oil film bearing capacity.

Principal approaches to the creation of a structural and thermodynamic friction model for a limited mode of lubrication have been developed on the basis of physical model of friction and the basic thermodynamic laws for open tribological systems [26]. Processes of the formation and destruction of adsorbed and chemically modified films under the limited supply of lubricant should be considered as processes of self-organization in thermodynamic friction systems. Herein the equations for transition temperatures used in this paper for description of the processes occurring in tribosystems under the limited mode of lubrication are nonlinear. Transitions to new steady levels occur in the case of deviation of the critical system parameters from equilibrium with subsequent self-organization at a new level.

In [27], rheological and thermodynamic models are proposed which describe melting of an ultrathin lubricating film located between atomically-smooth solid surfaces. The film melting under friction is presented as a result of the action of spontaneously arising shear stresses caused by external supercritical heating. The critical temperature of the friction surfaces which leads to the lubricant melting was established to increase with increasing a certain characteristic value of the shear viscosity and to decrease with increasing the oil shear module in a linear way. A thermodynamic model of melting of a thin lubricating layer has been constructed. Melting and solidification of lubricant are considered as first-order phase transitions. Depending on the system parameters, three lubricant states are possible under friction: solid or liquid states, or periodically melting-solidification transitions occur, which lead to a discontinuous motion of friction pairs [28].

The obtained in [29] time dependences for the friction force, the relative speed of friction surfaces during shear, and the elastic component of shear stresses in the lubricant indicate that in the liquid state the oil shear module and elastic stresses are equal to zero.An experimentally observed stick-slip friction mode is described, for which it was established that with increasing oil temperature, the frequency of phase transitions between oil structural states and the amplitude of the total friction force and elastic stresses decrease. When temperature or elastic deformations overcome certain critical values, melting of oil occurs and a kinetic sliding mode sets, in which the elastic component of friction force equals zero. It was also shown [30] that in the course of movement, a lubricant tries to acquire a uniform slide plane structure, which leads to a periodic dependence of the main parameters on time in the stick-slip mode of operation.

Functional dependences for thermal oxidation of multipurpose mineral, partially synthetic, and fully synthetic oils were obtained at static and cyclic testing temperatures, which made it possible to quantify the influence of the base and additives on oxidation processes [31]. The intensity of oxidation product formation and the oxidation rate were suggested. as indicators of the potential resource of oils in their identification and classification according to the operation properties. The mechanism of thermal oxidation of lubricant, which characterizes redistribution of absorbed heat and acts as an indicator of oxidation products formation and their volatility was clarified. The possibility of using such indicators as criteria for evaluating thermal transformations in a lubricant and self-organization processes running during thermal oxidation was shown.

This review of studies in the field of structural and rheological properties of boundary lubricating layers demonstrates that there have not yet been definited criteria for evaluating boundary films formed on contact surfaces because of the complexity of processes of forming/destroying boundary films in the tribotechnical contact. Therefore the development of structural-dynamic models characterizing the influence of boundary lubricating layers on the tribotechnical properties of contact and the kinetics of formation of secondary structures in the process of structural adaptability of triboelements under friction will allow one to predict the kinetics of changes in tribotechnical properties of friction pairs and their durability.

General aspects for selection of techniques for tribological investigations and modeling of friction processes.

The structural adaptability and evolution of a tribological system during its operation can significantly change the parameters used in predicting the friction unit resource. A numerical simulation of friction mechanisms for limited and mixed modes of lubrication, dominant in a non-stationary operation of triboelements, is a promising trend in terms of estimating changes in the properties of structural materials during operation.

In order to obtain reliable results when studying tribocoupling and to reach their reproducibility and convergence in repeated experiments, a clear structure of tribological researches is required (Fig. 1). It should include such elements as experimental means for conducting experiments (scheme and design of plants), research objects (material, construction, accuracy of manufacturing), conditions for carrying out the experiment (loading, kinematic and temperature factors), measuringand controlling means, and techniques for processing experimental results.

The development of computer technology allows widespread propagation of simulation techniques for many engineering tasks. Simulation of tribological processes on the basis of empirical data allows one to develop adequate measures for control of tribosystems [32].

The knowledge obtained in such a way combined with practical experience in the field of chemotology and tribology will be used to improve operation of tribosystems in industry; herein it is possible to define the following main tasks:

– to optimize technological processes of designing and manufacturing materials for tribotechnical purposes in order to provide high physical and mechanical-chemical properties of materials for specific operation conditions;

– to provide continuity in the production process taking into account optimization of tribosystem design in order to increase the wear resistance of friction pairs required for a high level of product reliability;

– to reach effective characteristics of compatibility of structural elements by tribotechnical parameters for specific operation conditions on the basis of instrumental modeling techniques based on the contact mechanics calculations taking into account dynamic models of crack propagation, the depth of thermal stress propagation, and intensity of running tribochemical reactions;

– to predict the durability of tribosystems taking into account large-scale changes in their tribotechnical properties when operating on the nano-, micro-, and macro-levels.

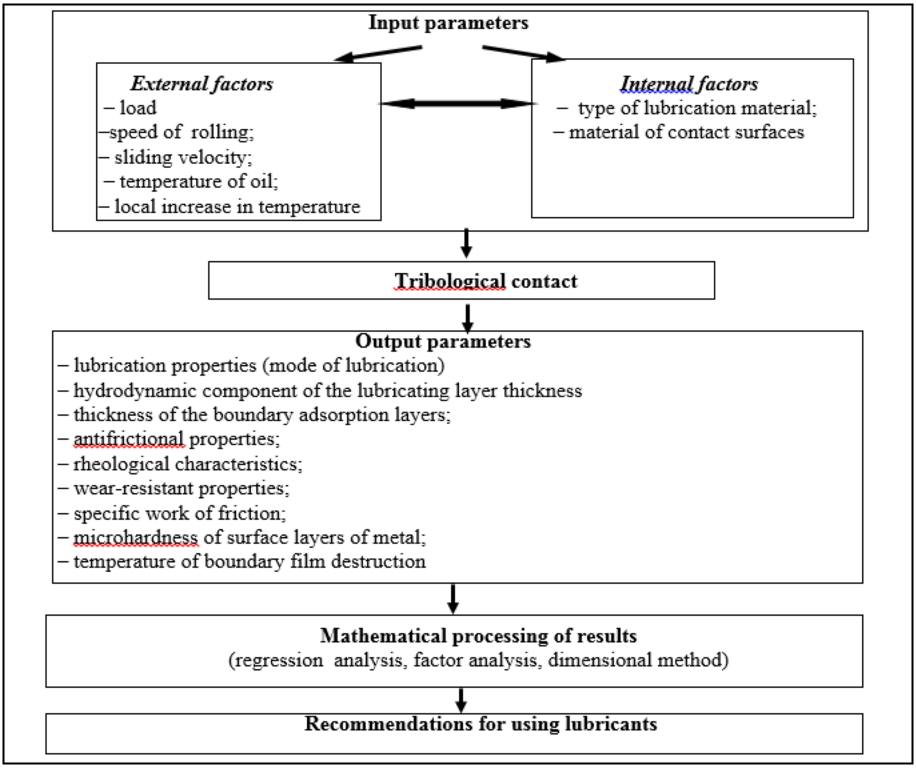


Fig. 1. Scheme of evaluation of tribological parameters in contact

The purpose of this research was to determine the dependence of the kinetics of change in the friction coefficient under the conditions of the stopping of lubricant supply on the lubrication and rheological properties of the boundary films formed on the friction-activated metal surface layers.

Investigation of the lubrication, antifriction and rheological properties of boundary films was carried out on an apparatus for testing tribological characteristics of triboelements described in [33]. The friction moment, speed of rollers, temperature of lubricant, stress drop in the lubricating layer in contact were recorded and processed using a PC (ProfiLab software) in real time with a graphical representation of their changes.

The investigated non-stationary conditions of friction implied carrying-out of cyclic experiments in a start – stationary operation – slowdown – stop regime (Fig. 2).

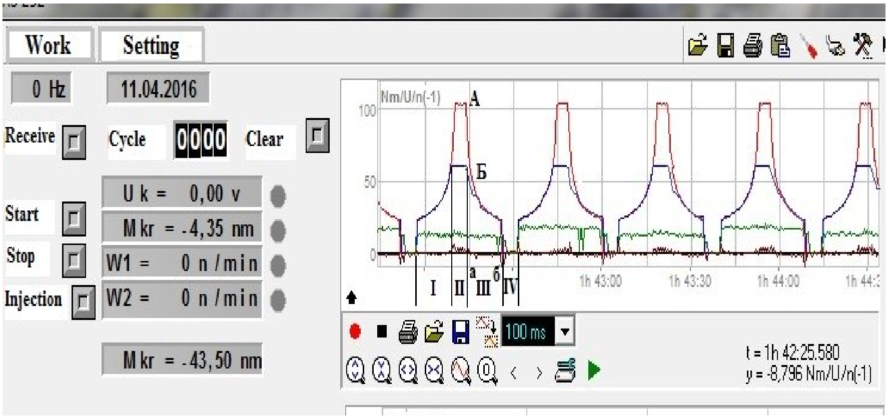

0 Hz
11.04.2016
Cycle 0000
U k = 0,00 v
M kr = -4,35 nm
W1 = 0 n / min
W2 = 0 n / min
M kr = -43,50 nm
100 ms
t = 1h 42:25.580
y = -8,796 Nm/U/n(-1)

Fig. 2. Scheme of tribosystem operation in non-stationary conditions of friction:
Region I – start; Region II – stationary operation; Region III– slowdown; Region IV – stop

Region I corresponds to the initial period of work of friction pairs and is characterized by a gradual increase in the rolling speed of rollers at $V_{sl} = 0$. In Region II, the specified maximum sliding of rollers is achieved at constant rolling speed of friction pairs. Region III corresponds to slowdown characterized by two periods: initial decrease in the speed of rollers with preservation of the specified sliding at point A and gradual decrease in the degree of sliding to zero at point B (IIIa). Further deceleration occurs in conditions of a simultaneous decrease in the speed of both rollers with maintaining $V_{sl} = 0$ (IIIb). Region IV corresponds to a stop. If the selected cycle is projected onto an involute gearing, the pole gearing zone corresponds to Regions I and IIIb, the near-pole zone – to Region IIIa, and extreme points of gearing with maximum sliding –to Region II.

The maximum rotation speed for the outlying surface was 1000 rpm. The simulated sliding degrees were 3, 10, 20, 30, and 40 %. Maximum contact stress by Hertz was 250 MPa.

Rollers from steel 45 (HRC 38, R_a 0.57 μm) were used as samples. Lubrication of contact surfaces was performed through immersing a low roller into a bath with oil. As a lubricant, mineral transmission oil for mechanical gearboxes and main gears of cars and trucks Okko GL-4 80w/90 was used. The oil volume temperature was 20 ^{o}C.

Adaptation of contact surfaces with a duration of 100 cycles and further work of friction pairs during 400 cycles were carried out in conditions of abundant lubrication, followed by the cut-off of lubricant supply. The total number of cycles in each experiment was as follows: 500 (abundant lubrication by immersing a low roller in an oil bath), 400 (simulation of oil starvation by stopping of regular supply of lubricant from the bath to the contact area), 100 (forced removal of lubricant from the contact surfaces by wiping the rollers).

In conditions of the absence of lubricant supply, lubrication properties of contact is only determined by the stability of the boundary layers formed on the friction-activated contact surfaces during abundant lubrication. Up to 400 cycles after start-up, an increase in the lubricant layer thickness by 0.5–2 μm was observed due to the availability of free lubricant material located in the contact area owing to the adhesion and cohesion forces of interaction. In case of abundant oil supply into the contact area, a hydrodynamic mode of lubrication is realized. The stopping of the lubricant supply creates preconditions for the tribosystem transition into harder operation conditions. In this case, different modes of lubrication, from semi-dry tohydrodynamic ones, take place (Table 1).

Table 1

Efficiency of lubrication at different sliding degrees of friction pairs

Sliding degree, %	Thickness of lubricating layer, μm	Mode of lubrication by parameter λ
Below 3	0.2–5.1	0–10.86 (semi-dry – hydrodynamic)
10	0.35–4.0	0.5–7.2 (semi-dry – hydrodynamic)
20	0.2–3.8	0.5–6.7 (semi-dry – hydrodynamic)
30	0.15–2.1	0.5–5.4 (semi-dry – hydrodynamic)
40	0–1.9	0–2.7 (semi-dry – mixed)

The decrease in the hydrodynamic component of the lubricating layer thickness by on average 70 % affects the antifriction properties of contact in different ways.In Region I, corresponding to the start-up in conditions of a pure rolling process, the friction coefficient *f* does not change for surfaces with subsequent sliding of 10–20 %, whereas for surfaces with sliding of 30 and 40 %, *f i*ncreases by 1.8 and 1.2 times, respectively. A more significant *f* increase (by 1.22–2.4 times) was established after 400 cycles of work, after the forced removal of free lubricant from the contact area, except for contact surfaces that further operated with a minimum sliding of 3 %, since reduction in the lubricating layer thickness does not affect the antifriction properties of contact and their friction coefficient is within 0.006–0.008, like in conditions of abundant lubrication.

In Region II, in the rolling-and-sliding conditions, a sharp *f* increase was fixed, by on average 3 times for sliding of 10–40 %, again except for contact surfaces characrerized by a minimum sliding: their antifriction contact properties remained unchanged (Fig. 3).

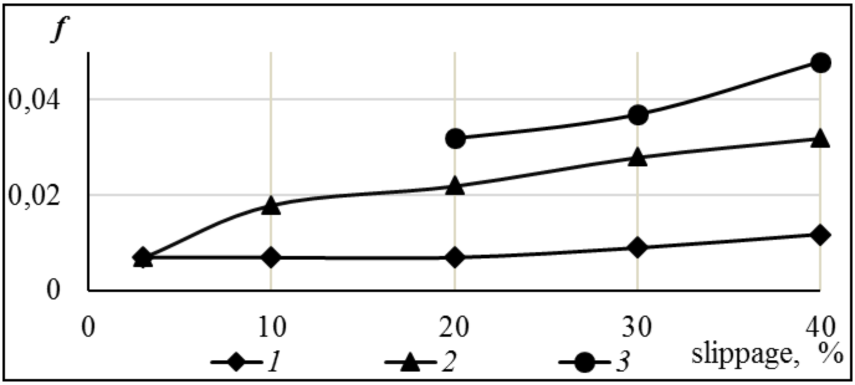
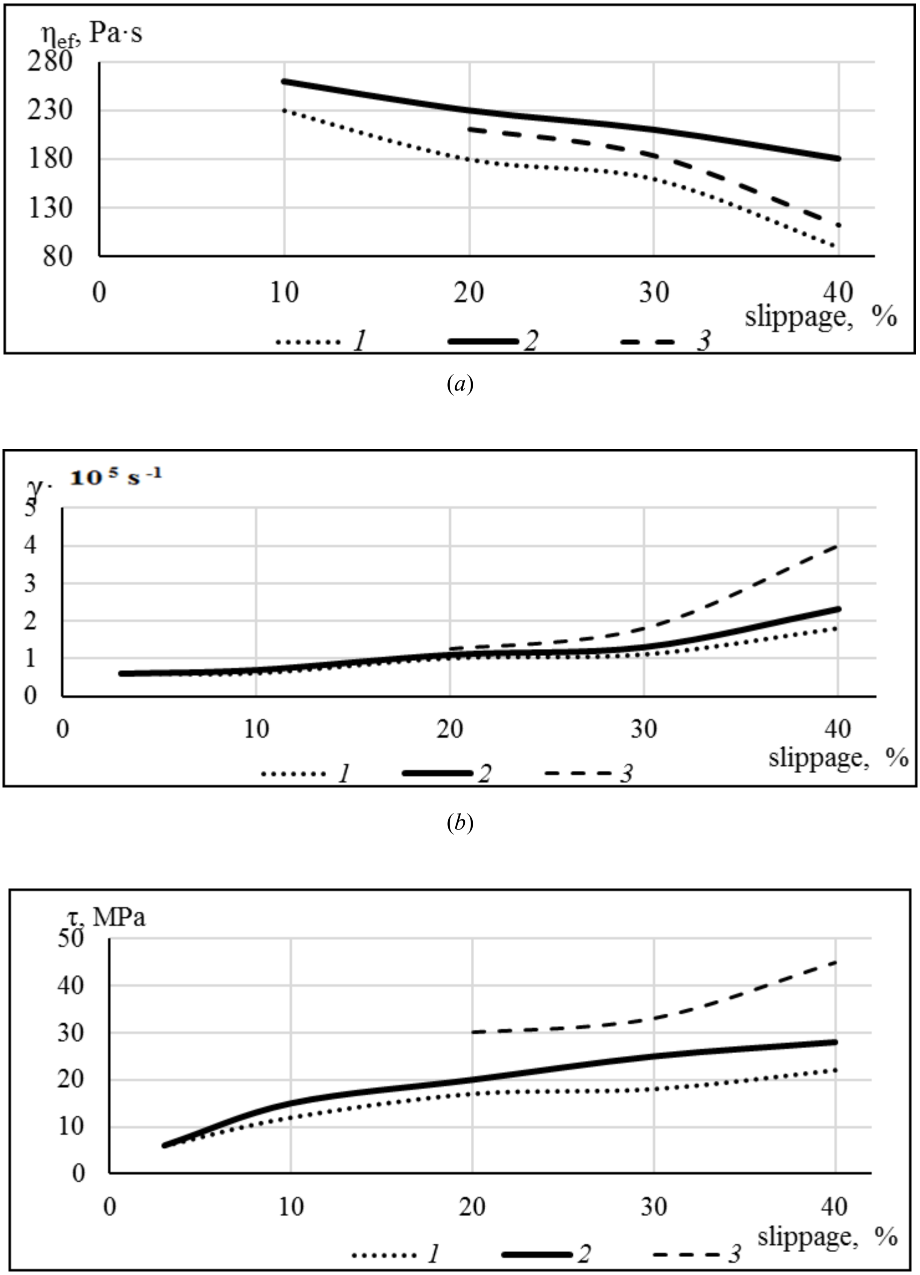


Fig. 3. Dependence of the friction coefficient on the sliding degree in conditions of limited lubrication: (*1*) pure rolling mode at start-up; (*2*) rolling-with-sliding mode; (*3*) moment of seizure during the rolling-with-sliding mode



(*a*)

(*b*)

(*c*)

Fig. 4. Influence of the sliding degree on the rheological characteristics of lubricant: (*1*) abundant lubrication; (*2*) limited lubrication; (*3*) forced removal of lubricant; *a* is the change in the effective viscosity η in contact; *b* is the change in gradient of shear rate, *γ*, in lubricating layers; *c* is the change in the shear stress, *τ*, of lubricant material

The absence of excess lubricant does not significantly affect the gradient of shear rate (γ) of the lubricating layers: the increase in this parameter was by 1.02–1.1 times, regardless of the degree of sliding of contact surfaces. The increase in sliding from 3 to 40 % causes growth of the shear rate gradient by 4.6 times (Fig. 4, *b*). It is this parameter that influences the stability of the formed boundary films: the increase in γ from 10^5 to $2.3 \cdot 10^5$ s^{-1} with increasing sliding degree from 20 to 40 % leads to the complete abrasion of the formed boundary layers during 30 % of the operation cycles on surfaces with maximum sliding (Fig. 5).

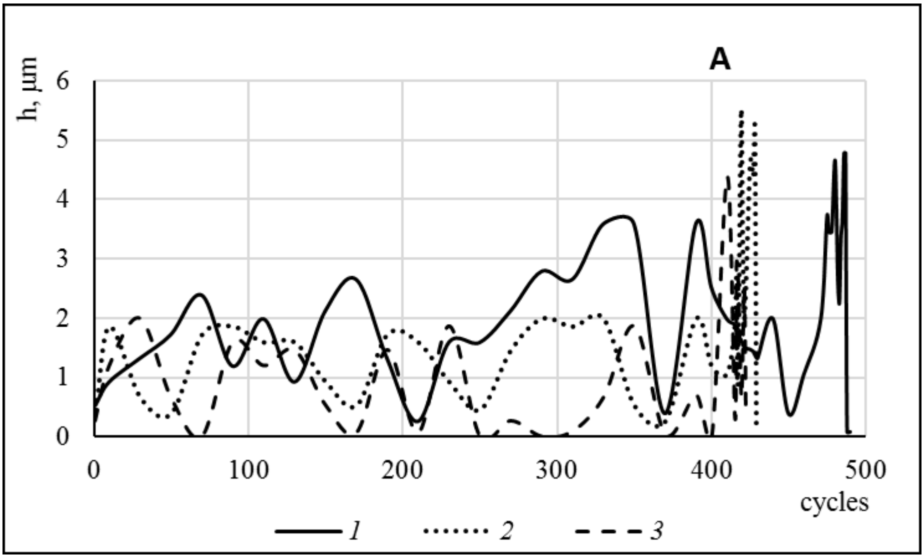


Fig. 5. Kinetics of change in the lubricating layer thickness in the stick-slip mode of operation during rolling-with-sliding at the sliding degree (*1*) 20 %, (*2*), 30 %, and (*3*) 40 %.
Point A indicates forced removal of lubricant

With an increase in the sliding degree from 10 % ($\gamma = 0.5 \cdot 10^5$ s^{-1}) to 40 % ($\gamma = 2.3 \cdot 10^5$ s^{-1}), the effective viscosity in contact decreases from 260 to 180 Pa s (Fig. 4*a*). Up to 400 operation cycles, when the oil had not yet forcibly removed from the studied surfaces, the shear stress of the lubricating layers at a sliding degree of 10 to 40 % increased by on average 1.25 times as compared with abundant supply of lubricant. In conditions of limited supply of oil, which leads to a decrease in the lubricating layer thickness, an increase in the effective viscosity of lubricant was revealed, which was by 1.13; 1.27; 1.31, and 2.0 times for sliding degrees of 10, 20, 30, and 40 %, respectively (Fig. 4*a*).

After 400 operation cycles, the lubricant was forcibly removed from friction surfaces by wiping the rollers. For contact surfaces with a degree of sliding of 3 and 10 %, the normal operation of tribocoupling was established to the 500th cycle, the friction coefficient was stable, which testifies to high antifriction properties of boundary lubricating films. The increase in the degree of sliding to 20, 30 and 40 % leads to reduction in the period of normal operation of contact surfaces because of the appearance of the first signs of seizure corresponding to 490, 430 and 415 operation cycles, respectively. In such extreme conditions there is observed a sharp change in the antifriction characteristics of contact, which manifests itself in the periodic growth and reduction of the friction coefficient (Fig. 6).

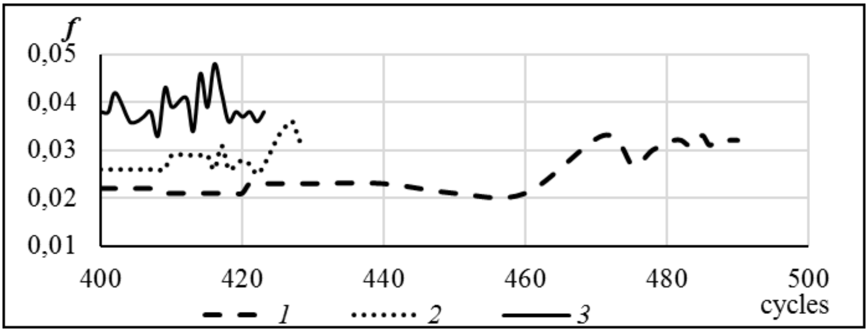
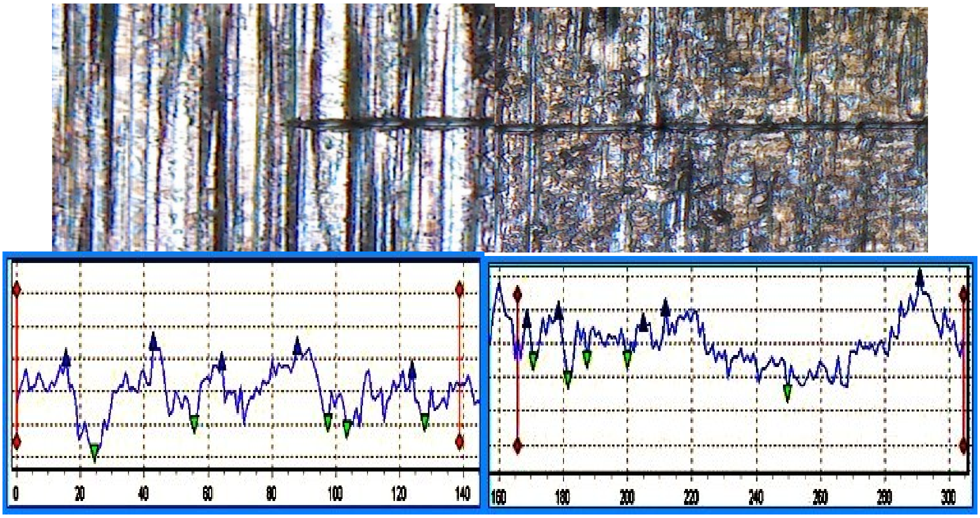


Fig. 6. Change in the friction coefficient during forced lubricant removal under rolling-with-sliding conditions at the sliding degree: (*1*) 20 %, (*2*) 30 %, and (*3*) 40 %

For contact surfaces that operate under minimal sliding of 3 %, no significant changes in the rheological properties of boundary lubricating layers were observed during the tribosystem transition to the mode of stopping the supply of lubricating material: stability of the shear stress of lubricating layers indicates weakness of cohesive forces of interaction.

However, with the evolution of cycles within $400 < N < 500$, in conditions of forced lubricant removal, no sign of seizure was detected in spite of the formation by transmission oil of boundary layers of physical nature during their structural adaptation. Two factors contribute to the preservation of normal work of friction pairs. Firstly, thanks to the reserve of lubricant in the roughness cavities of contact surfaces (operation R_a = 0.39 μm, Rz = 1.71), the lubricating layer thickness begins to grow from the 430th cycle of operation up to 3 μm, followed by its cyclic fluctuations of 0.2–3 μm, which prevents frictional seizure (Fig. 7).



(*a*) (*b*)

Fig. 7. Roughness of contact surfaces:
(*a*) initial (R_a = 0.57 μm, R_z = 2.33); (*b*) operational
(R_a = 0.39 μm, R_z = 1.71)

Secondly, strongly weakened surface layers of metal due to the plasticizing Rebinder effect are characterized by low resistance to tensile shear stresses. The microhardness of surface layers decreases, by on average 1000 MPa, and the depth of amorphizated weakened layer reaches 60 μm. Thus, these processes in contact contributes to maintaining the stability of the adhesion component of the friction coefficient at the level of values established for the sufficient supply of lubricant to contact.

The friction coefficient is equal to the sum of two components: an adhesion component related to the molecular interaction of solids on the actual area of contact, and a deformation component related to the deformation of surface layers of solids under friction [34]. Therefore, analysis of the kinetics of changes in antifriction properties of contact should be based on the consideration of issues relating to both the lubricity of materials used and changes occurring in the surface metal layers under friction. In the presence of lubricant incontact, the adhesion component can be determined by the tensile shear stresses predominantly in the lubricating layer.

Let us consider the kinetics of changes in antifriction properties of transmission oil from the position of self-organization of boundary lubricating films during the tribosystem transition into extreme operation conditions, that is, without reserve of lubricant. During the start-up period, in conditions of pure rolling with increasing speed, the tensile shear stresses are localized in the central part of the lubricating layer thickness, since there is no gradient of shear rate ($V_{\text{sl}} = 0$). Upon 400 cycles, owing to the growth of lubricant layer thickness due to the presence of free lubricant on the contact surfaces, the tensional stresses are localized mainly in this layer. Since the amount of lubricant is sufficient for the complete separation of the contact surfaces, in Region 1 no τ change for surfaces with subsequent sliding of 3 to 20 % is observed, τ is equal to 6–7 MPa like under abundant lubrication conditions. These processes contribute to the domination of the hydrodynamic mode of lubrication, in which the friction coefficient is determined by the volumetric properties of the liquid, smectic or nematic, phase of the lubricant [35]. The localization of tensile shear stresses in the liquid phase during a pure rolling process due to the minimal effect of solid surface provides the best antifriction characteristics of contact with a minimum friction coefficient at the level of 0.006–0.008 (Fig. 3).

On contact surfaces that operate at 30 and 40 % sliding, when the maximum velocity of sliding reaches 0.85 and 1.5 m/s, respectively, an intense lubricant spatter occurred. This resulted in decreasing the film thickness growth at the startup by on average 2 times, predominantly leading to a mixed lubrication mode. However, the shear stress of the lubricating layers during operation in Region I increases slightly (by on average 1.2 times) as compared with the conditions of abundant lubrication. With the lubricating film thickness decreasing, the effect of the solid metal phase on the lubricant components increases, which reduces antifriction properties: the friction coefficient increases to 0.01–0.013 (Fig. 3).

In conditions of sliding, the sliding velocity reaches maximum values, which results in appearing a gradient of the shear rate of lubricating layers through the thickness of lubricating film in contact. Because of the reduction of the hydrodynamic component of the lubricating layer thickness, the vector of tangential shear stress is localized mainly in the formed boundary layer, which is similar to the results obtained in [36].

Since the boundary layers are characterized by structuring and are subjected to the strong influence of the solid metal phase, the effect of rheological properties of lubricant on the kinetics of change in the adhesion component of the friction coefficient should be analyzed as well.

The analysis of lubricity of the investigated transmission oil in conditions of abundant lubrication revealed the formation of boundary lubricating layers of different nature. On contact surfaces with a minimum sliding of 3 %, predominantly physically adsorbed boundary films with weak Van der Waals interaction forces are formed which are characterized by low shear stresses similar to those in the bulk phase (Fig. 4*c*).

For contact surfaces with a sliding degree of 3 %, no change in the adhesion component of the friction coefficient was established in conditions of limited lubrication, unlike the case of abundant supply of lubricant to the contact area. First of all, this is due to low activation of surface metal layers at a slight sliding (V_{sl} = 0.07 m/s). The domination of rolling speeds creates preconditions for minimum mechanical and thermal effects of the speed gradient [37], resulting in the formation of physically adsorbed boundary films. The absence of strong adhesive bonds of lubricant components with the metal surface causes frequent disorientation of the boundary layers, which manifests itself in cyclic fluctuations of the lubricating film thickness from 0.2 to 3.5 μm in the course of 50 cycles. Such boundary layers are characterized by the rheological properties of the volumetric liquid phase of oil: their shear stress and effective contact viscosity are similar to those recorded in conditions of abundant lubrication (Fig. 4).

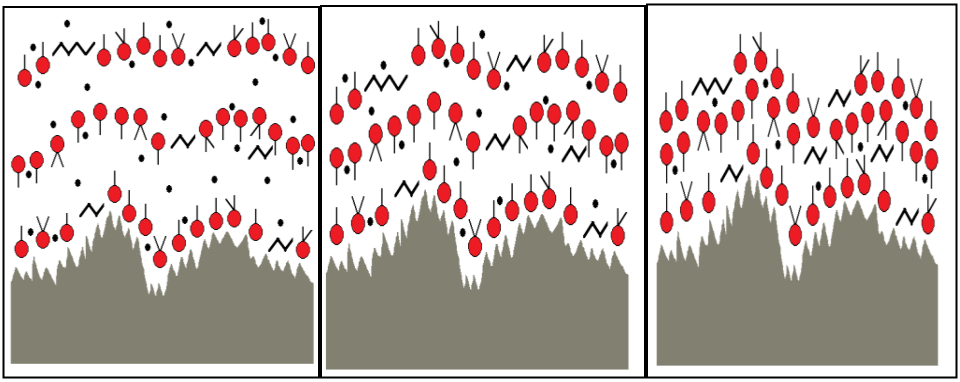
The increase in the degree of sliding and, consequently, in the gradient of shear rate, promotes formation of boundary lubricating layers of chemisorption nature. At a sliding of 10 to 40 %, the active lubricant components form chemisorption films and chemically modified layers on the surface, which are characterized by somewhat higher shear stresses as compared with the bulk phase owing to the action of cohesion forces.

According to [38], the shear rate gradient of about 10^5 ... 10^7 s^{-1} leads to the destruction of lubricant components, which manifests itself in reducing lubricant viscosity. Similar results were obtained in the present studies as well: the effective contact viscosity decreased by 1.45 times with increasing the degree of sliding from 10 to 40 %. However, an analysis of rheological characteristics of structured boundary lubricating layers revealed another regularity of the kinetics of change in the effective viscosity in conditions of interrupted supply of lubricant: effective viscosity increased, and the degree of its increase correlated with the sliding (Fig. 4). These layers are characterized by increase in the shear stress due to the growth of cohesive interaction forces in the formation of a more dense and stressed structure. According to [39], polymorphism of organic molecules of lubricants, when they are structured on a solid surface, is a source of boundary layer formation by the type of netlike (reticular) heterogeneous structures. In such a boundary layer, under high pressures, reorganization of its molecular structure takes place with the formation of denser ordering, since the structure of chain molecules changes due to the axial compression of the chains because of deformation of tetrahedral angles between carbon atoms.

The used mineral transmission oil was produced on the basis of residual oil, low-viscosity distillate, and a set of multifunctional additives. Thus, it contained molecules of different stoichiometric structure. Under the action of high shear rate gradients, due to the mechanical destruction of the lubricant components, the formation of reticular boundary layers with multiple cross-links between the active centers of molecules occurs. Herein, along the boundary layer thickness, planes of slight sliding are formed, which are oriented in the plane of the action of the vector of tangential shear stresses. Such a layered netlike structure serves as a kind of reservoir for chaotically arranged inactive free molecules. The presence of such molecules is characteristic for fractions of saturated and non-polar compounds contained in the base during compounding mineral transmission oil.

As follows, ordered solid-crystalline reticular structures, similar to the framework of the dispersed phase of lubricants and containing different number of free molecules of oil, analogous to the dispersed component of lubricants, are formed on friction-activated contact surfaces. The number of inactive free components in such structures decreases with increasing degree of ordering and density of the framework (Fig. 8). Accordingly, the denser a solid-crystal structure, the higher its shear stress, which is manifested at the maximum sliding (Fig. 4).

The kinetics of change in the thickness of boundary lubricating layers after the 400thcycle of work, that is, upon forced removal of free lubricant from contact, confirms the above statement. For contact surfaces with 10 % sliding, the thickness of boundary lubricating layers varies from 0.5 to 3.2 μm, while the rheological characteristics of chemosorption films remain unchanged.



(*a*) (*b*) (*c*)

Fig. 8. Structure of boundary film from oil with multifunctional additives at the sliding degree: (*a*) 10 %; (*b*) 20 %; (*c*) 40 %

Stable values of the shear rate gradient and tangential stress indicate the presence of strong adhesion and cohesive bonds. The tangential stress vector is localized in the boundary layer of lubricant, the strength properties of which are high enough for the solid-crystal structure of boundary layers to remain stable. This structure of boundary films provides their high antifriction and wear-resistant properties. By the 500th cycle of operation, the normal operation of friction pairs had been established, no signs of seizure of contact surfaces were observed.

A similar peculiarities were revealed for sliding 20 % before the 450th cycle of work. Then there was observed a sharp increase in the lubricating layer thickness by 2.5 times, in shear stress by 1.5 times, and in shear rate gradient by 1.25 times. All this is connected with the destruction of cohesive and adhesive bonds in the solid-crystalline boundary layer, which leads to its disordering, melting, and transition to a smectic phase. Herein the effective viscosity in contact decreases by 1.2 times, whereas the friction coefficient drastically increases from 0.008 to 0.017 in the presence of lubricant in the friction zone. At the moments of breaking of the lubricating layer integrity, the friction coefficient increases to 0.032 and there appear the first signs of seizure of contact surfaces after the 490th operation cycle (Fig. 6).

A more intense destruction of boundary layers and earlier appearance of the first signs of seizure were revealed at 430th and 415th cycles under sliding of 30 and 40 %, respectively, after forced removal of free lubricating material from the friction zone. Thus, the strength properties of chemisorption boundary layers directly depend on the sliding velocity in contact, whose increase creates high shear rate gradients, which leads to mechanical and thermal destruction of the formed lubricating films. For example, at the moment of seizure of contact surfaces at a sliding of 40 %, the shear rate gradient increases by 2 times, the shear stress of lubricating layers does by1.6 times, while the effective viscosity in contact decreases from 180 to 112 Pa s. In this case, there are observed sharp fluctuations in the lubricating layer thickness, whose increase can reach 4 µm, which provides a low friction coefficient, about 0.006 (for comparison, 0.014 at the minimum film thickness). The mechanism of this process includes disorientation of boundary lubricating layers under the action of shear stresses and temperature rise in contact due to increasing sliding velocity rate, which causes melting of the solid-crystalline layer due to mechanical and temperature effects. The lubricant reacquires Newtonian properties, becomes liquid; cohesive, and adhesive forces of interaction weaken, and the volumetric liquid phase of oil increases in contact, which leads to a short-term manifestation of a hydrodynamic lubrication mode, characterized by high antifriction properties of lubricant.

The obtained data are in agreement with the postulates of the models for the first-order phase transitions between solid and liquid states [40, 41]. According to them, , a sharp change in the friction force occurs at the moment of rapid change in the lubricant properties during the solid-liquid phase transition. Melting of boundary layers of lubricant can occur at the limit values of shear deformation, when the lubricant is in a liquid state, regardless of temperature [42]. In the moments of breaking the integrity of lubricating layer, the friction coefficient rapidly increases to 0.038 and 0.047 at a sliding degree of 30 and 40 %, respectively (Fig. 6).

As follows, sharp fluctuations of the friction coefficient in the manifestation of the first signs of seizure of contact surfaces are resulted from the destruction of boundary lubricating layers, which leads to a decrease in operation reliability of lubricant. These processes are characterized by the manifestation of two opposite effects. One of them causes an increase in the adhesion component of the friction coefficient owing to increasing degree of direct contact with surface metal. The other decreases the friction coefficient and provokes short-term hydrodynamic effects in contact due to local melting of boundary layers.

Reduction in the lubrication capacity of mineral transmission oil with increasing degree of sliding of contact surfaces from 3 to 40 % was established upon the tribosystem transition to extreme conditions of lubrication, which is related to decrease in the thickness of lubricating layer by 1.43 times when the tribosystem is transferred to the more rigid modes of operation, in which semi-dry and limited modes of lubrication dominate.

In conditions of pure rolling, high antifriction properties of contact are due to localization of the tensile shear stress in the liquid phase of lubricating film. In conditions of rolling-with-sliding, the vector of tangential stresses is localized in the boundary structured chemisorption films, which reduces the antifriction characteristics of contact.

The boundary layers of physical nature formed on contact surfaces with a sliding of 3 % are characterized by the identity of their rheological properties to those of the volume liquid phase of lubricant. Such structures have a strong plasticizing effect on the surface layers of metal, which manifests itself in reducing the adhesion component of the friction coefficient.

An increase in the sliding degree from 10 to 40 % causes the creation of high shear rate gradients of the lubricating layers and activates contact surfaces. These factors promote the formation of chemisorption films with an ordered layered crystalline reticular structure on friction surfaces.

An increase in the sliding degree promotes an earlier seizure of the contact surfaces, which manifests itself in the growth of the adhesion component of the friction coefficient under desorption of boundary layers. Locally, in extreme conditions, an oscillatory process of decreasing the friction coefficient was revealed, resulted from short-term hydrodynamic effects due to local melting of boundary layers.

РЕФЕРАТ

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ХІММОТОЛОГІЧНІ, ТРИБОТЕХНІЧНІ ТА РЕОЛОГІЧНІ ВЛАСТИВОСТІ ГРАНИЧНИХ ЗМАЩУВАЛЬНИХ ШАРІВ ПРИ ОЦІНЦІ ЕКСПЛУАТАЦІЙНОЇ НАДІЙНОСТІ ТРИБОСИСТЕМИ

Проаналізовано процеси фізико–хімічної взаємодії компонентів мастильних матеріалів з активованими в процесі тертя поверхневими шарами металу; розглянуто моделі, що враховують реологічні властивості мастильних матеріалів, що сприяють розкриттю механізмів формування граничних плівок мастильного матеріалу в триботехнічному контакті. Метою досліджень було встановлення залежності кінетики зміни коефіцієнта тертя від змащувальних та реологічних властивостей граничних плівок. Експериментально визначено закономірності зміни антифрикційних властивостей контакту від міцністних характеристик граничних плівок. Розглянуто механізми, які призводять до підвищення адгезійної складової коефіцієнта тертя при порушенні суцільності змащувального шару або до її зниження при плавленні твердокристалічного змащувального шару.

Ключові слова: граничні плівки змащувального матеріалу, коефіцієнт тертя, напруга зсуву, ефективна в'язкість, градієнт швидкості зсуву.

РЕФЕРАТ

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ХИММОТОЛОГИЧЕСКИЕ, ТРИБОТЕХНИЧЕСКИЕ И РЕОЛОГИЧЕСКИЕ СВОЙСТВА ГРАНИЧНЫХ СМАЗОЧНЫХ СЛОЕВ ПРИ ОЦЕНКЕ ЭКСПЛУАТАЦИОННОЙ НАДЕЖНОСТИ ТРИБОСИСТЕМЫ

Проанализированы процессы физико-химического взаимодействия компонентов смазочных материалов с активированными в процессе трения поверхностными слоями металла; рассмотрены модели, учитывающие реологические свойства смазочных материалов, способствующих раскрытию механизмов формирования граничных пленок смазочного материала в триботехнических контакте. Целью исследований являлось установление зависимости кинетики изменения коэффициента трения от смазочных и реологических свойств граничных пленок. Экспериментально определены закономерности изменения антифрикционных свойств контакта от прочностных характеристик граничных пленок. Рассмотрены механизмы, обусловливающие повышение адгезионной составляющей коэффициента трения при нарушении сплошности смазочного слоя или ее снижение при плавлении твердокристаллического смазочного слоя.

Ключевые слова: граничные пленки смазочного материала, коэффициент трения, напряжение сдвига, эффективная вязкость, градиент скорости сдвига.

ABSTRACT

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CHEMMOTOLOGICAL, TRIBOTECHNICAL AND RHEOLOGICAL PROPERTIES OF BOUNDARY LUBRICATING LAYERS USED IN EVALUATION OF OPERATION RELIABILITY OF TRIBOSYSTEMS

The processes of physicochemical interaction of epy components of lubricating materials with friction surface layers of metal are analyzed; models that take into account the rheological properties of lubricants that facilitate the discovery of mechanisms for the formation of boundary films of a lubricant in tribotechnical contact are considered. The aim of the studies is to determine the dependence of the kinetics of the coefficient of friction on the lubricating and rheological properties of the boundary films. The regularities of the change in the antifriction properties of the contact from the strength characteristics of the boundary films are determined experimentally. The mechanisms responsible for the increase in the adhesion component of the coefficient of friction when the continuity of the lubricating layer is disturbed or its decrease during melting of the solid-crystalline lubricating layer are considered.

Key words: boundary films of a lubricant, friction coefficient, shear stress, effective viscosity, gradient of shear rate.

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2.2 FORMATION OF COPPER (II) COORDINATION COMPOUNDS UNDER THE FRICTION PROCESS AND THEIR IMPACT ON THE TRIBOTECHNICAL CHARACTERISTICS OF THE LUBRICATING COMPOSITIONS

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If we take into considerationthe friction as a fundamental matter property, characterized by the energy transfer of physical bodies in contact, gravitational, electromagnetic and nuclear fields, then, for example, physicists point of view concerning friction, only as a complex physico-mechanical process of contacting bodies, is quite simplified. Therefore, for today, there are no definite friction laws and, as a sequence, it is revealed the difficulty of the complete physical concept representation of the frictional forces origin, as well as their quantitative evaluation and determination of all forces dependent factors. In fact, when friction forces are taken into consideration, mainly, laws of the qualitative origin are used and represented only by some approximations, which are related to actual laws, for example, the law of Amonton (1699) and the more definite law of Coulon's experimental studies (1781). According to these facts, it is logical to consider tribology (P. Jost, 1966) as an applied science of the friction, wear, lubrication and interaction of contacting friction pairs, which is based on a vast array of practical physico-chemical, mechanical, material science, technological and design studies. In this context, tribochemistry should be considered as a tribology component, which studies the chemical and physico-chemical solid surfaces transformations under the friction process,which are sequentially activated by the mechanical friction energy.

Nowadays, 20–25 % of the world's produced energy is consumed / absorbed, under the functioning of any mechanical systems related to the friction. This leads to the formation of the important tribological tasks, which should improve the economic and environmental efficiency, durability and reliability of the machinery, mechanisms and technological equipment, which are used for various purposes. In addition, nowadays, the modern world has the fast-track developing nanotechnology related to obtaining of new materials with the unique, physico-chemical properties, micro-optoelectronic and microelectromechanical systems, which are characterized by the new friction and wear conditions, applied in the contacting microsurfaces sector [1–3]. This formed another developing tendency of tribology, specifically, nanotribology (G. Newbauer, 1990), which studies bodies friction of micro- and nanoscale. Thus, in order to study the friction of the thresholding layers with the width from 0.04 μm to 0.08 μm (critical width) [4], in our opinion, first of all, it is necessary to take into consideration an atomic and molecular, and adhesive / chemisorption interaction of the friction surfaces, which forms the derivation of the highly structured, liquid-crystal layers, which have high, wear-resistant properties and a low friction coefficient. Thus, in this case, under the investigation of the friction and wear, first of all, it is necessary to take into account the adhesion / chemisorption, atomic and molecular transformations, which occurr on the friction surfaces, and only then, the friction pair volume properties variation. To prove this thesis, there is the discovery of the selective transfer phenomenon (Garkunov D. M., Kragelsky I. V., 1956), which is characterized by the formation of a nano-sized servo-film in the friction pair «bronze – glycerol – steel» [5–6]. This can be applied as fundamentals for considering the selective transfer phenomenon from the outlook of nanotribology, taking into account the chemisorption phenomena and chemical transformations, which occur on the surface of the contacting friction pairs. Thus, in the study [7] the authors explain the selective transfer mechanism by a series of consecutive probable triboelectrochemical mechanoactivation reactions. The authors explain the formation on the friction surface of the servovitic film by the work of macroscopic galvanic cells, in which the surface of steel can be represented as anode, and bronze – as cathode. The reaction also proceeds on the cathodic and anodic surfaces of micro-galvanic cells. In our opinion, it is given more accurate consideration of the chemical transformations in the tribochemical system «bronze – organic additive / medium – steel» from the point of view of the direct mechanically activated dissolution of the more active metal in the donor-acceptor electron transport chain (ETC) system, which is a matrix for the formation of the corresponding copper(II) coordination complexes [8]. According to this thesis, this study is carried out concerning the investigation of the possibility of the direct synthesis of copper(II) coordination complexes with thioamide ligands in the tribochemical system «bronze BrAZ 9-4 – thioamide – organic solvent – oil I-20A – steel 45» and their influence on tribotechnical characteristics of the lubricating compositions.

Methods of the lubricating compositions preparation and investigation of their tribotechnical characteristics are given below.

Preparation of lubricating compositions 1–5. 3 ml of an organic solvent (except composition 3) was added to 97 ml of industrial oil I-20A, and the mixtures were thoroughly mixed, using a magnetic stirrer until homogenization. The mixing process, as a rule, was carried out under the room temperature.

Preparation of lubricating compositions 7–11. 0.06 g of thioamide (HL^1 – HL^5) was added to 99.9 ml of industrial oil I-20A, and it was heated to 70–90 °C, and mixed until dissolved. The obtained lubricating compositions were cooled and the tribotechnical investigations were carried out.

Preparation of lubricating compositions 12, 15. 0.06 g of thioamide (HL^1 – HL^5) was added to 3 ml of DMF, then it was mixed until the full dissolution of thioamide and added to 97 ml of industrial oil I-20A. If it was necessary, the homogenization of the lubricating composition was carried out with heating to 70–90 °C, then cooled and the tribotechnical investigations were performed.

Preparation of lubricating compositions 13, 16. 0.06 g of coordination compound (CuL^1_2 – CuL^5_2) was added to 3 ml of DMF, then heated to 70 °C and stirred until the solution was homogenized. The obtained homogeneous mixture was added to 97 ml of industrial oil I-20A that was preheated to 70–80 °C. The mixture was stirred until it was completely homogenized, cooled and the tribotechnical investigations were performed.

Preparation of the lubricating compositions 14, 17 were carried out similarly to the lubricating compositions 13, 16. In this case, for example, instead of the coordination compound CuL^1_2, a mixture of HL^1 + CuL^1_2 in a ratio of 1 : 1 was taken.

Methodology of the investigation. The lubricating compositions were investigated using a friction machine SMC-2 (Fig. 1) with the friction pairs «shoe-roller», sliding velocity was 3.0 m/s and friction displacement – $3 \cdot 10^3$ m. Material of the roller was steel 45, shoe material – bronze BrAZ 9-4. The initial roughness was from 0.30 μm to 0.62 μm applied for a steel sample and from 0.62 μm to 0.80 μm for a bronze sample [9]. The duration of testing of one composition was 40 minutes. The temperature change in the friction zone was determined by the chromel copel thermocouple and marked on the corresponding strip chart curve of the electronic potentiometer KSP-4. The frictional force was determined with the means of a strain gauge sensor. The wear of the sample was indicated by a weighting method, which was applied on the analytical balance of the second accuracy classe VLR-200 type (GOST 24104–80). The change of mass of the samples was determined:

$$\Delta m = m_n - m_k \qquad (1)$$

where m_{n} – initial mass of the sample, g; $m_{\text{к}}$ – mass of the sample at the end of the experiment, g.

From the friction torque curve in a strip chart was taken the value of l in mm, corresponding to the deviation of the movable carriage of the KSP-4 potentiometer at the beginning and at the end of the experiment (the mode of stable selective transfer in the friction couple). With the calibration chart, it was determined the corresponding friction torqueM_{fr} by the l (mm) deviation magnitude of the potentiometer's carriage. The friction coefficient was determined by the formula:

$$f = \frac{M_{fr}}{r \cdot N} \qquad (2)$$

where M_{fr} – friction torque in the investigated friction pair, N·m; r – radius of a movable roller, m; N – total load in the friction pair, N.

The installation schematic diagram of the investigated tribotechnical characteristics of the lubricating compositions in a friction pair «bronze– steel» is given in Fig. 1.

Investigation of the tribotechnical system «bronze BrAZ 9-4 – organic solvent – oil I-20A – steel 45» [11]. It is known [12, 13] that in the friction pair «bronze-steel», the friction mechanical effect leads not only to the wear of its surface, but also due to the presence of complexing reagents in the oil medium, the friction mechanical effect leads to the formation of the metal-complex compounds, which are different in the composition and structure. Initially, this phenomenon was observed in the friction pair «copper alloy – steel» in glycerine, which was oxidized as a ligand, and formed the multiplex metal-complex compounds [14, 15].

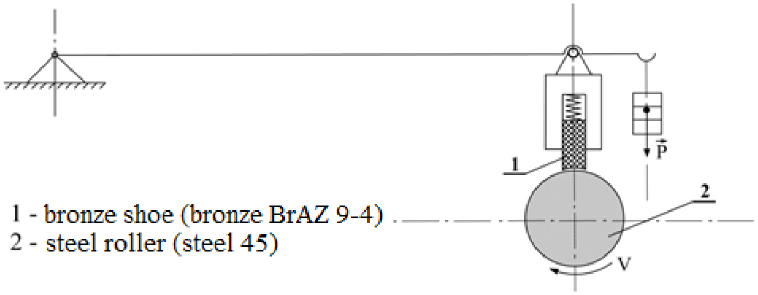


Fig. 1. The installation schematic diagram of the investigated tribotechnical characteristics of the friction pair bronze BrAZ 9-4 – steel 45, using a friction machine of SMC-2 type

The next persistent investigations of this friction pair, under the presence of N-, O-containing organic ligands, were proved the formation of copper(II) coordination complexes, the presence of which, substantially improved the tribotechnical properties of the lubricating compositions [12, 16, 17]. Specifically, the wear (I_g) and the friction coefficient (f_{fr}) decrease was unambiguously associated with the oxidation of metals during the friction in the oil medium and with the formation of their coordination compounds [18].

A sufficient number of scientific surveys is devoted to the problem of the metals oxidation in the aprotic solvents. In the studies [21–23] it was frequently considered that the metals oxidative solubility, especially, the direct organometallic and coordination complexes synthesis, is determined both by the nature of the metal (the ionization potential U, the standard redox potential E^0, the resonant potential I_r), and by the nature of the organic aprotic solvent (dipole moment μ, dielectric permittivity ε^{20}, donor number DN_{SbCl_5}). In the researches [23–26] it is stated that metals oxidation rate W depends on the donor numbers DN_{SbCl_5} of the organic solvents and has an extreme character, thus, $W = f(DN_{SbCl_5})$ correlation can be applied. This can be explained by the selective adsorption on the metallic surfaces, which have the diverse nature. Thus, Kuprin V. P. [27, 28] demonstrated the correlation of copper and bronze adsorption of the organic substances / solvents and their resonant potential (I_r), which also has the similar extreme character. However, it can be assumed, that there is a direct correlation between the organic solvents donor force (DN_{SbCl_5}) and their resonant potentials (I_r), if there is an adsorption of organic substances / solvents on the metal surface, the metals oxidation of this surface, where M^{n+} cations are formed, and the probability of their complexation in the solution is maximum (triple conditional «resonance») then, as a consequence, the friction pair has the minimum values of the wear (I_g) and friction coefficient (f_{fr}), in the case of using such tribotechnical systems. An example of this assumption is the analysis and comparison of the different authors' investigation results, which are given in Fig. 2. The curve I represents the extreme correlation of the cadmium oxidation rate (I_r = 7.4 eV [25]) and diphenylbismuthchloride, under involving of the organic aprotic solvents, and of their donor numbers [24]. It was found that the maximum dissolution rate (W_{rel}) of cadmium is observed in solvents with the highest donor activity: DMSO and DMF. The II curve shows the correlation between the obtained wear (I_g) of the friction pair «bronze BrAZ 9-4 – steel 45» of the lubricating composition «oil I-20 A + organic solvent», and the donor numbers of the investigated organic solvents.

According to the study [27], the resonant potential is equal to I_r = 7.2 eV for zero-valent copper and for its oxides CuO and Cu_2O I_r = 7.9 eV, and for bronze with the different composition, for example, with the tin composition, I_r^1 = 7.25 eV and I_r^2 = 8,00 eV. If we assume that with the same donor force of the investigated organic solvents (curves I and II, Fig. 2) and approximately the same values of the resonant potentials for cadmium and copper, their dissolution rate coincides, and the wear in the friction pair «bronze-steel» is inversely proportional to the metals dissolution rate, then the correlation $W_{rel} = f(DN_{SbCl_5})$ and $I_g = f(DN_{SbCl_5})$, should be implemented, i.e., $W_{rel} = 1/I_g$, which is proved by the given graphical data in Fig. 2.

The results of the antiwear and antifriction properties investigation of the lubricating compositions 1–5 (Table 1) in a wide range of the contact load (Table. 2 and 3).

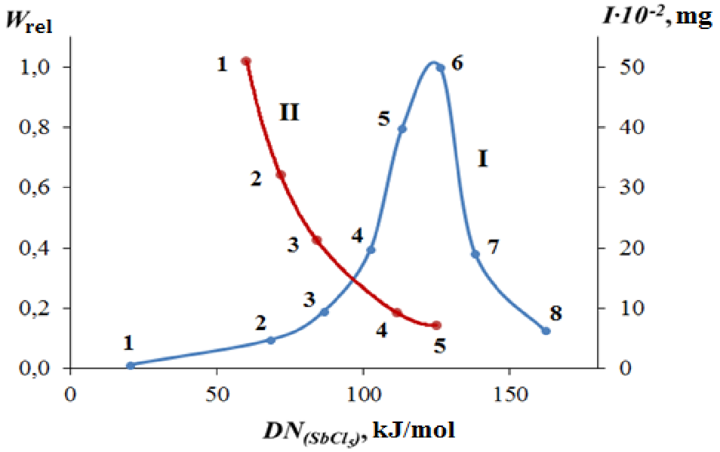


Fig. 2. The correlation of the relative dissolution rate between cadmium and bismuth diphenyl chloride and the donor numbers of the used organic solvents (I, conditions: $t = 20$ °C, $C_{ox} = 0,4$ mol/l): *1* – *p*-xylene; *2* – ethyl acetate; *3* – tetrahydrofuran; *4* – diglyme; *5* – DMF; *6* – DMSO; *7* – pyridine; *8* – hexamethylphosphoramideand the correlation of the wear in the friction pair «bronze BrAZ 9-4 – steel 45» with the lubricating composition «oil I-20 A + organic solvent» and donor numbers of the used organic solvents (II, conditions: $t = 20$ °C, $\tau = 3$ h, $P = 8$ MPa): *1* – dipropyl oxalate; *2* – ethyl acetate; *3* – TCM : DMF = 1 : 1; *4* – DMF; *5* – DMSO

Table 1

The compounds of the lubricating compositions «oil I-20A + organic solvent» and their physical, antiwear and antifriction properties

Composition	Compounds of the composition			Physical properties [29]			Tribotechnical properties	
	Organic solvent		Base oil I-20A	μ, C · m · 10^{-30}	ε^{20}	DN_{SbCl_5}, kJ/моl	I_g, mg	f_{fr}
	Title	% mass						
1	dipropyl oxalate	3,0	до 100	–	–	60,00	0,5106	0,32
2	ethyl acetate	3,0	до 100	6,03	18,51	71,57	0,3215	0,23
3	TCM	1,5	до 100	–	–	84,00	0,2128	0,19
	DMF	1,5						
4	DMF	3,0	до 100	12,70	36,7	111,33	0,0928	0,12
5	DMSO	3,0	до 100	13,03	48,9	124,73	0,0733	0,10
6	I-20A	100	–	–	–	–	0,6004	4,24

Note. Investigation of the tribotechnical properties of the lubricating compositions *1–5* was carried out under the contact load of 8.0 MPa in the friction pair «bronze BrAZ 9-4 – steel 45» under the 20 °C temperature condition during 3 hours.

Table 2

Antiwear properties of the lubricating compositions «oil I-20A + organic solvent» under the various loads

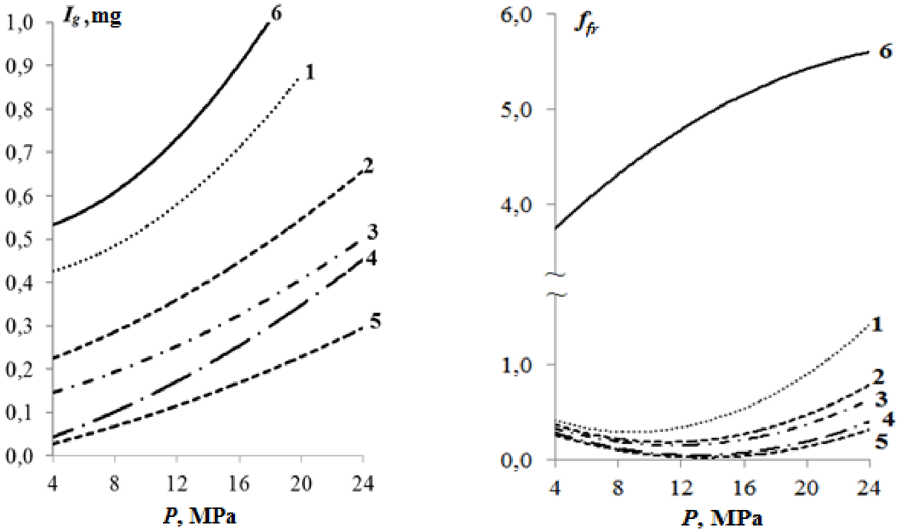
Composition	Wear of the sample I_g, mg, under the contact pressure P, MPa					
	4	8	12	16	20	24
1	0,4134	0,5106	0,5747	0,6933	0,8892	–
2	0,2200	0,2856	0,3805	0,4301	0,5408	0,6647
3	0,1402	0,2008	0,2567	0,3200	0,4001	0,5066
4	0,0433	0,0928	0,1867	0,2534	0,3332	0,4607
5	0,0267	0,0733	0,1005	0,1800	0,2267	0,2940
6	0,6003	0,6004	0,7406	0,9002	–	–

Table 3

Antifriction properties of the lubricating compositions «oil I-20A + organic solvent» under the various loads

Composition	The friction coefficient f_{fr} under the contact pressure P, MPa					
	4	8	12	16	20	24
1	0,41	0,32	0,33	0,51	0,96	1,41
2	0,37	0,23	0,19	0,27	0,48	0,80
3	0,34	0,19	0,15	0,21	0,40	0,63
4	0,29	0,12	0,06	0,08	0,19	0,41
5	0,27	0,10	0,03	0,05	0,15	0,32
6	3,76	4,24	4,85	5,20	5,15	5,64

The results of the investigation (Table 2, 3) are represented graphically in Fig. 3.The data shown in Fig. 3*a* represent that in the range of contact load from 4 MPa to 24 MPa, the lubricating compositions, which contain organic solvents with high value of donor numbers DN_{SbCl_5} (compositions *4* and *5*), have the best antiwear properties in the friction pair «bronze BrAZ 9-4 – steel 45», which unequivocally indicates the determining donor activity character of the organic aprotic solvents under the oxidation of metals. The determining influence on the wear decrease of the donor activity of organic solvents in the compounds of the lubricating compositions remains unchanged irrespectively to the contact load (4–24 MPa) in the investigated friction pair. It should be noted that the additional DMF dilution with 50 % of tetrachloromethane (DN_{SbCl_5} = 0) reduces the overall value of the donor activity (DN_{SbCl_5} = 84,4; the value is obtained by the graphic data interpolation (Fig. 2) and increases the wear in 1.6 times compared to «pure» DMF, which again proves the important character of the aprotic solvents and their donor activity during the metals oxidation.



(*a*) (*b*)

Fig. 3. The correlation between the wear (*a*) and the friction coefficient (*b*) under the contact load in the friction pair «bronze BrAZ 9-4 – steel 45» with the lubricating composition «oil I-20A + organic solvent» (conditions: $t = 20$ °C, $\tau = 3$ h): *1* –dipropyl oxalate, *2* –ethyl acetate, *3* – TCM : DMF = 1 : 1; *4* – DMF; *5* – DMSO; *6* – «pure» oil I-20A

It was found out a similar correlation between the decreasing of the friction coefficient under the growth of the donor activity of the organic aprotic solvents within the pressure range from 4 MPa to 24 MPa for the investigated lubricating compositions (Fig. 3*b*). It should be considered a significantly less range of the friction coefficient change in the definite range of contact pressure. It is obviously, that it is revealed due to another mechanism of the antifriction action of the compounds of the compositions *1–5* in comparison to the mechanism of antiwear action of the same solvents.

Investigation of the tribotechnical system «bronze BrAZ 9-4 – thioamide – oil I-20 A – steel 45» [8, 30]. In addition to the nature of aprotic solvents (Solv), the metals dissolution rate is greatly influenced by the presence of a complexing agent in the investigated systems:

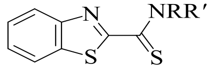
$$M^0 + m \cdot L \cdot \xrightarrow[-n\bar{e}]{+Ox,(+Solv)} L_m M^{n+} + \mathrm{Re}d + P \qquad (3)$$

where M^0 – zero-valent metal; L – complexing agent; Ox – oxidant; $L_m M^{n+}$ – formed coordination complex; Re*d* – reduced oxidant form; *P* – by-products of the chemical interaction.

In our case, different substituted thioamides have been investigated as complexing agents. The thioamides, as additives to industrial oils, have been studied in detail in the following surveys [19, 31–36], however, the improvement of the tribotechnical properties of the friction pair «bronze-steel» was previously related only to the implementation of copper (II) selective transfer from the bronze surface to the steel surface without taking into consideration the character of the organic solvents in this process. In the studies [9, 19] there were investigated the lubricating compositions, which are based on the industrial oil I-20A, complexes of the mixed ligand thioamides and DMF, as an aprotic solvent. However, DMF was used to homogenize the lubricating composition and to improve the copper(II) metal-chelates dissolution, and not as an active component of additional dissolution of zero-valent copper in the friction pair «bronze – steel». In the context of these studies tasks, which are related to the direct synthesis of copper(II) thioamide complexes, we conducted an additional investigation of the effect of the aprotic solvents on the tribotechnical properties of the industrial oil I-20A. At first, for this purpose, the system «bronze BrAZ 9-4 – thioamide – oil I-20 A – steel 45» was investigated. In this case, the obtained data (Table. 4) and their corresponding graphical correlation is represented in Fig. 4. The investigated thioamides HL^1 – HL^5, containing benzothiazole and amine –NRR' fragments, as additives to the oil I-20A, in various ways influence on the antiwear properties of the investigated lubricating compositions *7–11*. We have determined that the obtained data in the range of the 8–16 MPa contact pressure are the most important and informative.

Table 4

Compounds of the lubricating compositions «oil I-20 A + thioamide» and their antiwear and antifriction properties

Composition				Compounds of the composition, %			Wear of the sample $I_g \cdot 10^{-1}$, mg					Friction coefficient $f_{fr} \cdot 10^{-2}$				
	R	R′	designation	thioamide	DMF	oil I-20A	contact pressure *P*, MPa									
							8	12	16	20	24	8	12	16	20	24
7	H	C_6H_5	HL^1	0,06	–	до 100	0,43	0,88	1,33	4,95	8,50	2,3	2,4	2,5	2,9	3,2
8	CH_3	CH_3	HL^2	0,06	–	до 100	0,33	0,50	0,67	3,50	6,00*	2,5	2,6	2,7	5,1	8,0
9	$(CH_2CH_2)_2O$		HL^3	0,06	–	до 100	0,00	1,30	2,67	4,31	5,87	3,0	3,1	3,3	5,2	7,3
10	H	C_6H_4Cl-4	HL^4	0,06	–	до 100	0,00	1,28	2,50	3,88	5,25	3,3	5,0	6,7	6,6	6,4
11	H	C_6H_4Br-4	HL^5	0,06	–	до 100	0,00	0,93	1,80	2,35	3,00	5,7	5,8	5,9	5,7	5,5

Note: * – the value was obtained under the 22 MPa contact pressure.

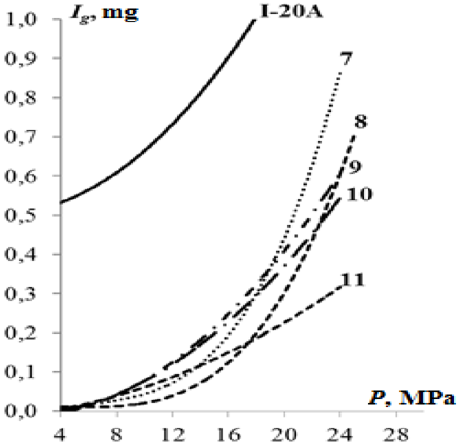


Fig. 4. The correlation between the wear and the contact pressure in the friction pair «bronze BrAZ 9-4 – steel 45» with the lubricating composition «oil I-20A + thioamide» (*t* = 20 °C, *τ* = 3 h)

It should be highlighted that thioamides with *N*-aryl fragment (HL^1, HL^4, HL^5) from 8 MPa to 16 MPa contact pressure range have the best results, while under the increasing of the contact pressure to 24 MPa, the antiwear activity series changes into this:

$$HL^5 > HL^4 > HL^3 > HL^2 > HL^1,$$

that at the first approximation can be explained by the thermicpermanence increase of the investigated heterocyclic thioamides. Thus, in the heat-resistant correlation, in the given series, *N*,*N*-dimethylamidobenzothiazole-2-thiocarboxylic acid (HL^2) is the least stable compound and is the latest in the given antiwear activity.

Fig. 5 illustrates the graphical correlation between the antifriction properties of the investigated lubricating compositions *7–11* (Table 4) and the contact load.

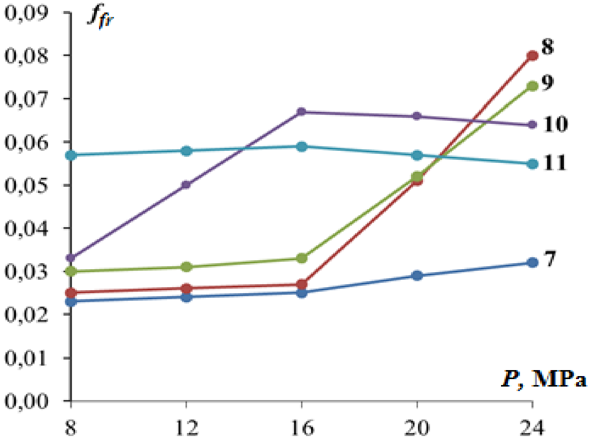
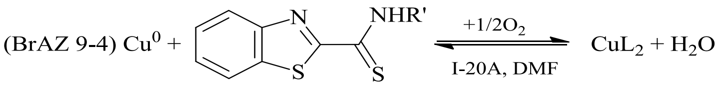


Fig. 5. The correlation between the friction coefficient and the contact pressure in the friction pair «bronze BrAZ 9-4 – steel 45» with the lubricating composition «oil I-20A + thioamide» ($t = 20$ °C, $\tau = 3$ h)

It should be taken into consideration that on the correlation curves $f_{fr} - P$ the investigated lubricating compositions have a «critical» inflection point, which is equal to 16 MPa. Under the growth of contact load, for all compositions *7–11* the friction coefficient linearly increases up to 16 MPa. A further contact pressure growth leads to the linear increase of the friction coefficients only for compositions *7–9*, whereas for compositions *10* and *11* the friction coefficient unexpectedly decreases. In the composition of the investigated thioamides, which revealed such properties, there were contained the chlorine atom (HL^4) and bromine atom (HL^5) in the *N*-aryl fragment, that explains such an anomalous correlation.

A comparison of the obtained antiwear and antifriction properties (Table 4) of the lubricating compositions shows that in some cases the tribotechnical properties improvement does not occur simultaneously, and it can be interpreted by the means of different mechanisms of additives action in the investigated friction pair «bronze – steel».

Investigation of the tribotechnical systems «bronze BrAZ 9-4 – oil I-20A – thioamide – DMF – steel 45» and «bronze BrAZ 9-4 – oil I-20A – Cu(II) chelate – DMF – steel 45». Previous, simpler tribotechnical systems studies revealed the organic aprotic solvents effect on the direct dissolution of zero-valent copper, which is contained in bronze BrAZ 9-4, and impact on the improvement of the antiwear and antifriction properties of the lubricating compositions, based on industrial oils. During the investigation of the same friction pair and aprotic solvent replacement with heterocyclic thioamides of the different substitutions, which included the benzothiazole fragment, their high efficiency was demonstrated, concerning the improvement of the antiwear and antifriction properties of the «bronze – steel» friction pair. According to Kuzharov A. S. [12] and our previous studies, this can be explained due to the fact, that in the friction process, coordination complexes of general formula CuL_2 are formed. At the same time oxygen is the oxidant, and zero-valent copper is the reductant, which is contained in bronze:



However, the composition of the previously studied tribotechnical system «bronze BRAZ 9-4 – thioamide – oil I-20A – steel 45» (tables 4 and Fig. 4, 5) did not include organic aprotic solvents with high donor activity, for instance, DMF (DN_{SbCl_5} = 111.33 kJ · mol^{-1}), which significantly increase the metallic copper dissolution rate, and the formation of CuL_2 metal chelates, and, accordingly, improve the tribotechnical properties.

In order to eliminate this disadvantage, we conducted investigations of such tribotechnical systems:

– «bronze BrAZ 9-4 – oil I-20A – thioamide (HL^1, HL^5) – DMF – steel 45». It was assumed that a comparison of the obtained results concerning the antiwear properties of the lubricating compositions, which contain active additives (HL^1, HL^5), (HL^1 + DMF) and (HL^5 + DMF), would reveal the character of the aprotic DMF solvent, as an active component of the tribotechnical system (additional factor), with the direct copper dissolution in the friction process;

– «bronze BrAZ 9-4 – oil I-20A – chelate (CuL^1_2, CuL^5_2) – DMF – steel 45». It was assumed that in the case of similar results, concerning the antiwear properties, obtained by the investigation of the given systems: (HL^1 + DMF) and (CuL^1_2 + DMF), (HL^5 + DMF) and (CuL^5_2 + DMF), it is possible not only indirectly to prove the formation of metal chelates CuL^1_2, CuL^5_2, but also to reveal the active character of the aprotic solvents, because such investigations have not been carried out previously.

The results, obtained under the investigation of these systems are given in Table 5.

Table 5

Compounds of the lubricating compositions «I-20A oil + thioamide + DMF» and «I-20A oil + chelate Cu(II) + DMF» and their antiwear properties

Composition	The compounds of the composition, %				Wear I_g, mg, under the contact pressure P, MPa				
	thioamide HL	complex CuL^n_2	DMF	I-20A	8	12	16	20	24
7	HL^1, 0,06	–	–	до 100	0,043	0,088	0,133	0,495	0,850
12	HL^1, 0,06	–	3,0	до 100	0,040	0,027	0,030	0,038	0,039
13	–	CuL^1_2, 0,06	3,0	до 100	0,010	0,014	0,018	0,027	0,013
14	HL^1, 0,03	CuL^1_2, 0,03	3,0	до 100	0,024	0,034	0,026	0,041	0,034
11	HL^5, 0,06	–	–	до 100	0,000	0,093	0,180	0,235	0,300
15	HL^5, 0,06	–	3,0	до 100	0,035	0,022	0,011	0,032	0,030
16	–	CuL^5_2, 0,06	3,0	до 100	0,000	0,011	0,016	0,025	0,021
17	HL^5, 0,03	CuL^5_2, 0,03	3,0	до 100	0,000	0,019	0,034	0,040	0,033

In the friction pair «bronze BrAZ 9-4 – steel 45» of the lubricating compositions *12–17*, the results of the investigation regarding the wear and contact load correlation (Table 5) and represented in Fig. 6 and 7, and can be formulated as following:

– under the condition of the contact load change, in the investigated lubricating compositions, in the friction pair «bronze BrAZ 9-4 – steel 45», the wear magnitude variation is represented as a constrained values range I_g: for the lubricating compositions *12–14* (Fig. 6) the magnitude variation is 0.013–0.041 mg, and for compositions *15–17* (Fig. 7) the magnitude variation is 0.011–0.04 mg;

– in the friction pair «bronze BrAZ 9-4 – steel 45», given intervals of the wear magnitude variation are practically identical, thus, as a sequence, we obtained the same antiwear effect mechanism of the investigated additives and lubricating compositions (Table 5);

– similar $I_g$values of the investigated compositions *12–17*, for example, under the condition when P = 16 MPa demonstrate, that the active substances, which provide the antiwear properties of the investigated friction pair, are absolutely CuL^{1}_{2} and CuL^{5}_{2} coordination compounds, which are present in the I-20A industrial oil;

– the difference in I_g values is 4.4 times for compositions 7 (HL^1) and 12 (HL^1 + DMF) (Table. 5, Fig. 6), for instance, under the condition when P_c = 16 MPa, and for compositions 11 (HL^5) and 15 (HL^5 + DMF), Table. 5, Fig. 7, under the same contact pressure, the difference in I_g values is 16.4 times, and it can be considered as a very significant aprotic DMF solvent effect regarding the process of zero-valent copper dissolution according to the previously given scheme (4)

It was demonstrated the series of the antiwear and antifriction action of the investigated organic solvents under the P = 8 MPa contact load.

f_{fr}	DMSO	>	DMF	>	(DMF + CCl_4)	>	$CH_3C(=O)OC_2H_5$	>	$(C(=O)OC_3H_7)_2$
I_g, mg	DMSO	>	DMF	>	(DMF + CCl_4)	>	$CH_3C(=O)OC_2H_5$	>	$(C(=O)OC_3H_7)_2$
DN_{SbCl_5} kJ/mol	124,73		111,33		84,00		71,57		60,00

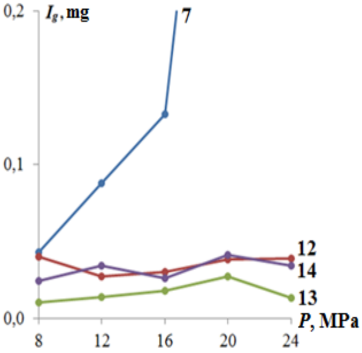


Fig. 6. The correlation between the wear and contact load in the friction pair «bronze BrAZ 9-4 – steel 45» with the lubricating compositions «oil I-20A + thioamide HL^1 + DMF» and «oil I-20A + chelate CuL^{1}_{2}» (t = 20 °C, τ = 3 h)

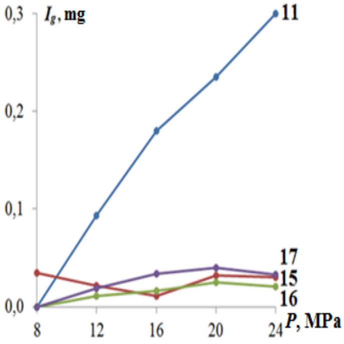


Fig. 7. The correlation between the wear and contact load in the friction pair «bronze BrAZ 9-4 – steel 45» with the lubricating compositions «oil I-20A + thioamide HL^5 + DMF» and «oil I-20A + chelate CuL^{5}_{2}» (t = 20 °C, τ = 3 h)

These data specify a linear correlation of the I_g and f_{fr} decrease in relation to the increasing of the donor activity of the investigated aprotic solvents ($DN_{\mathrm{SbCl_5}}$) and their ability to, additionally, increase the dissolution of zero-valent copper in the friction pair «bronze – steel» with the formation of the corresponding coordination compounds. It was found that the serial complication of the lubricating compositions *1–5*, *7–17* by the addition of the organic solvents, thioamide complexones (HL^1 – HL^5), copper(II) metal chelates, based on them (CuL^{1}_{2}, CuL^{5}_{2}), to oil I-20A allowed not only to find out a number of antiwear activity of additives, for example, for the aprotic solvent DMF:

Additives to the oil I-20A	I-20A	>	DMF	>	HL^1	>	HL^1 + DMF	>	CuL^{1}_{2} + DMF
I_g, mg	0,6004		0,0928		0,0430		0,0400		0,0100

but also to investigate the influence of each of the factors on the tribotechnical characteristics in the friction pair «bronze BrAZ 9-4 – steel 45».

Thus, the conducted investigations allow us to draw the following conclusions:

1. Organic solvents, whch are included in the lubricating compositions «oil I-20A + organic solvent» in 1,2–8,2 and 13,3–42,4 times improve, respectively, the antiwear and antifriction properties of the friction pair «bronze BrAZ 9-4 – steel 45» in comparison with «pure» oil I-20A.
2. Antiwear properties of the lubricating compositions «oil I-20A + organic solvent» in the friction pair «bronze BrAZ 9-4 – steel 45» are determined by the donor activity ($DN_{\mathrm{SbCl_5}}$) of the organic solvents: $I_g = f\,(DN_{\mathrm{SbCl_5}})$. The minimum wear values are observed during there were used organic solvents (DMF, DMSO), which have the maximum values of $DN_{\mathrm{SbCl_5}}$.
3. The injection of the organic solvent (DMF) into the lubricating composition «oil I-20A + thioamide HL^1» provides the wear decrease in the «bronze BrAZ 9-4 – steel 45» friction pair in 4.4 times, under the contact pressure of 16 MPa. Thus, the organic solvent (DMF) is an active dissolution zero-valent copper component, which is contained in bronze.
4. Similar values of the wear in the friction pair «bronze BRAZ 9-4 – steel 45», within the presence of the lubricating compositions «oil I-20A + thioamide HL^1 + DMF», «oil I-20A + chelate CuL^{1}_{2} + DMF», «oil I-20A + thioamide HL^1 + chelate CuL^{1}_{2} + DMF» (according to 0.030, 0.018 and 0.026 mg under the contact pressure of 16 MPa) prove that in all cases the active antiwear additive to oil I-20A is the coordination compound CuL^{1}_{2}.
5. Coordination compounds of the general formula $\mathrm{CuL_2}$ are the effective antiwear and antifriction additives to industrial oils and can be recommended for industrial use and can be applied for the general friction pairs «bronze – steel».

РЕФЕРАТ

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ФОРМУВАННЯ КООРДИНАЦІЙНИХ СПОЛУК МІДІ (ІІ) ПІД ЧАС ПРОЦЕСУ ТЕРТЯ ТА ЇХ ВПЛИВ НА ТРИБОТЕХНІЧНІ ХАРАКТЕРИСТИКИ ЗМАЩУВАЛЬНИХ РЕЧОВИН

Досліджено трибохімічну систему «бронза БрАЖ 9-4 – органічний додаток – олива І-20А – сталь 45», у якій під дією механічного активування металевих поверхонь пари тертя та органічних додатків утворюються координаційні сполуки купруму (II), що забезпечують високі протизношувальні й антифрикційні властивості мастильних композицій. Послідовне ускладнення мастильних композицій шляхом додавання до базової оливи І-20А органічних розчинників, тіоамідних лігандів та метал-хелатів купруму (II) на їх основі дозволило встановити ряд протизношувальної активності додатків до індустріальної оливи І-20А та дослідити вплив кожного із чинників на триботехнічні характеристики в парі тертя «бронза БрАЖ 9-4 – сталь 45». На основі отриманих результатів зроблено висновок, що покращення експлуатаційних характеристик мастильних композицій визначається утворенням у процесі трибохімічних реакцій координаційних сполук купруму (II).

Ключові слова: трибохімія, мастильні композиції, координаційні сполуки купруму(II), протизношувавльні і антифрикційні властивості

РЕФЕРАТ

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ФОРМИРОВАНИЕ КООРДИНАЦИОННЫХ СОЕДИНЕНИЙ МЕДИ (II) ВО ВРЕМЯ ПРОЦЕССА ТРЕНИЯ И ИХ ВЛИЯНИЕ НА ТРИБОТЕХНИЧЕСКИЕ ХАРАКТЕРИСТИКИ СМАЗЫВАЮЩИХ ВЕЩЕСТВ

Исследована трибохимическая система «бронза БрАЖ 9-4 – органическая присадка – масло И-20А – сталь 45», в которой под действием механического активирования металлических поверхностей пары трения и органических присадок образуются координационные соединения меди(II), обеспечивающие высокие противоизносные и антифрикционные свойства смазочных композиций. Последовательное усложнение смазочных композиций путем добавления к базовому маслу И-20А органических растворителей, тиоамидных лигандов и металл-хелатов меди (II) на их основе позволило установить ряд противоизносной активности присадок к индустриальному маслу И-20А и исследовать влияние каждого из факторов на триботехнические характеристики в паре трения «бронза БрАЖ 9-4 – сталь 45». На основании полученных результатов сделан вывод, что улучшение эксплуатационных характеристик смазочных композиций определяется образованием в процессе трибохимических реакций координационных соединений меди(II).

Ключевые слова: трибохимия, смазочные композиции, координационные соединения меди (II), противоизносные и антифрикционные свойства

ABSTRACT

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FORMATION OF COPPER (II) COORDINATION COMPOUNDS UNDER THE FRICTION PROCESS AND THEIR IMPACT ON THE TRIBOTECHNICAL CHARACTERISTICS OF THE LUBRICATING COMPOSITIONS

It has been investigated the tribochemical system «bronze BrAZ 9-4 – organic additive – oil I-20A – steel 45» in which due to mechanical activation of metal particles of the surfaces of friction pair the copper(II) coordination compounds have been created. These complexes provide high antiwear and antifriction properties of the lubricating compositions. The sequential complication of lubricating compositions by adding organic solvents, thioamide ligands and metal chelates of copper(II) based on them to base oil I-20A allowed to establish an order of anti-wear activity of additives to industrial I-20A oil and investigate the influence of each of the factors on tribotechnical characteristics in friction pair «bronze BrAZ 9-4 – steel 45». Based on the obtained results, it is concluded that improvement of the operational characteristics of lubricating compositions is determined by the formation of copper(II) coordination compounds during the tribochemical reactions.

Key words: tribochemistry, lubricating compositions, copper (II) coordination compounds, antiwear and antifriction properties.

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2.3 DEVELOPMENT OF ALTERNATIVE JET FUELS MODIFIED WITH CAMELINA OIL BIO-ADDITIVES

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Constant increase of aircraft fleet and exhausting crude oil deposits promote worsening of the world energy crisis. As a result we observe rise in prices for jet fuel (JF) that today comprise about 25–30 % of passenger travel [1]. Moreover, products of fuel combustion cause detrimental impact on environment. Thus, the task of search and development of alternative JFs became especially important.

This work is devoted to the study of possibilities of partial replacement of conventional JFs with components of biological (plant) origin. It will allow decreasing the dependence on exhaustible energy sources and minimizing negative impact of aviation on environment.

Today alternative fuels from various renewable feedstock are actively developed and studied. Among them are fuels made of biomass, plant oils, animal fats, microalgae, waste from agriculture, wood processing industry, municipal waste etc [2]. JFs produced from biomass via FTsynthesis and fats hydration were successfully tested and now are already implemented [3]. Theses alternative fuels possesss high quality, however its' chemical structure looks as completely synthetic paraffinic kerosene [5]. It means that entering the environment fuel causes negative impact on nature similarly to conventional JFs.

There is a good experience in use of conventional JF mixture with bio-additives produced from plants oil up to 50 % [6]. These bio-additives are methyl or ethyl esters of plant oils or animal fats. The most rational feedstock is rapeseed or camellina oils (CamO) [7]. Camelina relates to energy crops with high oil content. The main consumers are the producers of biofuels. Camelina is used in agriculture as crop rotation, which prevents reduction of soil fertility and provides increasing of crop resistance to diseases and pests. It is not demanding to climatic conditions and does not require substantial cultivation and care. Camelina seeds contain 40–50 % of oil, providing oil output of about 1250 l/ha [1–5]. Another advantage of this culture is the use of meal as feed for livestock and poultry. The scientists believe these camelina characteristics provide "sustainability" of the process of aviation biofuels production without creating competition in the food industry. Nowadays this culture is widespread in the US, Canada and some European countries [2].

However, today application of these bio-additives as components of JF is at the early stage of development and need to be studied completely. In this regards, the work is devoted to studying persectives of development new alternative JFs with CamO bio-additives.

The *purpose* of this work is to study key physical-chemical and exploitation properties of JFs modified with CamO bio-additives and to consider the possibility of using JF, blended with bio-additives in aircrafts' jet engines.

In order to reach the set purpose it was necessary to fulfill the next *tasks*:

– To study experimentally the main physical-chemical and exploitation properties of JF and CamO bio-additive;

– To study experimentally the main physical-chemical and exploitation properties of JFs modified with CamO bio-additives in quantity 10 %, 20 %, 30 %, 40 % and 50 %;

– To analyze and explain the influence of bio-additives on physical chemical and exploitation properties of JFs.

The quality of fuel samples was determined according to the following physical-chemical and exploitation properties: density, fractional composition, heat of combustion, kinematic viscosity, freezing point, anti-wear properties, fire safety and corrosiveness. The mentioned properties are considered to be identifying for quality control of conventional and blended JFs.

For fulfilling experimental studies conventional JF of grade Jet A-1 was used. This type of fuels was produced by Polski Koncern Naftowy «ORLEN» (Plok, Poland), and its quality parameters meet requirements of specifications ASTM D1655, Def Stan 91-91.

For obtaining alternative JF CamO fatty acids ethyl esters (FAEE) bio-additive were used. It was produced in the Institute of bioorganic chemistry and petrochemistry of the National Academy of Sciences of Ukraine.

Within the scope of the work physical-chemical and exploitation properties of pure JF, pure sample of bio-additive and JF blends, which contained 10 %, 20 %, 30 %, 40 % and 50 % of bio-additive were studied. The list of studied fuel samples and its designations are presented in Table 1.

Physical-chemical and exploitation properties of JF, bio-additives and JFs blended with bio-additives were studied using standard methods and equipment based in the Laboratory of Exploitation Materials at the Department of Internal Combustion Engines and Transport of Rzeszow University of technology and in the Laboratory "Aviatest" of the Scientific-Research Center of Chemmotology and Certification of Fuels, Lubricants and Technical Liquids of the National Aviation University. Density (denoted as ρ) was estimated according to ASTMD4052 using device for density determination "AntonPaar", DMA 4500M. Density was determined at temperature 15 °C that is specified by ASTM D1655. Fractional composition was determined according D86 using automatical fractional composition analyzer "Herzog Optidist".

Table 1

Description of fuels samples used for studying physical-chemical and exploitation properties

No	Sample description	Sample designation
1	Jet fuel of grade Jet A-1	JF
2	Bio-additive – fatty acids ethyl esters of camelina oil	CamO FAEE
3	Jet fuel blended with 10 % of bio-additive	JF+10 % CamO FAEE
4	Jet fuel blended with 20 % of bio-additive	JF+20 % CamO FAEE
5	Jet fuel blended with 30 % of bio-additive	JF+30 % CamO FAEE
6	Jet fuel blended with 40 % of bio-additive	JF+40 % CamO FAEE
7	Jet fuel blended with 50 % of bio-additive	JF+50 % CamO FAEE

Viscosity (denoted as ν) was determined according to ASTMD445 using automatic device for viscosity determination “HerzogLow temperature viscometer”, HVU 482. Viscosity was determined at temperature -20 °C that is specified by ASTM D1655 and also in a temperature range from -20 °C to 100 °C. Heat of combustion (denoted as Q) was determined according to ASTM using Automated Bomb Calorimeter IKA C 200 produced by IKA Werke GmbH&Co. KG. Flash point (denoted as t_{fl}) was determined according to ASTM D93 using Pensky-Martens Flash Point Analyzer HFP 339 (produced by Walter Herzog. Corrosiveness was determined according to ASTM using Analyzer for Corrosion Testing of Fuel (also LPG) To Copper produced by ANKO. Freezing point (denoted as t_{f}) was determined according to ГОСТ 5066–91 (ИСО 3013–74) using Petroleum products low-temperature properties analyzer UTF 70 produced by Crioholod. Antiwear properties were investigated using a T-02U four-ball tester by means of determining the scuffing load applied to the friction pair of the tester. The rotation speed during tests was 500 rpm, with the load increase rate of 409 N/s. The initial temperature of the fuel sample at the start of the test run was 20 ± 1.0 °C.

Today there are strict requirements to JFs connected with efficiency, reliability durability of aircraft equipment and environmental safety [1, 2, 7]. Among the general technical requirements special attention should be paid to:

- High level of evaporability that provides reliable flammability and completeness of fuels combustion;
- Good low temperature properties, which provide reliable fuel pumpability at low temperatures;
- Chemical and thermal stability with minimal tendency to form deposits in the fuel system of theair craftengine;
- Absence of negative impact on metal and non-metal parts of the engine fuel system, equipment for fuel storage and transportation;
- Good lubricating properties thate liminate excessive wearing of fuel assemblies friction parts;
- The optimal level of electrical conductivity, which excludes fuel electrification and provides safe fuel transfer and filling of fuel tanks;
- Absence of toxic components, impurities and additives, minimum content of sulphur compounds, which lead to harmful products in there sultof fuel combustion.

This complex of requirements is provided by physical-chemical, exploitation and ecological properties of jet-fuels, which are determined by nature and properties of raw material, methods of basic fractions productions, methods of their purification and mixing, additive sapplied [3].

At thef irst stage of the work we were studying physical-chemical properties of conventional JF Jet A-1 and CamO FAEE bio-additive. Characteristics of conventional JF and bio-additive are presented in Table 2.

It is seen from the table that properties of conventional JF completely meet the requirements of standard. However, bio-additive differs from properties of JF. Next, the compatibility of bio-additive with conventional JF and its influence on key physical chemical and exploitation properties of modified JF were studied.

Table 2

Physical-chemical properties of conventional jet fuel and biocomponents

No	Property	ASTM D1655	Jet fuelJetA-1	CamO FAEE
1	Density at temperature 15 ^{o}C, kg/m3	775–840	794.03	874.49
2	Fractional composition ^{o}C: - 10 % distilled at temperature - 50 % distilled at temperature - 90 % distilled at temperature - final boiling point	 max 205 max registered max registered max 300	 169.15 186.2 217.13 243.44	-
3	Kinematic viscosity, mm^2/s: - at minus20 ^{o}C - at 20 ^{o}C	 max 8.0 -	 3.2923 1.5004	 16.413 (-10) 6.422
4	Freezing point, ^{o}C	max minus 47	minus 57	minus7
5	Flash point, ^{o}C	min 38	43	35
6	Higher heat of combustion, kJ/kg	-	46368	39842
7	Copper strip test	1	1a	1b
8	Lubricity: Scuffing load, N	-	523	2644

Density. The density ρ of JFs is one of its main physical characteristics that influences directly on the flammability of fuel: the processes of evaporation, fuel-air mixture formation, completeness of combustion and fuel flow of the aircraft. The required density of JFs ensures reliable operation of fuel system of JE [4, 8].

The density of the JFs depends on its chemical and fractional composition. The increase of heavy fractions, aromatic hydrocarbons and reduction of paraffinic hydrocarbons contribute to increasing fuel density [8].

Fuel density plays an important role for evaluation its energy properties, including energy value and heat of combustion. Increase of aromatic hydrocarbons content in JF leads to increase of density and to rise of fuel boiling point, and as a result, increase of JF energy value [9].

The density of the JFs depends on its chemical and fractional composition [4]. CamOFAEE bio-additivepossesses much higher density value comparing to conventional JF (Table 2). It can be explained by its chemical structure. Unlike hydrocarbons of conventional JFs, which contain 5÷16 carbon atoms, acyl radicals of ester molecules contain on average 15÷26 carbon atoms [4]. This is the reason of a strong dispersion interaction forces between them and, consequently, higher density compared to JFs.

According to the research of bio-additives samples impact on JFs' density (Fig. 1), it was found that density dependence is additive in nature and may be depicted as a straight line.

Density of blended JFs increases with increasing content of bio-additives, which happens due to strengthening of the dispersion forces of interaction between molecules of hydrocarbons and acyl radicals of esters on one hand, and the appearance of induction force of interaction between hydrocarbons of JF and carboxylic groups of esters on the other [3, 4, 9].

It is known that JFs of greater density and higher final boiling point were developed in order to improve the energy properties of JFs, mainly its energy content, [6]. However, this was limited by negative impact on fuel evaporability and their low-temperature properties. It can be assumed that the addition of bio-additives to JFs will expand the range of boiling points also. Thus, the next step is to study the fractional composition of JFs blended with bio-additives.

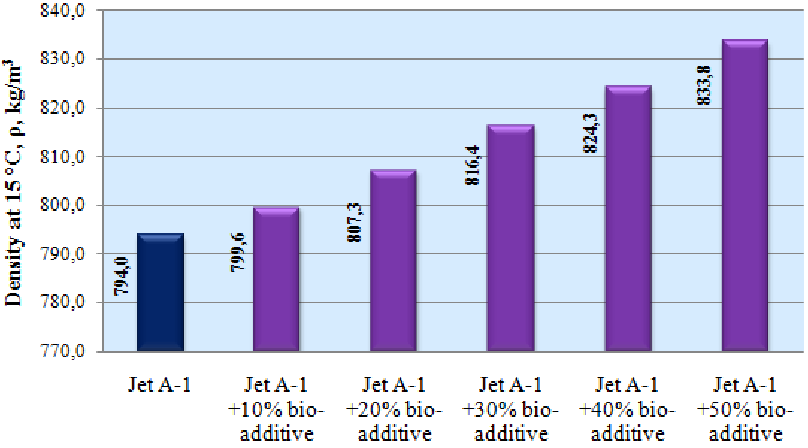

Fig. 1. Density of tested fuel samples with CamO bio-additive at *t* 15 °C

Fractional composition. JFs are a mixture of hydrocarbons of various structures [2, 7]. The data on JF's fractional composition allow evaluating the exploitation properties of JF and operation of the aircraft's fuel system: fuel evaporability, tendency to vapor locks, completeness of fuel combustion, absence of smoke and carbon inside the combustion chamber [8, 9].

Since bio-additives are also a mixture of organic compounds, a range of boiling points is also typical for it [2, 4, 5]. They belong to another class of organic compounds, which differ from petroleum hydrocarbons and from each other by structure, molecular weight and boiling points [5, 8].

Next, the influence of bio-additives on fractional composition of JFs was studied (Fig. 2). Fuel samples containing CamO FAEE in JF of grade Jet A-1 in quantities of 10 %, 20 %, 30 %, 40 % and 50 % (v/v) were studied.

The graph shows that blending JF with bio-additives affects its fractional composition, extending toward the final boiling point. Increasing of boiling points of modified JFs is explained by much stronger intermolecular bonds between esters molecules and higher heat of evaporation values of ester consequently: 58.6–69.3 kJ/mol for FAEE comparing to JF's hydrocarbon 31–47 kJ/mol.

From the graph it may be seen that boiling of fuel samples starts at about 76–77 °C. This means that CamO bio-additive contains some amount of ethanol that left in esters mixture after production process. Analyzing the data on the graph it may be concluded that the content of ethanol is up to 5–7 % The final boiling points of fuel sample are about 347–350 °C, which are similar to final boiling points of pure bio-additives.

Widening of the fractional composition in a result of JF modification with esters, mainly towards the final boil point ensures reduction of light fractions, thus reducing its evaporabiity. This in turn will reduce fuel losses from evaporation, reduce the possibility of vapor locks formation of and improve its fire safety.

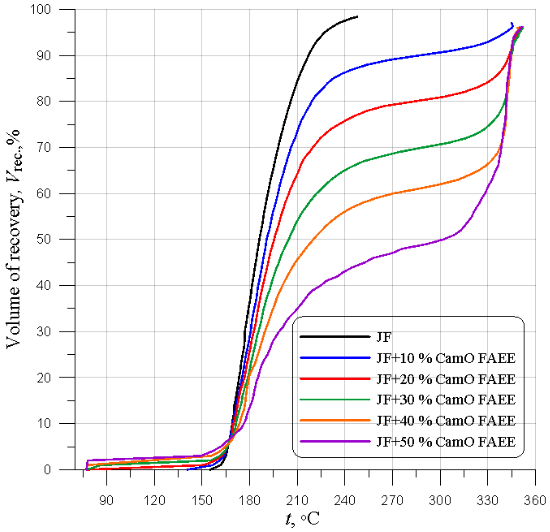

Fig. 2. Fractional composition of JF of grade Jet A-1 blended with CamO FAEE

However, the lighter fraction composition and higher vapor pressure, the better starting properties of JFs. Thus, fuels with high evaporability are able to provide jet engine launch with poor fuel-air mixture comparing to fuels with lower evaporability. In addition, increased volatility of fuels contributes to the increase of completeness of combustion and reduction of carbon formation in combustion chambers [4, 6, 9]. Studies of modified JFs showed that initial boiling point and temperature of 10 % (vol.) of recovery, which characterize evaporability and starting properties of JFs are within the values, which are set by specifications for JF of grade Jet A-1. Thus, the use of blended fuels should not have a negative impact on the launch of JEs. The final boiling point of modified JFs (up to 350 °C) significantly exceeds the norms established by specifications (up to 300 °C). This heavy fractional composition due to increased density of blended JFs will increase their energy value.

Energy properties. The heat of combustion is one of the most important physical and chemical parameters of JF quality that characterizes its energy properties [5, 6]. The purpose of the fuel in the engine is converting its chemical energy into heat one for heating of air that entering the turbine and jet pipe of the aircraft [4, 9]. For heating the required amount of air and obtaining the desired thrust characteristics of the engine it is better to use JF with the highest energy value.

According to specifications for JF the standard value is net heat of combustion. The heat of combustion is determined by its elemental composition: the more content of hydrogen in fuel, the higher is heat of combustion. Besides elemental composition, heat of combustion depends on the structure of fuel hydrocarbons. Thus, hydrocarbons of different structure have different energy of intramolecular bonds distruction. Among the components of JFs the maximal heat of combustion is typical for alkanes, then cyclic alkanes (naphtenes) and then aromatic hydrocarbons.

Data about the elemental composition of JF allows calculating its heat of combustion. *Higher heat of combustion* Q_h takes into account the heat of condensation of water vapors, which are formed during combustion. During the process of water condensation 2500 kJ/kg of energy is released. It is known that heat of vapors condensation is not used during engine operation, so the *lower heat of combustion* $Q_l$is used to characterize the fuel. Its value is less than higher heat of combustion on heat of water vapors condensation.

The method ASTM D4809 allows experimental determination of Q_h of fuel samples. Thus, within the scope of this work energy properties of fuel samples were estimated by the value of higher heat of combustion.

The results of measurements and calculations of heat of combustion of JF and CamO bio-additive are presented in Table 2. It is seen that heat of combustion of bio-additive is lower on about6600 kJ/kg, that is explained by differences in elemental composition of bio-additive: esters contain ~12 % of hydrogen, while JF – 14 %. Esters contain 11–11.5 % of oxygen, which almost absent in conventional JF.

Later the higher heat of combustion Q_h of JFs modified with bio-additives was investigated. It was found that blending of conventional JF with bio-additives reduces its higher heat of combustion (Fig. 3).

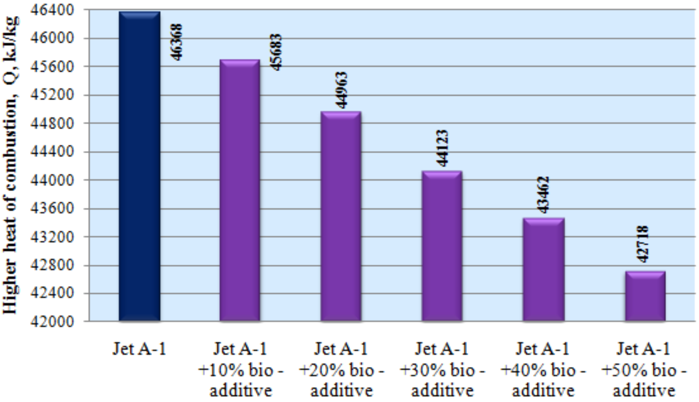

Fig. 3. Net heat of combustion of tested fuel samples

The results have shown that the blending JFs with bio-additives decreases its heat of combustion. Due to the fact that esters and blended JFs have higher density, it is reasonable to analyze in future works the changes in heat of combustion and energy value with increasing content of esters in JFs.

Kinematic viscosity. Stable operation of jet engine's fuel system at low temperatures largely depends on the fluidity of JFs that is measured by viscosity – a property of liquids to resist deformation of its volume by external forces. According to specifications for JF the standard value for describing viscosity is kinematic viscosity ν, mm^2/s.

The viscosity affects pumpability of JF within fuel system. Using high-viscous fuels can cause reduction of productivity of fuel pumps, reduction of injection pressure and quality of fuel spraying, especially at low temperatures [3, 6]. This leads to the deterioration of JF volatility and completeness of combustion. Low viscosity is also undesirable. Fine dispersion of fuel causes local oversaturation of fuel-air mixture and narrowing range of the stable operation of combustion chamber. In addition, low viscosity values adversely affect the anti-wear properties of JFs [3].

Bio-additive based on FAEE of CamO is characterized by much higher viscosity values comparing to petroleum-derived JFs (Table 2).

The reason for this is chemical structure of bio-additives. Chain length determines the large size of the compounds, which leads to higher energy of intermolecular interaction [9]. Viscosity characterizes the strength of intermolecular interaction within the fuel [1, 2]. The greater energy of intermolecular interaction, the greater is viscosity. It explains stronger dependence of esters' viscosity on temperature.

Viscosity-temperature dependence of esters can be explained by the fact that decreasing of temperature causes reduction of thermal energy of motion as well as mobility of molecules [3]. Temperature decrease leads to association increasing and rising of esters' viscosity. Hydrocarbon are characterized by smaller sizes and the energy of it's interaction is lower comparing to esters [3, 8].

CamO FAEE bioaditive possesses comparatively low viscosity values (if to copare with other types of bio-additives). Probably, this may be explained by the presence in bio-additive of small quantity of ethanol that possesses much smaller viscosity. Later the influence of CamO bio-additives on kinematic viscosity of modified JFs at 20 °C was studied (Fig. 4).

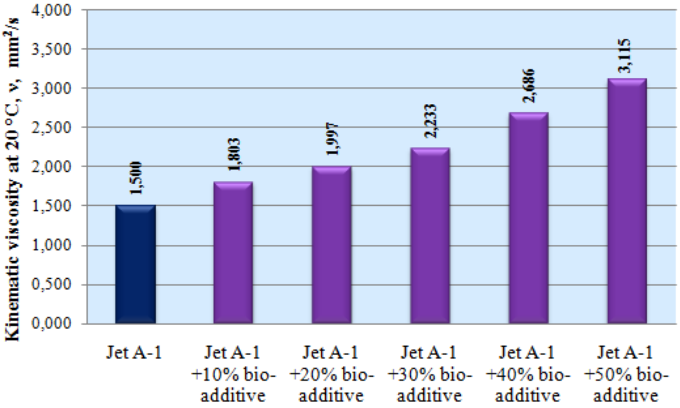

Fig. 4. Kinematic viscosity of tested fuel samples with CamO bio-additive at 20 °C

It was found that blending of JFs with bio-additives causes increase of its kinematic viscosity. We suppose that this happens due to the appearance of forces of intermolecular interaction between JF's molecules and esters' molecules [4, 7].

Low-temperature properties. Low-temperature fuel properties of JFs are characterized by its behavior at low temperatures [6, 9] and are strictly controlled by specifications. During exploitation jet engines usually have to work at very low temperatures, especially in winter. In summer period fuel also can be cooled during high-altitude flights of subsonic jet aircrafts. The reason for this is that the ambient temperature at an altitude of 9–12 km reaches minus 50–70 °C [1, 3]. Cooling of JFs may be accompanied with clogging of fuel filters that may be associated with aircrafts accidents and disasters. Cooling of fuel also reduces spraying efficiency by fuel nozzles and worsening fuel pumps operation [2, 5].

Low-temperature properties of fuels are characterized by physical and chemical phenomena, which occur in fuels at temperatures below 0 °C. Low temperature is a condition for occuring insoluble organic precipitates that affect fuel system operation. The reasons for its occurrence are the sharp decrease of solubility of some components in fuel at low temperatures and phase transitions [2, 7, 8].

The main source of low-temperature precipitate in JFs is the crystallization of fuel's hydrocarbons when freezing point (FP) is reached. Decreasing of temperature causes crystallization of hydrocarbons, rise of crystals concentration and fuel gradually loses its fluidity and then freezes [7, 8].

Bio-additives based on FAEE of CamO are characterized by significantly higher values of FP comparing to JF (Table 2). High value of bio-additive's FP is stipulated by chemical structure of molecules and by Van der Waals interactions between them. The length of the hydrocarbon chains ($C_{15}÷C_{25}$) defines the large size of the compounds. Due to this binding energy between molecules is higher comparing to conventional JFs [2, 3].

Due to the existence of intermolecular interaction forces the speed of random motion of esters molecules is insignificant. With temperature decrease its association is growing fast. Further temperature decrease causes viscosity rise to such a degree that esters freeze and loose mobility [8]. Presence of double bonds in esters makes them curve-shaped, that makes it difficult to locate compactly [8, 9].

The experimental results have shown that modifiying JFs with bio-additives increases its FP (Fig. 5). When concentrations of bio-additives are small, they are uniformly distributed in the volume of JF and distances between esters' molecules are not enough for interaction appearance. Further increase of esters content causes rise of FP that gradually approaches to values typical for pure esters.

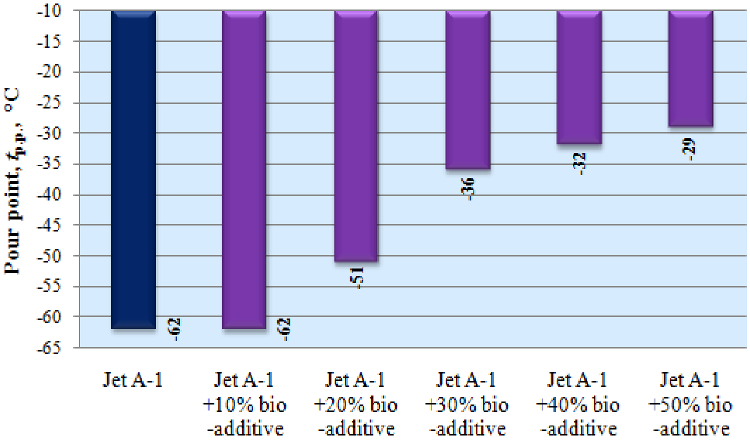

Fig. 5. PP of tested fuel samples with CamO bio-additive

When content of bio-additives in JF exceeds 30 % the content of comparatively large esters molecules is sufficient for their associations due to attraction forces, and also due to the interlinking of molecules chains. A special role in the process of "interlinking" is played by unsaturated esters of curved form. Thus, associated esters' molecules initiate formation of structure within blended JFs. The other explanation of FP rise may be proposed: during temperature decrease small molecules of JF bond with single molecules or group of associated esters molecules. This promotes association of hydrocarbons and freezing of blended JFs.

Basing on the results of experiments we can make the conclusion that sample of modified JFs, which contain up to 20–25 % of CamO FAEE, satisfy requirements of specifications.

From the studies [8] it is known that the reason for the decreasing of fuel pumpability at low temperatures is a significant increase in fuels' viscosity. In order to evaluate viscosity of modified JFs at low temperatures we have studied the mutual influence of temperature and concentration of bio-additives on the above mentioned property (Fig. 6).

Increasing the concentration of esters and reduction of the temperature are factors that contribute to the association of molecules of modified JFs primarily due to increasing the number of collisions (contacts) of esters' molecules. And reduction of temperature is a factor that strengthens the ties between associated molecules by reducing the speed of molecules thermal motion and, consequently, increases the viscosity and FP.

From the studies [3, 5] it is known that curves of JFs viscosity dependance on temperature change in the area of low temperatures very rapidly. Fig. 5 shows that even insignificant increase of temperature causes a significant decrease in fuels' viscosity. To avoid potential problems with blended JFs spraying at low temperatures it is possible to increase fuel pressure before the nozzles. This technical solution is well-known for a long time and has been successfully used during JEs exploitation. This allows achieving the required fineness of spraying and sufficient quality of fuel-air moxture in the combustion chamber.

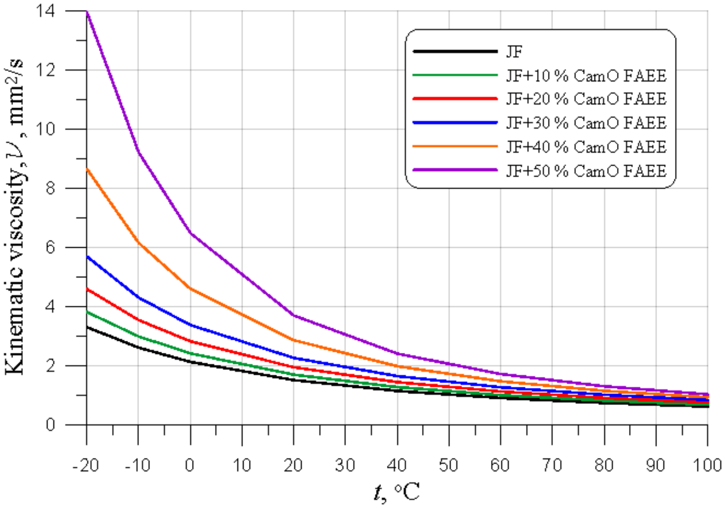

Fig. 6. Kinematic viscosity of tested fuel samples with CamO FAEE bio-additive asafunction of temperature

Anti-wear properties. It is known that antiwear properties of JFs determine reliability and operational life of aircrafts' fuel system equipment and friction pairs in particular [3, 7]. These pairs usually work in regimes of rolling friction, sliding friction and combined friction at various loads, temperatures, pressure, speed of relative movement [9]. At semi-liquid friction the antiwear properties of JFs are determined by:

- JF viscosity that provides hydrodynamic effect of wearing surfaces division by liquid,
- presence of surfactants in fuel that form high strength absorption layer at the wearing surface and divide surfaces with decreasing of friction coefficient and wearing details.

As it is noted in works [2, 3, 7] using of fatty acids esters positively influences on lubricating properties of fuels. The data in Table 2 shows that conventional JF's lubricity evaluated by the value of scuffing load P_S is significantly lower, comparing to CamO FAEE.

Surfactants in fuel cause its surface activity – ability of fuel or its components to absorb at the surface of metal, form the boundary film and thus prevent dry friction of details [2, 3, 7]. Fuel hydrocarbons almost do not protect friction pairs from wear. Substances, which are considered to be surface active, are gums, oxygen-, sulfur- and nitrogen-organic compounds. But presence of these substances is undesired, because of thermal stability and corrosion properties of fuel.

Fatty acids esters are natural surfactants. Presence of oxygen atom in carboxyl group in molecules stipulates strong polarity of esters. Such structure provides ability to absorb on surfaces of solid bodies and thus, ability to form polymolecular film – boundary layer. In a result of experimental data processing the dependence of scuffing load P_S of the friction pair in the medium of studied modified JFs on the content of bio-additives (Fig. 7) was obtained. In general obtained results indicate that increasing portion of bio-additives in modified JFs improves its antiwear properties [3].

Such view on lubricating properties of fatty acids esters allows us explaining obtained experimental results: gradual improvement of antiwear properties of JF with increasing content of bio-additives. During modifying JF with bio-additives the total content of surfactants in fuels rises. In a result the boundary film between friction pair become stronger. We can make a conclusion that blending conventional JFs with bio-additives improves its antiwear properties.

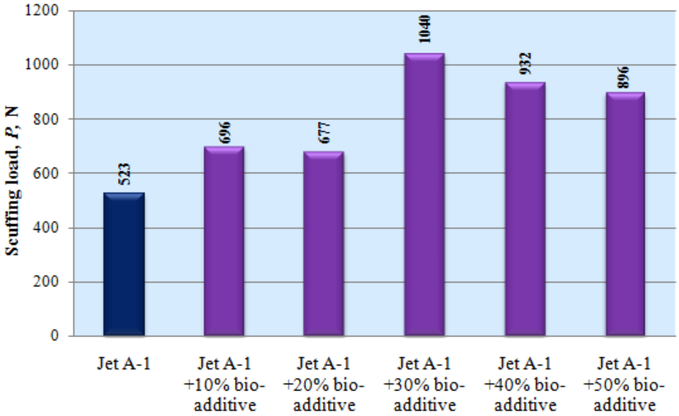

Fig. 7. Friction pair load in medium of tested fuel samples as a function of CamO bio-additives content

Fire safety. According to modern international specifications one of the dominant operational properties of JFs is its fire safety [7, 8]. JFs belong to flammable liquids. They are characterized by high volatility, easy form a flammable mixture with air, during combustion form a large number of products of combustion and are good insulators. According to its fire safety JFs belong to hazardous liquids at high temperatures.

Traditionally fire safety of JFs is characterized by its flash point (FlP) t_{fl}. This parameter shows the conditions under which the fuel becomes fire dangerous. Specifications for JFs regulate the lower limit of this parameter. Thus, the fuels of grade Jet A-1 should have FlP values, which are not lower than 38 °C. According to experimental results of fire safety researches it was found that CamO FAEE is characterized by lower value of FlP comparing to conventional JFs (Table. 2). This result is explained by the presence of ethanol in bio-additive, left after the production process.

Corrosiveness. It is known that corrosivenessis one of the most important exploitation properties of JFs [3, 4]. It influences on durability, and reliability of jet engines. During exploitation details of fuel system equipment are the most subjected to corrosive influence of fuel; details of the jet engine’s jet pipe are subjected to corrosive influence of fuel combustion products [8]. Corrosiveness is characterized by the presence of corrosively aggressive components in fuel. These components include sulfur and sulfur containing compounds, where the most aggressive are hydrogen sulfide and mercaptanes (thiols). Except that, the reasons of JFs corrosiveness are oxygen-containing heterogenic compounds, water-soluble alkalis and acids, dissolved oxygen and insoluble moisture [4, 6].

The process of chemical corrosion takes place during chemical interaction of corrosively-active substances, which are present in fuel, with color metals or their alloys that are used for producing details of aircrafts' fuel systems. The processes of corrosion are especially intensive when the water is present. The highest activity among sulfur compounds is typical for mercaptanes, elemental sulfur and hydrogen sulfide. Sulfides, disulfides, thiophenes and thiophanes are related to neutral sulfur compounds. However, at temperatures more than 120 °C these compounds decompose and form mercaptanes and hydrogen sulfide. Other words, they become corrosively active. Copper (bronze) alloys and steel details with coating (usually cadmium) are subjected to most intensive corrosion during exploitation.

Among JFs the highest corrosive activity is typical for fuels, which are produced from sulfur oils. Hydrogen sulfide is removed from fuels completely during crude oil processing. However, because of the technological reasons elemental sulfur and mercaptanes are still present in JFs is small quantities.

Corrosive action of JF sisrevealed at firstin destruction of copper surface; later significant corrosive sediments of black color appearon copper details. With time these sediments cut from surface and accumulate in fuel in the form of black in soluble particles, which cause clogging of filtering equipment. Corrosion of fuelling equipment, which are made of copper alloys, also depends on products of JF oxidation that are contained in fuel [4].

The method for JFs corrosiveness control is copper strip test. The degree of copper strip corrosion is estimated comparing to etalon sample (Fig. 8).

Fig. 8. The standard samples for determination copper strip corrosion

The results of tests of JF, bio-additives and samples of JFs blended with bio-additives on copper strip are presented in Table 3.

Table 3

The result of copper strip test of fuel samples

Bio-additive	JF of grade Jet A-1	100 % bio-additive	JF + 10 % of bio-additive	JF + 20 % of bio-additive	JF + 30 % of bio-additive	JF + 40 % of bio-additive	JF + 50 % of bio-additive
CamO FAEE	1a	1b	1a	1a	1a	1b	1b

According to the requirements of ASTM and Def Stan specifications for JF of grade Jet A-1 the degree of copper strip corrosion have to be not more than 1 according to the scale on Fig. 8. As we can see from the data in Table 3 the degree of corrosiveness of JFs modified with bio-additives completely satisfies requirements of existing specification.

This diversity of technologies provides the ability for JF production using various feedstocks. Scientists believe that the most promising feedstocks are plants with high oils content, algae and some types of industrial and household waste. This work was devoted to studying alternative JF produced by it modifying with CamO components.

In are sultof the work the complex of physical-chemical and exploitation properties and quality parameters of JF and Cam O esters were studied. The results have shown that the main characteristics of bio-additives differ from conventional JFs.

The dependencies of JF density, fractional composition, heat value, viscosity, freezing temperature and lubricity on the content of bio-additives were obtained. It is found that modification of JF with CamO esters results in increasing of fuel density and viscosity, rising of freezing temperature, decreasing of heating value and widening of fractional composition due to the rise of final boiling point. At the same time addition of CamO esters improves anti-wear properties of JFs. It was determined that jet fuel modification by biocomponents will have controversial effect on exploitation properties of new fuels. On one hand it may negatively influence on combustion process, and on the other hand it allows improving certain exploitation characteristics and making new JF more environmentally clean.

It may be concluded that modification of conventional JF by CamO bio-additives is possible. At the same time there is a need in more detailed influence of bio-additives on fuel properties for optimization of jet engines operation using new kind of fuel.

РЕФЕРАТ

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РОЗРОБЛЕННЯ АЛЬТЕРНАТИВНИХ АВІАЦІЙНИХ ПАЛИВ, МОДИФІКОВАНИХ БІОДОБАВКАМИ НА ОСНОВІ РИЖІЄВОЇ ОЛІЇ

Стаття присвячена розробленню та вивченню фізико-хімічних та експлуатаційних властивостей нових альтернативних авіаційних палив, модифікованих біодобавками на основі рижієвої олії. Проаналізовано сучасний стан навколишнього середовища, а також вплив авіаційної промисловості на навколишнє середовище. Під час дослідження було вивчено такі фізико-хімічні властивості зразків палив: густина, в'язкість, фракційний склад, теплота згоряння, змащувальна здатність, корозійна активність та температура кристалізації. Встановлено, що властивості біодобавок істотно відрізняються від властивостей авіаційних палив. В результаті проведеної роботи розроблено комплексну порівняльну характеристику фізико-хімічних та експлуатаційних властивостей та показників якості авіаційних палив, біодобавок на основі рижієвої олії та зразків сумішевих авіаційних палив.

Ключові слова: авіаційне паливо, альтернативне паливо, біопаливо, біодобавка, модифікування, рижієва олія, фізико-хімічні властивості.

РЕФЕРАТ

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РАЗРАБОТКА АЛЬТЕРНАТИВНЫХ АВИАЦИОННЫХ ТОПЛИВ, МОДИФИЦИРОВАННЫХ БИОДОБАВКАМИ НА ОСНОВЕ РЫЖИКОВОГО МАСЛА

Настоящая статья посвящена разработке и изучению физико-химических и эксплуатационных свойств новых альтернативных авиационных топлив, модифицированных биодобавками на основе рыжикового масла. Проведено анализ современной состояния окружающей среды, а также влияния авиационной промышленности на окружающую среду. В ходе исследования были изучены следующие физико-химические свойства образцов топлив: плотность, вязкость, фракционный состав, теплота сгорания, смазывающая способность, коррозионная активность и температура кристаллизации. Было установлено, что свойства биодобавок значительно отличаются от свойств авиационного топлива. В результате работы была разработана комплексная сравнительная характеристика физико-химических и эксплуатационных свойств и качественных показателей авиационного топлива, биодобавок на основе рыжикового масла и образцов смесевых авиационных топлив.

Ключевые слова: авиационное топливо, альтернативное топливо, битопливо, биодобавка, модифкация, рижиковое масло, физико-химические свойства.

ABSTRACT

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DEVELOPMENT OF ALTERNATIVE JET FUELS MODIFIED WITH CAMELINA OIL BIO-ADDITIVES

This paper is devoted to the development and study of physical-chemical and exploitation properties of new alternative jet fuels modified with camelina oil bio-additives. The current condition of environment is analyzed as well as the impact of aviation industry on the environment. During the study the following physical-chemical properties were investigated: density, viscosity, fractional composition, heat of combustion, lubricity, corrosiveness and freezing point. It was found that properties of bio-additives are significantly different from properties of jet fuels. As a result of the work, the complex comparative characteristic of physical-chemical and exploitation properties and quality parameters of jet fuel, camelina oil bio-additive and blended jet fuel samples, was developed.

Key words: jet fuel, alternative fuel, biofuel, bio-additive, modification, camelina oil, physical-chemical properties.

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2.4 MEANS OF QUALITY CONTROL OF BIOFUELS, THEIR PRODUCTION AND COMBUSTION

Artur Zaporozhets, *Serhii Ivanov*, *Roman Serhiienko*

In the structure of Ukraine's exports, products of the agricultural sector and the food industry occupy the highest position. This draws attention to Ukraine because of the potential for the development of bioenergy through the processing of biomass and agricultural waste into fuel briquettes and pellets. Moreover, according to the «New Energy Strategy of Ukraine» [1], by 2020 the share of renewable energy sources should be at least 11 %, a substantial part of which will be solid fuel of plant origin. For achieving these indicators, an integrated approach to improve the efficiency of pellet production is needed, as well as to control not only the quality of the finished product, but also the parameters of such fuel burning. This requires methodological and hardware control of informative parameters at each stage of the existence of this plant fuel: from the preparation to the combustion of raw materials.

Production control. The technology of manufacturing of fuel pellets from vegetable raw materials involves three main stages: preliminary grinding, drying, and the formation of the finished product by pressing.

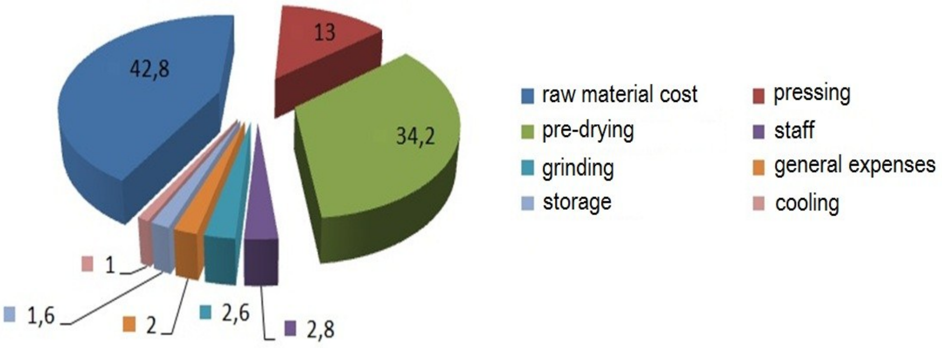
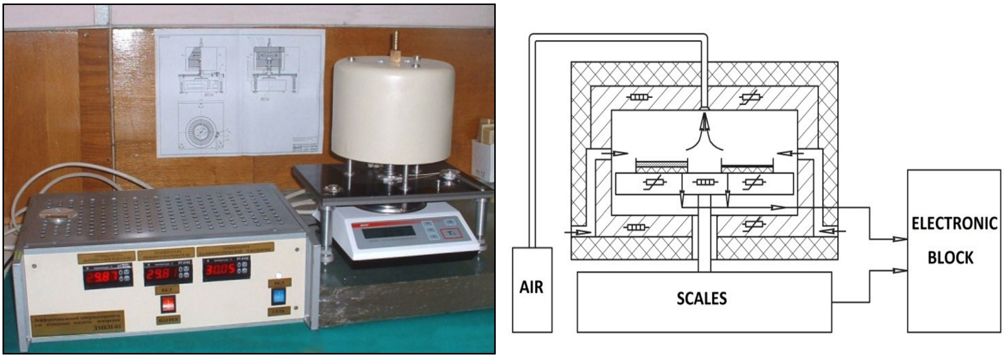


Fig. 1. The diagram of the cost of production of vegetable pellets

In the cost structure of production of fuel briquettes or pellets from woodworking or food industry waste, the cost of drying raw materials can reach 45 %, therefore one of the promising ways to reduce the cost of such fuel is the efficient using of energy for the drying process.

The criterion for optimizing the drying process of any material is the Rebinder criterion [2], to determine which it is necessary to know the heat capacity of the material and the heat of evaporation of moisture from it for a specific temperature and humidity of the studied raw materials. Plant materials are heterogeneous in structure, biological material, drying of which is accompanied by secondary exothermic and endothermic processes, such as crystallization, structural changes in proteins, changes in the concentration of the components of organic substances during evaporation, etc. It is extremely difficult to take into account the influence of such factors on the amount of evaporation heat using analytical methods, therefore it is preferable to use data from direct experimental measurements. For an experimental study of the specific heat of evaporation and the heat capacity of inhomogeneous wet materials, a measuring system [3] was developed and created, which allows to implement two different research methods using a single device (Fig. 2).



(*a*) (*b*)

Fig. 2. Appearance of the device (*a*) and the structure of the thermal block (*b*)

The device is constructed as a block-modular system, each of the individual blocks of which implements separate functional tasks.

The thermal unit is designed to accommodate the sample and the implementation of the temperature conditions of the experiment. The sample is placed in one of two differentially connected calorimetric cells, which are mounted into a common high-heat conductive base and form a calorimetric platform.

Several calorimetric platforms with cells of different configurations have been designed for the device (Fig. 3).

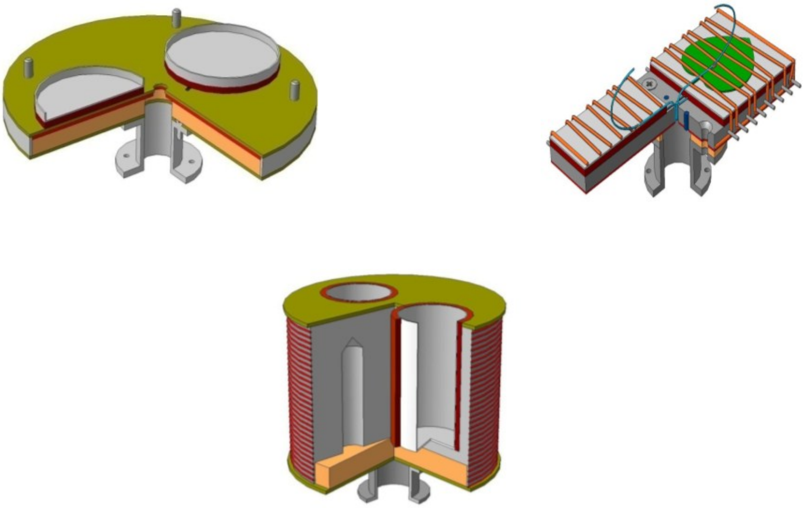


Fig. 3. Different types of calorimetric platforms

Platforms are designed as replaceable elements of the thermal unit, which allows to significantly expand the range of materials under study. Such solution makes it possible to obtain correct data on the heat capacity and heat of evaporation in the study of liquors, viscous samples, capillary-porous bodies, thin-sheet materials with a tendency to deform during drying, bulk materials of varying degrees of dispersion, etc. In the upper and lower parts of the working chamber, as well as directly in the calorimetric platform, electric heaters are mounted with an independent temperature control system to provide an isothermal environment in the working chamber of the device. The calorimetric platform is connected to an analytical balance, which ensures registration of the mass loss by the sample during drying. The air with the moisture, which was removed from the sample, are evacuated from the working chamber convectively through flexible tubes by a compressor.

The control unit is used for setting and maintaining the temperature conditions of the experiment. In addition, it is necessary to convert the data from the thermal block on the parameters of the sample under investigation into digital form for its further processing by software.

Determination of heat of evaporation. To determine the specific heat of evaporation, the device provides for the using of the method of synchronous thermal analysis and the simultaneous application of the methods of differential calorimetry and thermogravimetric analysis. The method is based on the assumption that under isothermal conditions, the heat that is supplied to a thin layer of inert moist material is consumed to evaporate the liquid from it. The system provides for the reproduction of the isothermal environment in which the sample under study is placed. Heat is supplied to the sample by conduction, and its quantity is recorded by heat flow sensors that are connected in a differential measurement circuit. At the same time, the amount of liquid that has evaporated from the surface of the sample in the same time is determined.

The heat of evaporation r for an arbitrary point in time in a generalized form is defined as the ratio of these quantities:

$$r(T) = \frac{(Q_1 - Q_2)}{dm/d\tau}, \tag{1}$$

where $r\,(T)$ − specific heat of evaporation at the temperature T; Q_1 − eat flux recorded by the cell sensor with the sample; Q_2 − heat flow recorded by the sensor of the empty reference cell; $dm/d\tau$ − sample mass loss rate.

Calibration device for the heat of evaporation is performed by examining the unknown quantities in pure well-characterized model substances. Distilled water and propanol were used as such exemplary substances. The results of the verification showed that the error in determining the heat of evaporation using the presented instrument does not exceed 1.5 %.

The determination of heat capacity in the presented device is carried out using a standardized method of step-by-step scanning. According to this method, the temperature range in which the research is planned to be carried out is divided into separate intervals (steps) of successive increase in temperature in the working chamber. The duration of each interval should be sufficient for the formation in the working chamber of a stationary temperature regime. A sample of a known mass is placed in the working cell of the device, after which the cells are hermetically sealed with a vapor barrier to prevent the sample from changing its mass throughout the experiment. Heat flow sensors measure the amount of heat that was spent on heating a sample in a sealed cell with an increase in temperature in the working chamber for a given interval, as shown in Fig. 4.

The specific heat $\tilde{n}$ in the generalized form for one interval is determined by the formula:

$$c = 1/m \cdot \left[\int_{\tau_1}^{\tau_2} (Q_1 - Q_2)\,d\tau \Big/ (T_2 - T_1) \right], \tag{2}$$

wherec − specific heat of the sample; $T_2 - T_1$ − the difference between the final and initial temperature values within the same interval.

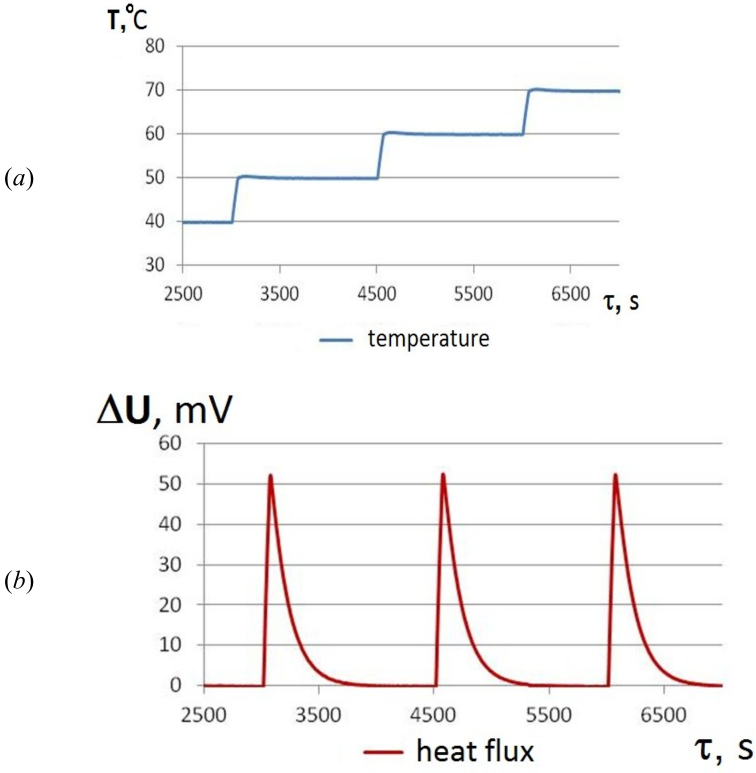


Fig. 4. Temperature change (*a*) and recorded heat flux (*b*) during using the step-by-step scanning method

The instrument is calibrated for heat capacity by studying the heat capacity of samples of pure inert materials with previously known well-studied thermophysical characteristics. According to the recommendations of the standard [4], a sample of leucosapphire with a purity of at least 99.99 % is used as such a reference material.

The results of verification showed that the study of heat capacity by the method of step-by-step scanning using the presented system does not exceed 2.5 %.

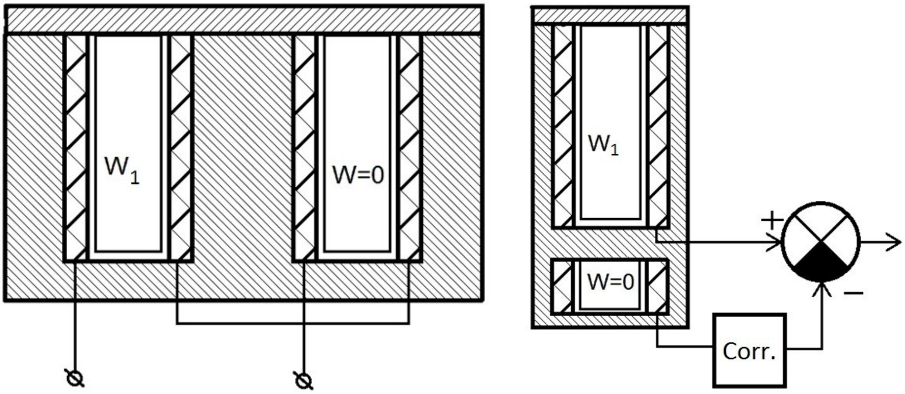
The system was used for studying a wide range of wet materials, including complex integrated studies of the thermophysical and thermodynamic parameters of the plant components of biofuels [5].

Quality control. Formed and ready-to-use biofuels (fuel pellets), depending on their characteristics and properties, are assigned a quality category according to one of the international standards, for example EN 14961-2. The most informative parameter is the calorific value of the fuel, which is traditionally used to determine the method of bomb calorimetry.

The method of bomb calorimetry is based on measuring the amount of heat that is released when a sample of the fuel under investigation is burned in an oxygen atmosphere. Since solid fuel of plant origin is heterogeneous in structure and characteristics, special requirements are placed on bomb calorimeters for studying such material, including the need to ensure high capacity to accommodate a sufficient amount of the material under study, the ability to measure relatively powerful heat fluxes and, at the same time, the ensure high accuracy of measurement.

Improving the accuracy of measuring the heat of combustion is achieved by using a differential measurement scheme, which is not always convenient when studying heterogeneous types of fuel, because the calorimeter with two full-sized cells has a significant inertia, high mass and low speed. An alternative could be a quasidifferential bomb calorimeter on Fig. 5. The appearance of the structure of the core of such a calorimeter is shown on Fig. 6. As in the classical calorimeter to determine the heat of combustion, this device has two cells, in one of which (the bomb) the sample is located, and the second (auxiliary) remains empty and serves to reduce the environmental impact on the measurement result. Both cells have their own heat flow sensor which has a cylindrical shape and covers the entire side surface of the cell.

A feature that distinguishes a quasidifferential bomb calorimeter from the classical one is the presence of an auxiliary cell, the dimensions of which are much smaller than the main one. Comparing the signals of the working and auxiliary cells is achieved by selecting the thermophysical parameters of the auxiliary cell's bomb simulator and amplifying its signal using a separate correction unit. The signal gain is determined at the instrument calibration stage.



(*a*) (*b*)

Fig. 5. Differences between differential (*a*) and quasidifferential (*b*) scheme of a bomb calorimeter

(*a*) (*b*)

Fig. 6. The appearance of a quasidifferential bomb calorimeter (*a*) and the design of the devices's core (*b*): *1* – fuel sample bomb; *2* – bomb simulator

The principle of operation of the calorimeter is based on measuring the heat flux generated during the combustion of a fuel sample, and its integration, as a result of which it is determined the heat released during the fuel combustion.

Compared to other models of KTS calorimeters [6], a number of improvements have been added to the design of the KTS-4 device (Fig. 6), aimed at improving manufacturability, reducing preparation time and improving measurement accuracy. The measurement range of the calorimeter is from 10 to 40 kJ, the measurement error is ± 0.1 %, the duration of the preparation process is no more than 90 minutes, the duration of the measurement process is 30 minutes. Technical characteristics of the KTS-4 bomb calorimeter are given in Table. 1.

Table 1

Main technical characteristics of the KTS-4 bomb calorimeter

Parameter	Value
Range of measured quantity of heat, kJ	10–40
The limits of permissible relative error, %	±0.1
Total preparation time for measurements, min	≤90
Measurement time, min	30
Power (220 V, 50 Hz), W	≤850
Indication of measurement results	digital
Mass, kg	
- thermal unit	50.0
- electronic unit	15.0
- calorimetric bomb	2.5

The KTS-4 bomb calorimeter includes:

1) a thermal unit designed to place a sample of fuel in it, to ensure the required temperature mode of operation and to measure heat generation from a bomb when a sample of fuel is burned;

2) two calorimetric bombs BKU-2 intended for burning a sample of fuel in the oxygen atmosphere;

3) an electronic unit designed to regulate the thermal regime, measure and process signals from the primary transducers, generate an electrical pulse to burn a fuel sample, and transfer measurement information to a personal computer.

The thermal unit of the device (Fig. 7) has a cylindrical sensitive heat-metering shell *6*, in the internal space of which a calorimetric cell *5* is placed. Externally the heat-metering shell is surrounded by a thermal diffusion case *7*. A reaction vessel is placed in the cell − a calorimetric bomb containing a cup *3* with a lid *1* and a seal *2*. In the lower part of the case, a compensation cell *10* is coaxially mounted, surrounded by its own calorimetric shell *9*, which has the same diameter, design and density of thermoelements as the main shell. The compensation cell contains a simulated reaction vessel simulator with elements *12*, *13*, *14* and has a specific heat capacity per unit area of the shell surface identical to the main one. There is an air gap *4* between the bomb glass and the working cell, and a gap *11* between the simulator and the compensation cell, and the case is protected by end insulation *8*.

Analytical solution of the non-stationary problem of heat conduction for the described model is almost impossible to obtain. At the same time, the presented model consists mainly of two types of structural elements, some of which have low thermal resistance and high heat capacity, while others have high resistance and low heat capacity. Such a system is quite well modeled as a system with lumped parameters.

Measurement of the amount of heat released during the combustion of a fuel sample is as follows. A fuel sample, prepared in accordance with the standards, is burned in a calorimetric bomb, which is installed in the thermal unit of the calorimeter and filled with oxygen with a pressure of 2.5...3 MPa. The surface temperature of the heat unit is stabilized with an electronic regulator.

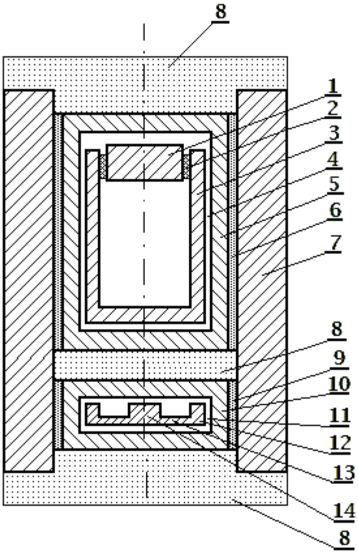


Fig. 7. Simplified model of the thermal unit of a quasi-differential calorimeter

The heat that is released during the combustion of a fuel sample is determined by integrating the heat flux, which is measured by a thermoelectric heat flux converter. Measurement and processing of information are carried out on the basis of a microprocessor device, and the result is displayed on a digital display of an electronic unit in the form of units of the amount of heat released during fuel combustion (J/kcal). The result is transmitted to a computer for further processing, specifically for the calculation of the highest and lowest calorific value, amendment, printing of the protocol. To eliminate the influence of temperature and air convection, the heat block of the calorimeter is placed in the climate chamber. To stabilize the supply voltage in the network using the mains voltage regulator.

During preparing the sample, the masses of the sample of the fuel material M_{fuel}, copper inflammatory wire M_{w1}, plastic packaging M_p and filler M_{fill} are measured. During conducting a calorimetric experiment, the heat Q_{fuel} generated by the sample burning is determined. After the experiment, the residual mass of the inflammatory wire $M_{w2}$is measured. The specific heat of fuel combustion in a bomb is calculated by the formula:

$$q_b = \left[Q_{fuel} - q_w \cdot (M_{w1} - M_{w2}) - q_p \cdot M_p - q_{fill} \cdot M_{fill} \right] \big/ M_{fuel}, \qquad (3)$$

where q_b – specific heat of fuel combustion in the bomber calorimeter, J/g; Q_{fuel} – measured heat of fuel sample combustion, J; q_w – specific heat of burning wire combustion (2510 J/g); q_p – specific heat of the polyethylene packaging (46382 J/g); q_{fill} – specific heat of filler combustion (16700 J/g).

Fig. 8, for example, shows graphs of the change in heat flux Q during the measurement time t at the transition between stationary levels during the combustion of biomass samples in a bomb calorimeter.

In the course of experimental studies, two separate measurements of the heat of combustion of identical samples of wood pellets were carried out. It was established that the heat of combustion (after integrating the signal from the heat flow sensors) of the 1st sample was Q_{b1} = 11243 J, the 2nd – Q_{b2} = 13273 J (in Fig. 8, the graphs of E_1 and E_2, respectively).

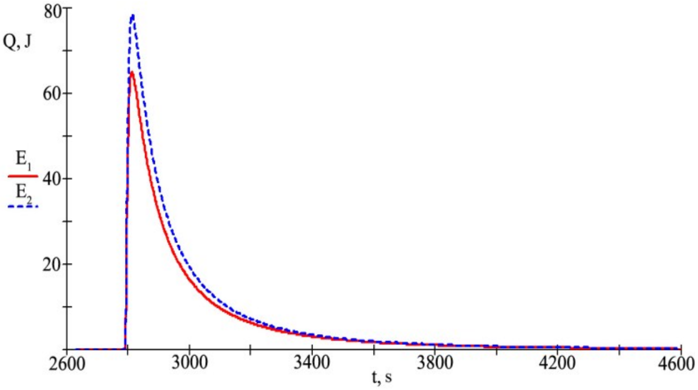


Fig. 8. Changes in heat flux during experimental studies on a bomb calorimeter

The work [7] confirmed the possibility of applying the method of reducing the time for measuring the specific heat of fuel combustion by interpolating the obtained data of the change in heat flux over time after reaching its peak value (≈90 s). To use this method, it is necessary to have empirical information about the nature of the non-stationary mode of combustion of a particular type of fuel in a bomb calorimeter.

The advantages of such calorimeter are: improved speed, weight and size parameters are reduced by 1.5…2 times (compared to a similar differential bomb calorimeter) while maintaining measurement accuracy in the range of 0.1 %. The effectiveness of the calorimeter was confirmed experimentally by studying biofuels of various nature [8].

*Combustion control.*To maintain high efficiency of the fuel system is not enough to use high-quality fuel, it is necessary to use effective modes of burning such fuel. Monitoring of the fuel combustion is reduced to monitoring the content of exhaust gases, while the objects of investigation are the fuel systems and air-fuel path [9]. The structural diagram of monitoring the fuel combustion is shown in Fig. 9.

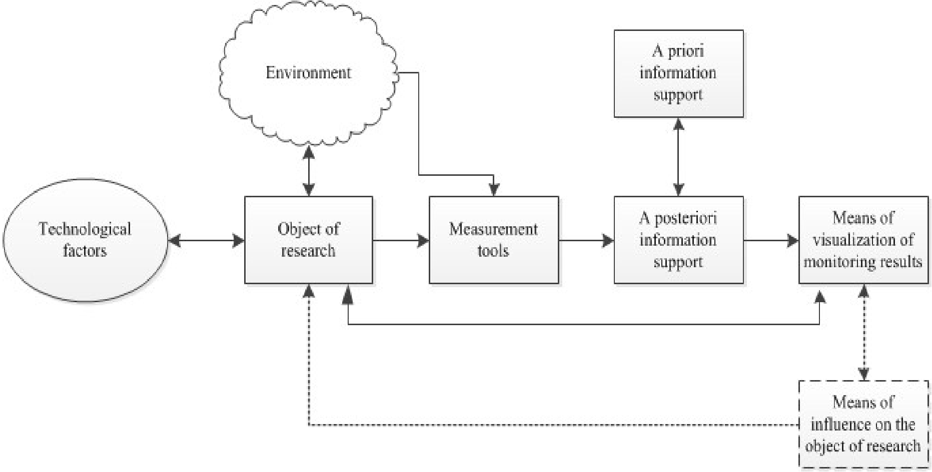


Fig. 9. Structural scheme of monitoring of combustion process

The efficiency of the fuel system unit is determined on the basis of the efficiency of its components: burners, heating surfaces, heat exchangers (economizers, air heaters), draft machines and other devices. One of the most important components of the combustion process is the efficiency of fuel combustion, that is, the economy of the operation of the burners themselves and associated equipment (fans and smoke exhausters).

The main losses of heat during the natural gas combustion are heat losses with outgoing gases; thermal losses associated with chemical incompleteness of combustion; heat losses from heating surfaces. The heat losses with flue gases depends on: the temperature difference between the exhaust gases and the air supplied to the boiler furnace, and the residual oxygen content in the off-gas, that characterized the air excess ratio (AER, α) or the air-fuel ratio. These losses are significant (for small and medium-sized fuel systems they can be from 10 % to 26 %, for gas fuel system and boilers of power plants – 6–12 %) and mainly affect the efficiency of the fuel system.

In Fig. 10 shows heat losses with exhaust gases, calculated by the method of M.B. Ravich, for different values of the temperature of the outgoing gases.

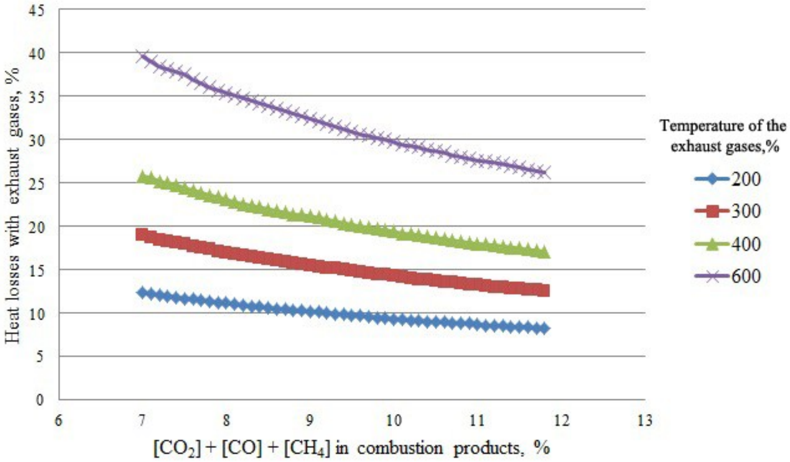


Fig. 10. Heat losses with exhaust gases in the fuel system with different composition of combustion products

According to the methodology based on the generalized characteristics of the fuel, during the combustion of natural and associated gases q_2 is determined by the formula (%):

$$q_2 = 0{,}01 \cdot z \cdot (t_g - t_a), \tag{4}$$

where z takes the tabulated value, t_g – the temperature of the exhaust gases, t_a – the ambient temperature. At the same time, increasing t_g by 10 °C above the normal value for a given fuel system load cause increasing q_2 by at least 0.5 %, and increasing α by 0.1 cause increasing q_2 by about 1 %.

A number of requirements are put forward for the design and use of burners operating on liquid gaseous fuels, including compactness and ease of use, long service life and relatively low cost. But one of the most important requirements is the need to ensure complete and reliable combustion of fuel with a minimum excess of air, that is, burners must ensure the formation of a stoichiometric air-fuel mixture. Fig. 11 shows the factors affecting on the process of fuel combustion.

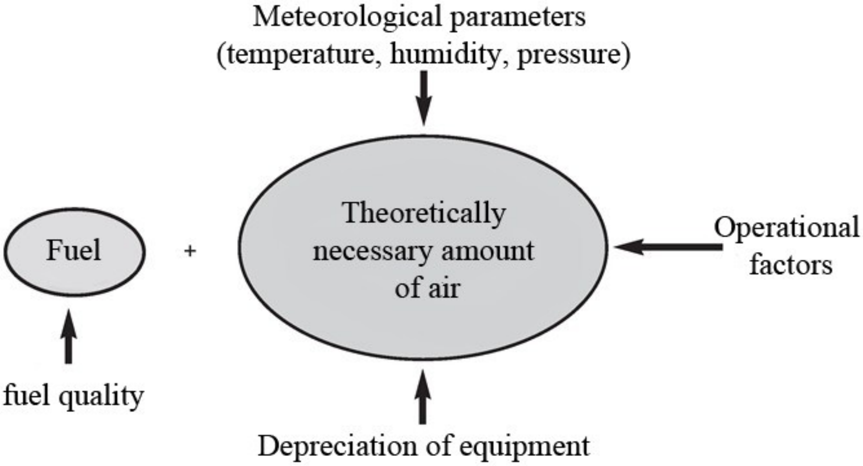


Fig. 11. Influencing factors for fuel combustion

A stoichiometric air-fuel mixture is a mixture containing exactly the same amount of oxidant as is necessary to completely oxidize the fuel. In practice, a lean air-fuel mixture is formed for fuel combustion, caused by a number of factors: insufficient fuel and oxidizer mixing, structural features of the fuel system, and the like.

Fig. 12 shows the theoretical dependences of the change in the mass ratio of the amount of air per unit of fuel for different AER values for some hydrocarbons [10].

Considering the problem of changes in combustion parameters over time, fluctuations in fuel quality and external factors of influence, it is effective not to use regime maps, but to regulate the parameters of their operation based on real-time computerized combustion control systems, by maintaining high efficiency of operation of fuel systems for solid fuel.

A fundamentally new approach to monitoring the fuel combustion is based on the using of a broadband oxygen sensor (Fig. 13)

A control block of the system of the fuel combustion in fuel systems of small and medium power based on an oxygen probe is shown in Fig. 14.

At present, oxygen probes are widespread in the automotive industry due to the constantly growing stringent regulations for the toxicity of off-gases. An essential advantage of such probes is the CO oxidation on the surface of the sensor containing ZrO_2 in its composition. This makes it possible to obtain information on the actual oxygen concentration in the combustion products. The disadvantage of their application is the impossibility of detecting chemical underburning in the zone of $\alpha > 1$, however, as experimental data showed, supporting the fuel system operation with an air excess ratio $\alpha \geq 1{,}1–1{,}15$ excludes the possibility of CO formation at a level of more than 200 ppm.

The probe construct assumes the presence of two chambers (cells): measuring and pumping (Fig. 13*b*). Through the hole in the wall of the pump cell, the output gases enter the measuring chamber (diffusion gap) in the Nernst cell. This configuration is characterized by a constant maintenance of the stoichiometric air-fuel ratio in the diffusion chamber. The electronic circuit for the supply voltage modulating maintains in the measuring chamber the composition of the mixture corresponding to $\alpha=1$. For this purpose, the pump cell removes oxygen from the diffusion gap into the external medium with a lean mixture and an excess of oxygen in the flue gases, and, with the enriched mixture and insufficient oxygen, pumps the oxygen molecules from the surrounding medium into the diffusion gap.

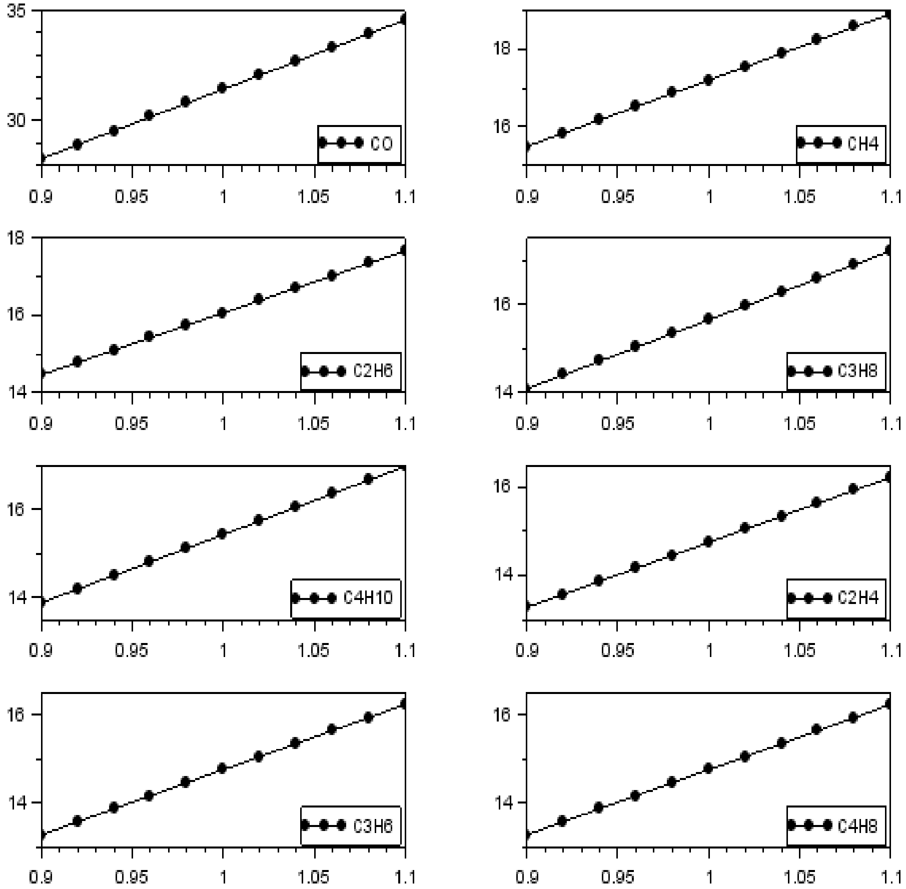
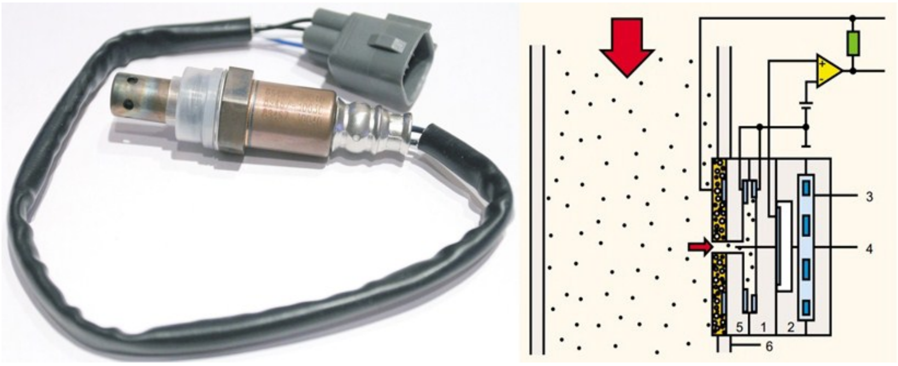


Fig. 12. The theoretical dependence of the change in air flow per unit of various types of fuel from the coefficient AER



(*a*) (*b*)

Fig. 13. Broadband oxygen probe: *a* – appearance; *b* – structural scheme
(*1* – Nernst cell, *2* – reference cell, *3* – heater, *4* – diffusion slit, *5* – pumping cell,
6 – air and fuel tract)

The main purpose of the control system is the speed regulation of the fan motor drive. This will encourage the optimum combustion regime in the boiler furnace, that is, provide the most favorable conditions for complete fuel combustion. The system supplies the required quantity of air to the furnace in terms of information received from its primary sensors (oxygen probe, temperature sensors and vacuum).

The task of maintaining the optimum combustion regime is ensured by selecting the necessary speed of motors rotation of the traction mechanisms with fully open guide devices in practically the entire range of the operating capacity of the O_2-corrected combustion.

Technical characteristics of the monitoring system for the fuel combustion in fuel systems are given in Table. 2.

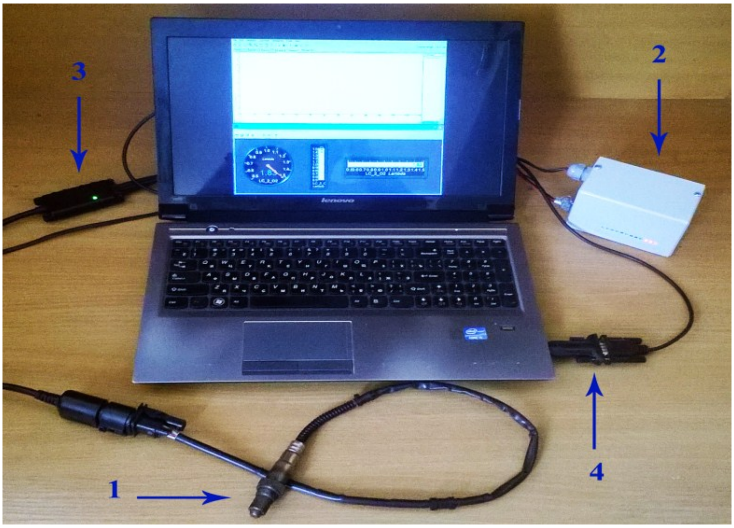


Fig. 14. A control block of the system of the fuel combustion in fuel systems:
1 – broadband oxygen probe, *2* – alpha indicator, *3* – controller, *4* – USB interface

Table 2

Technical characteristics of the monitoring system

Parameter	**Value**
Output signal of the measuring probe, V	+0.1…+5.0
Recall (time delay of indication) for 50 % step perturbation, s	0.1…0.3
Initial preparation time for measurements, s	≤30.0
Measuring range of the parameter α	0.5…1.5
Relative error, %	3
Indication of measurement results	LED
Cable length, m	≤ 5
Ambient temperature at relative humidity up to 80 %:	
display unit, ^{o}C	5…50
boxes of the measuring probe, ^{o}C	5…70
Conditions at the measurement point:	
ambient temperature, ^{o}C	50…250
flow rate, m / s	≤15
pressure, Pa	≤+-500

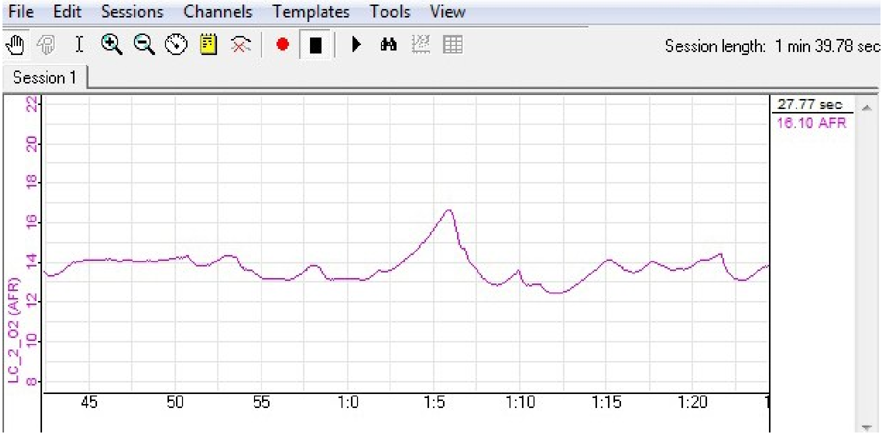


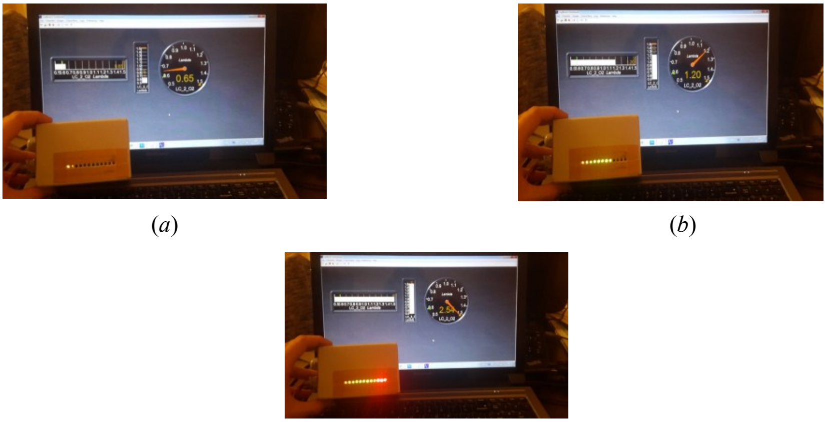
Fig. 15. Real-Time Log Environment

The program controls the air-fuel volume ratio depending on the duration of the analysis of the composition of the exhaust gases. The resulting graph can be obtained during the entire monitoring time and saved to a file with the *.log* extension for further analysis and information processing.

This software has a direct connection with the developed digital α-indicator, which allows controlling the PNC using a frequency controller, that is, to realize the possibility of correcting the operating modes of the fuel system by introducing feedback based on oxygen sensor signals. Fig. 3.23 shows the interaction of the α-indicator with the software for different values of the air-fuel ratio.

The specified control system provides:

- rational using of the natural gas (savings of 5–10 % per year);
- reduction of electric power consumption by asynchronous wire motors of traction mechanisms (savings of 30–75 % per year);
- reduction of harmful substances in the atmosphere due to the complete combustion of fuel.



(*a*) (*b*)

(*c*)

Fig. 16. The interaction of the α-indicator and the developed software product in various modes of operation of the fuel system: (*a*) enriched mixture; (*b*) a mixture close to stoichiometric; (*c*) lean mixture

A system was developed and tested to determine and control the amount of heat of evaporation and the heat capacity of wet inhomogeneous materials, the use of which allows to experimentally obtain correct data to optimize the process of drying raw materials and, consequently, reduce costs and improve the quality of the final drying facility.

The proposed method and means of quasidifferential bomb calorimetry, which reduces the impact of external interference by 3...7 times compared to single-cell bomb calorimetry, or allows reducing the weight and size characteristics by 1.5...2 times compared to the classical differential bomb calorimetry.

Experimental studies of environmental and thermal parameters of the created system of monitoring and control of the process of fuel combustion in fuel systems with a stepwise correction of the ratio of the air-fuel mixture components were carried out. The use of such a system allows you to increase the efficiency of the fuel systems by 6...20 % compared with manual adjustment, reduce fuel consumption by 10...25 %, maintain the concentration of CO and NO_x in the exhaust gases at the level of European Union standards.

The combined use of the presented methods and means of improving production efficiency, quality control and fuel combustion from plant biomass makes it possible to increase the share of high-quality biofuels for the domestic market and for Ukraine to enter the international market for biofuel energy resources as one of the exporters of plant fuel cells.

РЕФЕРАТ

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ЗАСОБИ КОНТРОЛЮ ЯКОСТІ БІОПАЛИВ, ЇХ ВИРОБНИЦТВА ТА СПАЛЮВАННЯ

Представлено пристрій для вимірювання теплоємності і теплоти випаровування вологи та органічних рідин з неоднорідних матеріалів, який реалізує метод синхронного термічного аналізу. Розглядаються конструкція пристрою і методи, що використовуються під час дослідження зразків біопалива. Наведено методи калібрування калориметричних платформ з використанням еталонного перетворювача теплового потоку. Представлено методи і технічні засоби калориметричного аналізу теплоти згорання біопалива. Запропоновано квазідиференціальний бомбовий калориметр для вимірювання питомої теплоємності спалювання зразків палива, розглянуто його структуру, модель і технічні характеристики. Запропоновано систему контролю якості процесу горіння в паливних системах, яка базується на зміні швидкості обертання дуттєвого вентилятора за сигналами сенсора кисню.

Ключові слова: біопалива, теплота випаровування, теплоємність, бомбовий калориметр, згоряння, контроль.

РЕФЕРАТ

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СРЕДСТВА КОНТРОЛЯ КАЧЕСТВА БИОТОПЛИВ, ИХ ПРОИЗВОДСТВА И СЖИГАНИЯ

Представлено устройство для измерения теплоемкости и теплоты испарения влаги и органических жидкостей из неоднородных материалов, которое реализует метод синхронного термического анализа. Рассматриваются конструкция устройства и методы, используемые при исследовании образцов биотоплива. Приведены методы калибровки калориметрических платформ с использованием эталонного преобразователя теплового потока. Представлены методы и технические средства для калориметрического анализа теплоты сгорания биотоплива. Предложен квазидифференциальный бомбовый калориметр для измерения удельной теплоемкости сжигания образцов топлива, рассмотрены его структура, модель и технические характеристики. Предложена система контроля качества процесса горения в топливных системах, которая базируется на изменении скорости вращения дутьевого вентилятора по сигналам сенсора кислорода.

Ключевые слова: биотоплива, теплота испарения, теплоемкость, бомбовый калориметр, сгорания, контроль.

ABSTRACT

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MEANS OF QUALITY CONTROL OF BIOFUELS, THEIR PRODUCTION AND COMBUSTION

A device for measuring the heat capacity and heat of evaporation of moisture and organic liquids from inhomogeneous materials is presented, which implements the method of synchronous thermal analysis. The installation design and methods used in the study of biofuel samples are considered. The methods of calibration of calorimetric platforms using a reference transducer of heat flow are given. Methods and technical means for calorimetric analysis of the calorific value of biofuels are presented. A quasidifferential bomb calorimeter for measuring the specific heat of combustion of fuel samples is proposed, its structure, model, and technical characteristics are considered. A system for monitoring the quality of the combustion process in fuel systems, which is based on the change in the rotational speed of the blower fan according to the oxygen sensor signals, is proposed.

Key words: biofuels, heat of evaporation, heat capacity, bomb calorimeter, combustion, control.

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2.5 INFLUENCE OF ELECTROMAGNETIC TREATMENT OF FUELS AND OILS ON THE FORMATION OF WEAR RESISTANCE OF FRICTION PAIRS

Igor Trofymov, Mykhailo Svyryd, Olena Matveyeva, Oleksandr Sydorenko

The studies referred to in the article relate to the engineering industry. In connection with the sharp rise in the cost of natural resources, increasing the performance properties of lubricants (L) becomes an urgent scientific and technical problem. Therefore, the issue of improving the operating properties of working fluids, in particular, by performance of electromagnetic field (EMF) or magnetic field (MF), is one of the components when considering priority areas to ensure the reliability of motor equipment and friction units.

Modern technic is equipped with complex hydraulic systems that perform important functions in the control of aircraft and ground equipment. The reliability of the fuel and hydraulic units largely depends on the performance of precision friction pairs. As a result of increased wear, destruction and jamming of friction pairs, failures of hydraulic units arise, and it becomes necessary to replace worn parts systematically. The most common defects include the jamming of plunger, plate and spool pairs, the destruction of rolling bearings, wear of the grommets of plungers, etc. The specificity of these friction pairs requires a critical approach in the matter of using to them the existing concepts of the relative influence of lubricants, the mechanical properties of materials, the roughness of the mating surfaces, the speed of their relative movement.

The purpose of the work is to increase the reliability of fuel systems parts by eliminating the causes of unit failures, analyzing the structural, technological and operational factors that determine their performance, and developing measures on this basis to ensure trouble-free friction pairs. In continuation of the research, the purpose of the work was also to study the change in the energy state of M10G2k oil under the influence of MF by passing a white light beam through it and determining the energy aspects of the interaction of oil with MF, which will allow adjusting the wear rate of friction surfaces, treated in MF media.

The most important condition for the implementation of reliability, embedded in the design of fuel-hydraulic units, is to improve the performance properties of operating fluids. Today, the requirements for the modes and operation properties of the fuels and lubricants determine the need to increase their anti-wear properties and search for new directions and methods for this.

In this work the electrophysical treatment is proposed to improve the operating properties of fuels, which occurs when they are passed through an electromagnetic or magnetic field.

Analysis of the literature [1–3] shows the interest of the authors in experimental and theoretical development of improving the antiwear properties of precision friction pairs and studies of the influence of the electromagnetic field on the state and property of working fluids.

One of the ways to extend the service life and restore tribo-triggers is tribomodification of friction surfaces due to the formation of metal-containing films, through the use of lubricants that are under the action of a magnetic field.

As it is known, lubricants, treated with MF possess high antifriction and wear-resistant properties [1], therefore they are used for lubricating magnetic bearings, gears, etc.

Nowadays, considerable attention is paid to research on the modification of motor oil by treating it with physical fields, the results of which are shown in the works of many scientists, namely, I.A. Portnoy, E.M. Lisikova, N. A. Pivovarova, E.S. Wenzel, L.I. Pogodaeva, S.V. Putintseva et al. [4–6].

In [7], it was shown that one of the ways to improve the operative properties of fuels is their electrophysical processing, which occurs when the working fluid is passed through a magnetic field while simultaneously applying a high-frequency electromagnetic field with a frequency equal to the proton precession frequency in a given magnetic field. The authors found that the electrophysical treatment of diesel fuel reduces the hourly and specific fuel consumption by 2 ... 4 % at all crankshaft rotational speeds, while the greatest effect was observed at idle (hourly fuel consumption decreased by 8 ... 12 %).

A number of researchers [8, 9] proved that when treating a fuel with an electric field, its drops, in addition to the molecular forces that determine their strength, also have aerodynamic and electric forces directed in the opposite direction. Reducing the surface tension of the droplet leads to a thinner dispersion of the liquid, improving combustion and, as a consequence, reducing the toxicity of exhaust gases.

The authors of [10] conducted research on the effects of the electromagnetic field on aviation fuel in order to extend the service life of rolling bearings on the fuel flow meter sensors. The authors established the effect of electromagnetic treatment on the antiwear properties of hydrocarbon interfaces. In their opinion, one of the features of chemical conjugations in organic compounds is the spatial orientation, in which the molecule acquires a certain geometric structure, the chemical bonds in it are covalent in nature and are relatively easily polarized. The shift of electrons in molecules, caused by the mutual influence on atoms, actively influences the physicochemical properties of hydrocarbons.

The quantum mechanics says that the greater the frequency of the light flux, or its change from red to violet, the greater its energy [11]. Therefore, a change in the color of a substance is an energy indicator in the formation of the internal state of hydrocarbon SS, which can be changed by the external influence of a magnetic field.

To understand the experiments conducted by us and described below, it is necessary to select something from the theory of magnetism: a magnet is a permanent source of photons; a photon is a movable discrete transverse electromagnetic disturbance, which consists of an electric quantum and a magnetic flux quantum and represents an excited state of the field. A photon that moves forms partial electromagnetic waves, which, according to Huygens' principle, due to interference, are not emitted, but move together with the photon as a single entity, representing a package of partial waves as a train. If we add two such quanta, we get a quantum of double energy (E = h.2), which is usually called a photon. The more quanta in a photon, the more powerful it is, since a photon consists of a larger number of minimal portions of energy. Although the photons have no mass, they have different energies. If we see a red ray of light, this means that the photons of which it is composed have energy at the level of 1.68–1.98 eV.

Planck's quantum hypothesis was that for elementary particles, any energy is absorbed or released only in discrete portions. These portions consist of an integer number of quanta with an energy proportional to the frequency ν with a proportionality coefficient determined by the formula: $E = h \cdot \nu = h\omega$, where: h is the Planck constant. Thus, a change in the color of light is the change in photon energy.

The color of the oil when light passes through it in the MP changes in the direction of an increase in frequency (in color from yellow to green), the frequency increases from 510 THz to 600 THz, which means that the photon energy that passes through the oil increases and thereby increases its activation.

In the presence of MF, the quantum part, which has a spin magnetic moment, receives additional energy $\Delta E = -\vec{\mu} \cdot \vec{B}$, proportional to its magnetic moment $\vec{\mu}$ (Zeeman effect). Acquired energy leads to the removal of atomic states by the magnetic quantum number m_j and the splitting of atomic lines. However, the authors of [11] experimentally confirmed that the quanta of the electromagnetic radiation flux have a field structure, that is, they consist of electric and magnetic fluxes and, accordingly, all laws of electrodynamics apply to them. According to electrodynamics, in an electromagnetic wave, the energy of an electric flux is always equal to the energy of a magnetic flux. Under the conditions of physicochemical interactions of lubricants with a metal surface under friction, besides adding chemicals to the lubricants, physical methods are known for its processing with sound and ultrasonic waves, irradiation with light of different wavelengths, etc.

The study of the influence of magnetic fields on liquid environment was carried out by the authors of [12], who determined the influence of external magnetic fields on the transfer processes in ferrosuspensions. The researchers argue that such a powerful influence is explained by the structure formation in a fluid-dynamic system as a result of the dipole-dipole interaction of ferromagnetic particles and the orientation of the structure elements along the MP force lines. At the same time, the geometry and magnitude of the magnetic field, the concentration and size of particles, their magnetic properties and other factors affect the transfer processes. The rheological properties of ferrosuspension, namely plasticity and effective viscosity (magnetorheological effect), are most intensively changed. Also, in [12], the results of studies of the magnetorheological effect are summarized – a sharp change in mechanical properties (viscosity, plasticity, elasticity) under the action of a magnetic field. It is shown that the electrical and magnetic permeability of liquids varies considerably.

The method of treating fuel and lubricants with an electric field has been improved, which makes it possible to increase the antiwear properties of fuels and oils several times [13, 14].

In this regard, the question of the influence of electrophysical treatment of fuels on the formation of wear resistance of friction pairs of fuel systems remains open.

In order to determine the influence of the magnetic field on the physicochemical and operational properties of hydrocarbon fuels, a method for treating fuel [14] and a filter activator fuel [15] were developed, the essence of which is that due to the influence of electromagnetic field pulses generated around coils wires of high voltage during the passage of high-voltage pulses of electric current from a source of high voltage pulses through it, frequency pulsed electromagnetic processing of fuel is carried out, as a result of which the fuel is activated, in particular, the physicochemical properties of the fuel are improved.

Processing (activation) of fuel by electromagnetic field pulse lines causes an improvement in fuel performance such as pumpability, evaporation, flammability, flammability, as well as an improvement in fuel energy characteristics such as volatility, a decrease in flammability temperature, and an increase in combustion stability.

Electromagnetic pulses provide fragmentation, changes in the structure and configuration of fuel molecules, weakening the bonds between them, reducing their surface tension. In addition, some fuel molecules are charged for a sufficient period of time, as a result of which they more actively combine with the oxidizing agent – oxygen. This contributes to a more optimal mixing of the air-fuel mixture in the combustion chamber and, as a consequence, an increase in the completeness of combustion.

It was found that the fuels subjected to this electromagnetic treatment were characterized by a decrease in viscosity and density, and for 12 hours after the treatment, an increase in the acidity index was observed.

«TC-1» jet fuel was selected as a working fluid, which has low anti-wear and rheological properties and provides friction at the nodes. Also, the gasoline A-92, which acts as fuel for cars, trucks and special vehicles, was amenable to electrophysical processing. The tests were carried out using the finger-plane friction scheme; material of samples ШХ15 – photographic glass ϑ = 0.30; 0.630 m/s, P = 5 N. The sample finger size: diameter – 4 mm, length – 25 mm. Sample No. 1 and No. 3 worked in the base (not processed) environment of aviation fuel «TC-1» and gasoline A-92, respectively. Sample No. 2 and No. 4 worked in the environment of aviation fuel «TC-1» and, respectively, gasoline A-92, treated with fields for 1 hour at a voltage of U = 32,000 V and field strength E = 4. 106 V/m Sample No. 5 worked in the environment of gasoline A-92, treated with EMF, after 24 hours of the relaxation period. The mass of prototypes was measured on an analytical balance of increased accuracy "ADV-200 2Kl".

Given these changes in the physicochemical properties of fuels, it would be legitimate to assume that similar changes in the anti-wear properties of the treated fuels are possible, which are an important performance indicator. In this regard, to study the effect of electrophysical treatment of fuels and low-viscosity liquids on the change in antiwear properties and friction coefficient, a complex was used to study the tribological characteristics of fuels and lubricants, developed by the authors [16]. The technical conditions of the complex make it possible to take photographic images and video footage of surface transformations in a dynamic mode.

The results of the experiments are given in Table. 1. From Table 1 it can be seen that under the same experimental conditions and with the same distance traveled (in the medium of jet fuel – 12 km, in gasoline – 3 km) for sample No. 1, the amount of wear after mass was 0.0013 g, for sample No. 2 – 0.0003 g, the difference was –0.001 grams. For sample number 2, the difference over the mass of 0.001 g was only after 22 km of the distance traveled. For sample No. 3, the amount of wear after mass was 0.0032 g, for sample No. 4, 0.0012 g, the difference was 0.002 grams. For sample number 5, the difference was – 0.0025 grams.

Table 1

The results of experiments conducted on the complex to study the tribological characteristics of fuels and lubricants

Sample Number/Environment	Mass, m, g	Distance, S, km	Friction velocity, ϑ, m/s	Load, P, N
Sample № 1 / «TC-1»	2,1478	0	0,630	5
	2,1465	12		
Sample № 2 / «TC-1»$_{\text{EMF}}$	2,1539	0		
	2,1536	12		
	2,1529	22		
Sample № 3 / A-92	2,1575	0	0,330	5
	2,1543	3		
Sample № 4 / A-92$_{\text{EMF}}$	2,1543	0	0,330	5
	2,1531	3		
Sample№ 5 / A-92$_{\text{EMF.p.}}$	2,1545	0		
	2,1520	3		

The results of studies of the friction coefficients of the tribocouples are shown in Fig. 1–2.

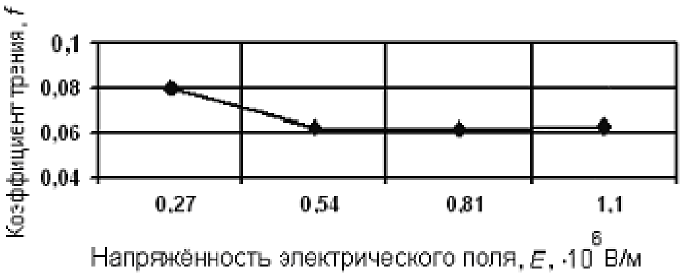


Fig. 1. Dependence of the friction coefficient of steel SHKh15 on the electric field strength at sliding speed = 0.6 m/s in «TC-1» jet fuel

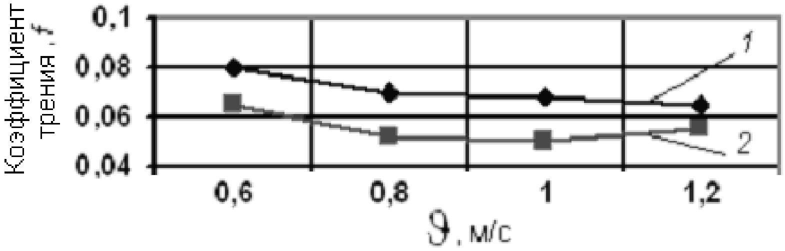


Fig. 2. Dependence of the friction coefficient of steel SHKh15 on the sliding speed at a specific load P = 5 kg/cm^2: *1* – in the «TC-1» jet fuel in the delivery condition; *2* – in the aviation fuel processed by the EMF for 1 hour at a voltage of *U* = 32000 B and field strength *E* = 4.10^6 V/m

It has been established that with an increase in the electric field strength, the coefficient of sliding friction decreases (Fig. 1). This can be explained by an increase in the mobility of parts of molecules, caused by the fragmentation of sedentary large molecules of lubricating media using an electromagnetic field.

A reduction in the friction coefficient of steel SHKh15 with an increase in the sliding speed was established. The friction coefficient during lubrication of the contact with jet fuel «TC-1», treated with an electromagnetic field is 1.3 times less in comparison with the coefficient of friction obtained in «TC-1» in the delivery condition (Fig. 2). The decrease in the friction coefficient can be explained by a decrease in the magnitude of the surface tension of the fuel during its processing by the EMF, which has also been established experimentally.

Optical comparison of the friction surfaces of the samples shows (Fig. 3) that in the case of their operating time at = 0.63 m/s and the same friction paths in the «TC-1» jet fuel treated with an electric field, oxidation films begin to form much later and in comparison with 1000 m of the traversed path of oxidative films is almost not found.

Investigating the surface of samples produced at ϑ = 0.8 m/s, after 1000 m of friction, the subsequent formation and accumulation of oxidative films was detected, after 12000 m of friction – films that occupy a sufficiently large area of friction are clearly visible. But for samples developed in «TC-1» treated with an electromagnetic field after 12000 m of friction, a sharp decrease in the number of secondary structures and a decrease in their area on the friction surface were found. This gives the right to argue about their destruction and removal of friction from the surface at the specified distance traveled. A similar picture was observed in micrographs of the surface of samples produced at ϑ = 1.2 m/s after 12000 m of the traversed friction path, and in the case of accumulation in the «TC-1» basic fuel, oxide films look clearly formed and have clear limits for the transition from the secondary structure to the main structure metal. At the same time, for samples developed in the aviation fuel processed by EMF – more subtle and elastic.

Comparing the friction surfaces of the samples (Fig. 4) developed in gasoline treated with EMF at a constant speed = 0.330 m/s and load P = 5 N, it was found that oxidizing films are thinner and more elastic, which fully explains obtaining a lower wear value at the same traversed friction path. On both surfaces, the secondary structures directed behind the movement of friction and at the stage of formation look the same.

After 3000 m of the path, the films of the sample produced in the EMF-treated gasoline become significantly larger with the length and width, and they also have destroyed areas that alternate with the sections of the films themselves (in comparison with the films of the sample obtained in the base gasoline).

Sample treated in gasoline with an EMF after 24 hours after treatment showed that the films looked completely formed and oriented behind the direction of movement, and the friction surface itself is very similar to the friction surface of the sample worked out in the base gasoline with the same path traveled.

Operation time of the samples in the base aviation fuel «TC-1»

Operation time of samples in the aviation fuel processed by the electromagnetic field «TC-1»$_{EMF}$

Sample surface through 1000 m friction path

Sample surface through 1000 m friction path

ϑ = 0,63 m/s, *P* = 5 N

Sample surface through 1000 m friction path

Sample surface through 1000 m friction path

Sample surface through 12000 m friction path

Sample surface through 12000 m friction path

ϑ = 0,8 m/s, *P* = 5 N

Sample surface through 1000 m friction path

Sample surface through 1000 m friction path

ϑ = 1,2 m/s, *P* = 5 N

Fig. 3. Micrographs of steel samples ШХ15 surfaces; ×150

Operation time of the samples in the base fuel **A-92** | Operation time of samples in the fuel processed by the electromagnetic field $\mathbf{A\text{-}92}_{\mathrm{EMF}}$

Sample surface through 1000 m friction path | Sample surface through 1000 m friction path

Sample surface through 3000 m friction path | Sample surface through 3000 m friction path

Sample surface through 3000 m friction path (Operation time of the samples in the gasoline after 24 hours of relaxation)

ϑ **= 0,330 m/s,*P* = 5 N**

Fig. 4. Micrographs of steel samples ШХ15surfaces; ×150

To determine the change in the energy parameters of oil in MF, we designed a device for assessing the energy-information state of liquid carbon materials (Fig. 5.), which consists of: a computer for capturing the image of changes in liquid carbon materials *1*; light sources *2*; lens for processing light *3*; permanent magnets *4*, which create a magnetic field for processing liquid SS; dielectric glass capacitance *5*, which is located between the magnetic field and the test material; microscope "MPD-1U11" *6*; “Quick Cam Express” cameras *7*.

The dielectric glass container *5* is placed between two permanent magnets *4*. Then it is filled with liquid carbon material and placed on the optical axis of the microscope *6*. Then, using a light source *2* and an objective for processing light *3*, they pass a beam of white light through the liquid material under study field. Its induction value is 0.3 Tl.

Next, using the camera *7*, the image of energy-information changes in liquid carbon materials is processed and recorded, which can be seen on the computer monitor *1*. Accordingly, all the necessary experimental results were recorded and stored on electronic device.

Thus, the change in the energy state of the oil depending on the change in its color under the action of a magnetic field was studied, namely, the orange color is characterized by the light energy

1.98 eV, green – 2.48 eV.The essence of the presented technique is to change the frequency of white light, that is, the light that passes through the layer of oil that is in the MF. Each color has its own energy component (see Table. 2).

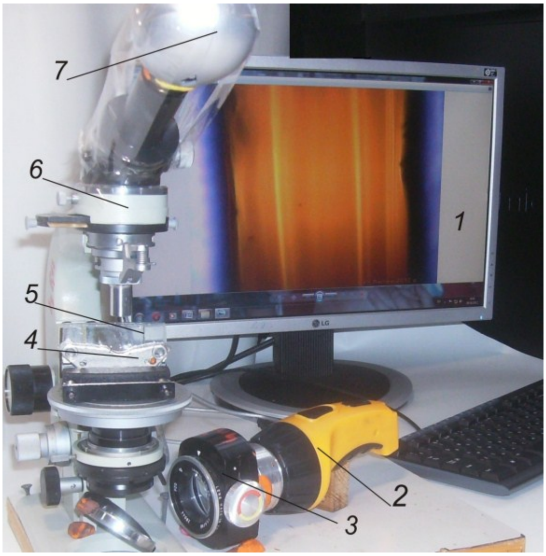


Fig. 5. A device for assessing the energy-information state of liquid carbon materials in a magnetic field: *1* – a computer for fixing the image of energy-information changes in liquid carbon materials; *2* – light source; *3* – lens for processing light; *4* – permanent magnets; *5* – dielectric glass capacitance; *6* – microscope "MPD-1U11"; *7* – "Quick Cam Express" camera

Table 2

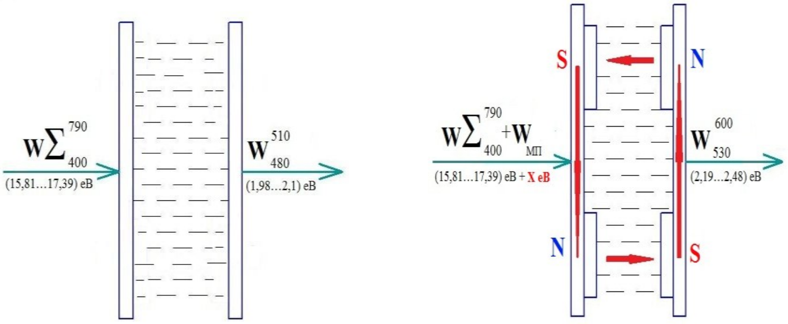
Energy parameters of light

Color	Wavelength range, nm	Frequency range, THz	Photon energy range, eV
Green	500–565	600–530	2,19–2,48
Yellow	565–590	530–510	2,10–2,19
Orange	590–625	510–480	1,98–2,10

The presented methodology for studying changes in the energy state of liquids is characterized by the possibility of monitoring changes in the energy-information state of liquid carbon materials in MF.

The conditions for changing the energy state of the medium are explained by the physical properties of the influence of the magnetic field on the magnets, which are in the composition of the oil and changes in their orientation in space (Fig. 6).

On the basis of the experiment, a beam of white light, which is characterized by a frequency range (400 ... 790 THz) and a photon energy (15.81 ... 17.39 eV) passes through the layer of the test oil. In the case of passing a beam of light through the oil without the action of the MP (Fig. 2a) after scanning, we obtain the energy of orange color, which has a value (1.98 ... 2.1 eV) and a frequency range (480 ... 510 THz). This color meets the conditions of the oil, which is located between the poles of the magnet (Fig. 7.)



(*a*) (*b*)

Fig. 6. The physical content of the experiment: (*a*) the study of the energy state of the oil M10G2k by passing a beam of white light through it; (*b*) study of the influence of MP on the energy state of the oil M10G2k by passing a beam of white light through it

In Fig. 7 shows the results of studies of the change in the energy state of motor mineral oil M10G2k in MF. The influence of MF on the change of the state of the environment was determined by the change in color to the lumen. Green color characterizes oil at the poles of a magnet that corresponds to energy (2.19 ... 2.48 eV) with the highest energy content. That is, in this position, the oil holds the auxiliary energy of the MF.

The energy component affects the placement of oil dipoles and we believe that they are located along the MF lines, that is, perpendicular to the surface of the magnet. The transition zone, which is located between the poles of the magnet, has an orange color of lower energy (1.98 ... 2.1 eV). Thus, the oil that is located between the poles has the same energy; in our case, we designated it as the initial one (No.0). The transition zones from the initial to the traits (Fig. 7.) N/S No.2 S/N or No.2 (to green) are characteristic of mixed shades of blue-violet and green, which indicates a change in the arrangement of the conglomerates of the environment (Fig. 7.) N/S No.1 S/N or No.1. In addition, each condensation has its own energy component, their chaotic location characterizes the preparation for changing the state of the oil, this can be expressed:

$$W^{790}{}_{400} = W^{510}{}_{480} + W_{\mathrm{lfr.}}$$

When studying the influence of MF on the energy state of the oil M10G2k by passing a beam of white light through it (Fig. 6*b*), in addition to the energy of white light, the energy of MF (W_{MF}) also affects the oil, and after translucent we get energy of green color, which has a value (2.19 ... 2.48) eV and a frequency range (530 ... 600) THz, plus the energy of the losses. Mathematically, it will look like this:

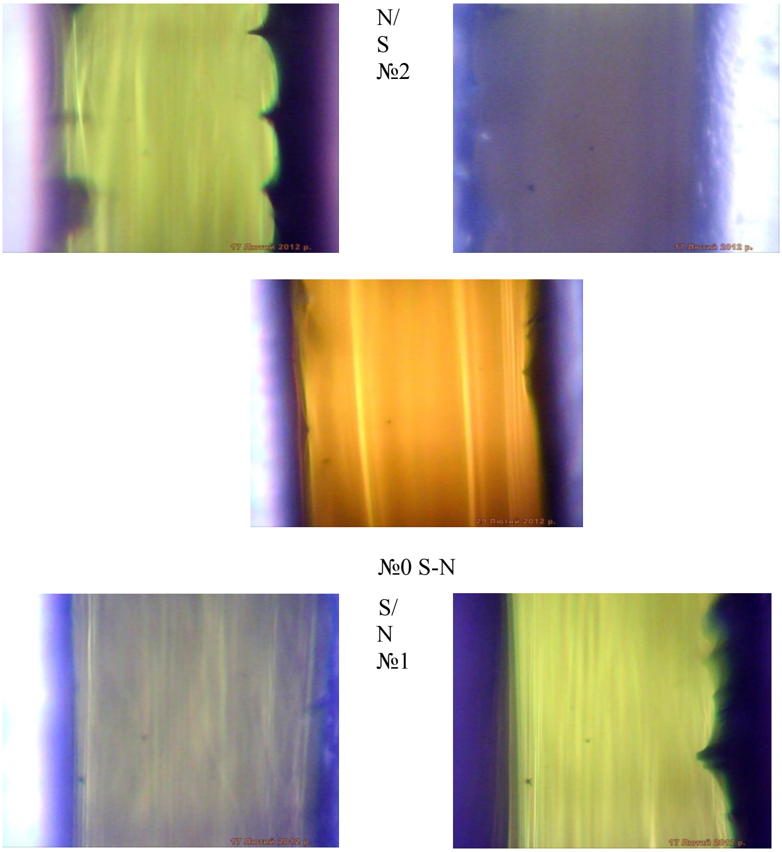
$$W^{790}{}_{400} + W_{MF} = W^{600}{}_{530} + W_{\mathrm{Lfr.}}$$

Thus, the energy of the MP, which acts on the oil, is determined from the previous two formulas, as:

$$W_{MF} + W^{510}{}_{480} + W_{\mathrm{Lfr}} = W_{\mathrm{Lfr}} + W^{600}{}_{530}$$

Here: $W_{MF} = W^{600}{}_{530} - W^{510}{}_{480} = (2{,}19\ldots2{,}48) - (1{,}98\ldots2{,}1) = (0{,}21\ldots0{,}38)$ eV.

Therefore, under the action of MF magnetic induction of 0.3 T on oil M10G2k, the amount of energy with which the MF acts on oil is (0.21 ... 0.38) eV.



N/S №2

N/S №1

№0 S-N

S/N №1

S-N №2

Fig. 7. The results of studies of the change in the energy state of mineral oil M10G2k, which is under the action of a permanent magnet MF with intensity $B = 0.3$ Tl, by passing a beam of white light through it

To determine the percentage contribution of MF energy to oil, the energy of orange color, without the action of MF (1.98 ... 2.1) eV, is taken as 100 %. Under the action of MF, the green color (2.19 ... 2.48) eV for x %. We get the following proportion:

$$(1{,}98\ldots2{,}1) \; - 100\ \%$$
$$(2{,}19\ldots2{,}48) - x\ \%$$

After calculations, we obtain that the percentage contribution of MF energy to oil is 11 %–11.8 %.

The change in the energy state of the system is reflected in the tribological parameters of the friction pair. Tribological studies were carried out according to the finger-plane scheme following the procedure described in [17]. The normal load was 1 kg per Hertz contact, the speed was 0.1 m/s. Friction pair: ШХ15 steel – LS59-1 alloy. Wearing of steel (regardless of the direction of the MF) is characterized by initial wear, but when the energy component changes, the processes of repairing the friction surface of steel ШХ15 take place. The results of the experiment are shown in Fig. 8.

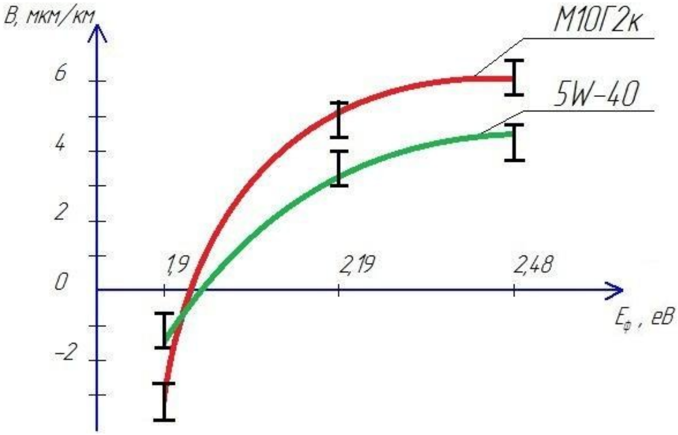


Fig. 8. Dependence of the level of wear on the value of the photon energy of light in oil

Thus, the dependence of the level of wear on the amount of energy of the oil shows that with an increase in the energy state of the oil, the wear of the material during friction decreases and goes into repair conditions. It has been established that the influence of MF on the antiwear properties of the oil is extremely positive, namely: the level of energy of the oil increases, the level of wear during friction decreases and other operational parameters do not deteriorate.

Consequently, the obtained results confirm the relevance of using the MF effect on the working environment during friction.

As a result of the experimental studies found that:

– treatment of aviation fuel «TC-1» and gasoline A-92 by EMF leads to an improvement in their antiwear properties;

– at the same values of sliding speeds and the traveled distance, the mass wearing of samples in the «TC-1» accumulated in the EMF-produced aviation fuel «TC-1» is 3.5 times less than that accumulated in the basic aviation fuel. For samples worked out in EMF-treated gasoline A-92, 2.5 times less than those worked out in base gasoline;

– it was established that the friction coefficient during lubrication of contact with jet fuel «TC-1», treated with an electromagnetic field is 1.3 times less compared to the friction coefficient obtained in «TC-1» in the delivery condition;

– a general view of the friction surfaces shows that the accumulated tribological films on friction surfaces, which worked in the EMF-treated «TC-1» fuel and A-92 gasoline, are more uniform and dense, compared with similar parameters of the samples working in the same media in the delivery condition;

– the energy aspects of the interaction of the oil with the MF, namely the amount of energy with which the MF acts on the oil is (0.21 ... 0.38) eV or 11 %–11.8 %;

– during the course of research, it has been established that with an increase in the photon energy, the level of wear decreases, and this makes it possible to adjust the wear rate of friction surfaces in the media of processed MFs;

– it is established that the higher the frequency, the greater the activation energy of the oil, respectively, increases the reliability of the interaction of the oil with the friction surface, which in turn is also activated at the points of actual contact.

РЕФЕРАТ

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ВПЛИВ ЕЛЕКТРОМАГНІТНОГО ОЧИЩЕННЯ ПАЛИВ ТА ОЛИВ НА ФОРМУВАННЯ ЗНОСОСТІЙКОСТІ ФРИКЦІЙНИХ ПАР

У статті проаналізовано вплив електромагнітної обробки палив і олив на формування зносостійкості пар тертя, подано результати деяких досліджень у цій галузі. Основною метою дослідження було поліпшення експлуатаційних властивостей палив електрофізичною обробкою, яка відбувалася при їх пропущенні через електромагнітне поле, аналіз впливу магнітного поля на зміну енергетичного стану змащувальних середовищ. У роботі використано комплекс для вивчення трибологічних характеристик паливно-мастильних матеріалів, який дає можливість робити фотографічні знімки і відеозйомку поверхонь у динамічному режимі. Представлена методика обробки палив електромагнітним полем дозволяє досягти покращення їх протизносних властивостей, зниження коефіцієнта тертя, отримання більш рівномірних і щільних окисних плівок на поверхнях тертя. Результати дослідження можуть бути застосовані в галузі машинобудування для підвищення надійності деталей паливних систем, вони можуть бути використані експертами з трибології, хімотології, фахівцями у сфері експлуатації паливних і змащувальних систем наземної й авіаційної техніки. Прогнози щодо розвитку об'єкта вивчення – продовження досліджень з впливу силових полів на протизносні властивості пально-мастильних матеріалів, а також можливість контролювати та регулювати електромагнітними полями параметри зношування.

Ключові слова:надійність, електрофізична обробка, електромагнітне поле, паливо, фотон, зносостійкість, протизносні властивості, коефіцієнт тертя, поверхня тертя, вторинні структури.

РЕФЕРАТ

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ВЛИЯНИЕ ЭЛЕКТРОМАГНИТНОЙ ОЧИСТКИ ТОПЛИВ И МАСЕЛ НА ФОРМИРОВАНИЕ ИЗНОСОСТОЙКОСТИ ФРИКЦИОННЫЕ ПАР

В даной статье проанализировановлияние электромагнитной обработки топлив и масел на формирование износостойкости пар трения,представлено результаты некоторых из наших исследований в этой области. Основной целью исследования было улучшения эксплуатационных свойств топлив электрофизической обработкой, которая происходила при их пропускании через электромагнитное поле, анализ влияния воздействия магнитного поля на изменение энергетического состояния смазывающих сред. В работе использован комплекс для изучения трибологических характеристик горюче-смазочных материалов, который позволяет делать фотографические снимки и видео съемку поверхностей в динамическом режиме. Представленная методика обработки топлив электромагнитным полем позволяет достичьулучшение их противоизносных свойств, снижения коэффициента трения, получение более равномерных и плотных окисных плёнок на поверхностях трения. Результаты исследований могут быть применены в отраслимашиностроения для повышения надёжности деталей топливных систем, они могут быть использованыэкспертами трибологами, химмотологами, а также специалистами в области эксплуатации топливных и смазывающих систем наземной и авиационной техники. Прогнозы по развитию объекта изучения– продолжение исследований по влиянию силовых полей на противоизносные свойства горюче-смазочных материалов, а такжевозможность контролировать и регулировать электромагнитными полями параметры изнашивания.

Ключевые слова: надёжность, электрофизическая обработка, электромагнитное поле, топливо, фотон, износостойкость, противоизносные свойства, коэффициент трения, поверхность трения, вторичные структуры.

ABSTRACT

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INFLUENCE OF ELECTROMAGNETIC TREATMENT OF FUELS AND OILS ON THE FORMATION OF WEAR RESISTANCE OF FRICTION PAIRS

This article discusses the effect of electromagnetic processing of fuels and oils on the formation of wear resistance of friction pairs and presents the results of some of our research in this area. The main goal of the research was to improve the performance properties of fuels by electrophysical treatment, which occurred when they were passed through an electromagnetic field and to study the effect of the influence of a magnetic field on the change in the energy state of lubricants. In the work, a complex was used to study the tribological characteristics of fuels and lubricants, which allows you to take photographs and video images of surfaces in a dynamic mode. The presented method of treating fuels with an electromagnetic field makes it possible to acheivean improvement in their anti-wear properties, a decrease in the friction coefficient, and a more uniform and dense oxide films on the friction surfaces. The research results can be applied in the field of mechanical engineering to increase the reliability of parts of fuel systems, they can be applied by experts by tribologists, chemotmologists, as well as experts in the field of operation of fuel and lubricating systems of ground and aviation equipment. Predictive assumptions on the development of the object of study – the continuation of research on the effect of force fields on the antiwear properties of fuels and lubricants, as well as the ability to control and regulate wear parameters by electromagnetic fields.

Key words: reliability, electrophysical treatment, electromagnetic field, fuel, photon, wear resistance, antiwear properties, coefficient of friction, surface of friction, secondary structures.

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2.6 INFLUENCE OF ANTIOXIDANTS AND ANTIWEAR ADDITIVES ON JET FUEL PROPERTIES

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Production of fuels for aviation engines is one of the developing directions of the oil refining industry. First of all, this is due to the increased number of aircrafts in the world. According to the Forecast International marketing company data, 5835 large air liners and transport planes were built in the world during 2004–2013. Today, according to World Air Fleet data [1], there are about 2,000 airlines in the world which are using 50,000 airplanes. Airlines of the world were transported about 2.5 billion passengers. According to Boeing's data [2], passenger transportation increases annually by 5.1 %, and cargo traffic (expressed in ton-kilometers) – by 5.6 %.

According to the analytical site [3], about 875,000 tons of jet fuel are produced and consumed in the world every day. In Ukraine (UPECO consulting company data [4]) the amount of consumed jet fuel is about 300–350 thousand tons per year, the half of which falls on Boryspil State Airport.

The quality of jet fuels in comparison with other petroleum products depends to a large extent on the nature of oil and the boiling range of fractions obtained by atmospheric distillation. Fractions of direct distillation are purified in various ways, depending on the oil composition and the quality specifications.

All jet fuels are divided into two subgroups: direct and thermostable ones. In each subgroup there are 2–3 grades of fuel of different fractional composition: i) fuels of wide-fractional composition; ii) flammable fuels (naphtha-kerosene); iii) fuels of heavy-fractional (kerosene-gasoil) composition with high flash point. The following operational properties of jet fuels are accepted: pumpability, evaporation, flammability, combustibility, deposits formation tendency, compatibility with structural materials, frictional, anti-wear, protective, cooling properties and toxicity. Each operational quality is characterized by a set of physico-chemical indicators of quality.

To classify jet fuels it is accepted in the world to use such indices as evaporation (boiling range), flammability (flash point) and pumpability (chilling point). The basic requirements for the fuels quality are formed by the International Air Transport Association (IATA), the American Society for Testing and Materials (ASTM), Directorate of Engine Research and Development (DERD, UK Ministry of Defense jet fuel specification) and the «CheckList» [1].

Oil is the main raw material for the production of aviation fuel, as well as other types of fuel. Traditionally, jet fuels are produced via direct distillation; as well as via cracking processing. Jet fuels are medium-distillate oil fractions with boiling range of 140–280 °C. [5–8].

Fuel of «TC-1» grade may be virgin (most often it is a fraction of sulfuric oil that boils in the range of 140–250 °C) or mixed. In the latter case, components after hydrofining or demercaptanization, as well as gas fraction after hydrodewaxing can be added to the straight-run fraction of oil. Hydrofining or demercaptanization are used when the total and sour sulfur content is high, hydrodewaxing is used to improve the low temperature properties of kerosene fractions. From literary sources it is known that hydrofining is used when the content of total and sour sulfur in kerosene distillates does not meet the requirements of the standard, demercaptanization – when only the content of sour sulfur does not meet the standard requirements. Fuel of «TC-1» grade is used as fuel for subsonic and supersonic aircraft with limited flight duration.

Fuel of RT grade is obtained by hydrofining of a straight-run fraction 135–280 °C from various oils, as well as by the addition of various additives to the hydrodeparaffined straight-line kerosene fraction. The raw materials for hydrofining are distillates, from which it is impossible to produce «TC-1» due to the high content of total and sour sulfur. When oil distillate is hydrofined, aggressive and unstable compounds containing sulfur, nitrogen and oxygen are eliminated; thermal stability increases and corrosion activity decreases. RT is a thermostable fuel for thermally stressed aircraft engines with an extended duration of supersonic flight. It fully meets the requirements for aviation fuel of the highest quality. Moreover, this aviation fuel is universal, since it can be used for both subsonic and supersonic aircraft.

Modern jet fuels must meet a number of requirements related to the cost-effectiveness, reliability, durability, as well as environmental safety [9].

Reliable and durable operation of the aircraft is ensured if the fuel has a fractional composition, capable of maintaining a stable combustion process in all modes of engine operation and does not form vapor locks in the fuel system during altitude flights; if the fuel and its products of combustion do not cause damage of the fuel system and engine details; if the fuel provides reliable operation of the engine in a wide range of external conditions (temperature, pressure, humidity, etc.).

Economic work of the aircraft is provided when the fuel has a low price, high heat of combustion and high density; has such a chemical and group composition, which guarantees the most complete combustion process, as well as low evaporation during altitude flights and long-term storage.

Environmental safety of fuel is provided in case of its least impact on the environment at all stages of operation (production, transportation, storage, refuelling of the aircraft, direct combustion, etc.).

The main technical requirements for jet fuels are the following:

– high level of evaporation, which provides reliable flammability and completeness of fuel combustion;

– satisfactory low-temperature properties, ensuring reliable pumpability at low temperatures;

– chemical and thermooxidative stability with minimal tendency to form deposits in the fuel system of the engine;

– absence of negative influence on metal and non-metallic details of engine fuel systems, equipment for storage and transportation of fuel;

– high lubricity, eliminating the increased wear of fuel assemblies;

– optimal level of electrical conductivity, which prevents the electrification of fuel and ensures safety during pumping and loading-unloading operations with fuel;

– the absence of toxic components, impurities and additives, the minimum content of sulfur-containing compounds that form environmentally hazardous combustion products.

The fuel stability, namely chemical stability and thermal oxidative stability, is the most important technical requirement for jet fuels. At elevated temperatures some components of fuel become thermally unstable, resulting in an intense formation of a deposit and increased corrosion activity, which leads to the fuel lines plugging and the plunger wear. This reaction is especially intensive at high temperatures typical of the aircraft fuel system.

Thermal oxidative stability is defined as the oxidation stability with the formation of resinous deposits at elevated temperatures (100–120 ºC, subsonic aircraft). Some of resinous deposits are insoluble in fuel and can lead to the filter plugging and engine failure.

Jet fuels must meet the increased requirements for thermal oxidative stability:

– under statistical conditions;

– under dynamic conditions.

In addition to temperature effect, the thermal oxidative stability of fuel can be affected by metals, which are used for the manufacture of fuel engines: copper, bronze, brass, alloy steels, etc. These metals at high temperatures are the catalysts of fuel oxidation.

The presence of resins in fuel leads to increased formation of deposits. At the same time, the negative role of these substances is revealed only at their certain concentrations, below which the presence of resins increases stability and anticorrosive properties of jet fuels. This inhibitory effect is explained by the presence of some sulfur-, nitrogen- and oxygen-containing compounds in resins.

Sulfur compounds play an important role in the formation of insoluble deposits and other oxidation products in fuels. Resins, carbon deposits and lacquer always contain a large amount of sulfur and oxygen. Partial transition of sulfur compounds from fuel to resins and from resin to solid deposits occurs at low temperatures during long-term storage, as well as at high temperatures for several hours. Sulfur compounds of different classes have different effect on the thermal stability of fuels. The least stable components at elevated temperatures are mercaptans and disulfides. The presence of elemental sulfur in reactive fuels, even at a concentration of 0.001 %, contributes to a sharp increase in the fuel corrosion activity.

Along with the corrosion activity and low thermal stability the sulfur compounds are characterized by antioxidant properties, which are clearly observed when the content of these compounds in fuel is low. The antioxidant properties of sulfur compounds, for example sulfides, can be explained by their easy interaction with the formation of hydroperoxides, subsequent destruction and, consequently, the prevention of the oxidation chain reaction development. The removal of nitrogen-containing compounds from fuels contributes to the increase of thermal oxidative stability.

The quality of jet fuels depends on used additives to a large extent. Antistatic and antiwear additives, fuel system icing inhibitors and antioxidants are added to the jet fuels. The main requirement for aviation fuel additives is their high effectiveness, i.e. they should be introduced in small concentrations without worsening the fuel quality relative other indices and retain their properties for a long time both in pure form and in fuel composition. In the world practice the additives quantity and composition must be approved by aircraft builders and engine manufacturers and specified by the relevant developers in the documentation.

In order to increase the chemical and thermal oxidative stability of jet fuels during storage and transportation the antioxidants (oxidation inhibitors) are added. Such additives should be introduced into fuels that undergo a hydrofining in order to prevent the formation of peroxides. «TC-1» may contain antioxidants by agreement. Antioxidants are compulsorily introduced into hydrotreated fuels («РТ», «Т-6», «Т-8В») to compensate the reduced chemical stability as a result of hydrofining. Antioxidants do not have any known side effects that could negatively affect the properties of fuel. The mechanism of antioxidants action is based on the idea that oxidation of hydrocarbons is a chain process, in which the origin of chains and their development occurs with the participation of free radicals. In other words, the action of oxidation inhibitors is aimed at preventing the formation of primary oxidation products – peroxides and consists in breaking and preventing the development of the oxidative reactions chain with the formation of hydroperoxide and stable free radical inhibitor:

$$\mathrm{InH + ROO \rightarrow In + ROOH.}$$

In order to increase the antiwear (protective) properties of jet fuels the antiwear additives are used. Their main purpose is to increase the lubricating properties of fuel. Components of the engine fuel system and fuel regulation devices are designed to be lubricated by fuel. Differences in structures and materials of the fuel system components lead to different sensibilities of the equipment to the fuel lubricity. Aviation fuels, in turn, differ in their level of lubricity. The incipient operational problems are classified starting from cost reduction to the unplanned mechanical failure, which may cause the engine shutdown during flight. Physico-chemical properties of jet fuels do not provide sufficient lubricity of fuel at high temperatures and high loads. Hydrotreated jet fuels are characterized by worse lubricating properties than those obtained via direct distillation.

Antiwear additives are intended to restore the lubricating properties of fuels after hydrofining. They are introduced into fuel at the refineries along with antioxidants. Among the substances that improve antiwear properties are fatty and naphthenic acids, their esters and salts. Such components of antiwear additives as surfactants have the following properties:

– they improve the lubricating properties of petroleum products in relation to metals in the «petroleum product – water» system and slow the anode process of metal ionization;

– they form strong chemosorption protective films on the metal surfaces that prevent corrosion.

One of the widely used additives is the antiwear additive Hitec-580. It is a transparent amber-colored liquid with flash point ≥ 66 °C and acid number of 80–100 mg KOH/g.

The purpose of this work was to study the efficiency and influence of antiwear additive Hitec-580 and antioxidants Agidol-1 and AO-80 on the properties of hydrotrated fraction of jet fuel.

For the experiments we used a hydrotreated fraction of jet fuel, the physico-chemical characteristics of which is presented in Table 1.

Table 1

Characteristics of hydrotreated fraction

Indices	Values
1. Fractional composition, °C	
initial boiling point	117
10 %	151
20 %	166
30 %	176
40 %	185
50 %	**196**
60 %	203
70 %	213
80 %	221
90 %	236
95 %	245
98 %	270
Weight content of sulfur compounds, %	0.037
Flash point, closed-cup, ºC	37
Viscosity at 20 ºC, mm^2/s	1.50
Weight content of aromatic hydrocarbons, %	19.2
Ash content, wt %	0.002

Antioxidants Agidol-1 and AO-80 and antiwear additive Hitec-580 were used to determine their influence on jet fuel properties.

The additive Agidol-1 (Ionol, (2,6-di-*tert*-butyl-4-methylphenol) is a white crystalline powder without foreign impurities, with a melting point ≥ 69.5–70.0 °C and chilling point ≥ 69 °C. This additive allows to completely prevent the oxidation of hydrogenation fuels, including that occurred at elevated temperatures (up to 150–160 °C).

The additive AO-80 is an alkylphenolic antioxidant containing at least 75 % of 2,4-dimethyl-6-*tert*-butyl-phenol and maximum 25 % of *tert*-butyl methyl and *tert*-butyl-dimethyl-phenol. Appearance – a colorless or yellowish-colored liquid that prevents the formation of resins, oxidation and prevention of peroxides formation during storage.

Hitec-580 is the antiwear additive without phosphorus for low-sulfur aviation fuels used to reduce the wear of fuel pumps and regulators of aviation engines. It is a clear amber oily liquid with the density of 920 kg/m^3, pour point of mines18 °C, flash point ≥ 66 °C and acid number of 80–100 mg KOH/g. Hitec-580 is a multicomponent mix, the main active substance of which is a dimer of linoleic acid.

Standard and analytical methods, as well as heuristic methods according to the Complex of Methods for Qualitative Assessment («KMKO») for jet fuels were used for the investigations.

At the first stage we tested hydrotreated fraction of jet fuel with different additives according to KMKO. The amounts of additives were chosen as maximum concentrations recommended by the manufacturer: Agidol-1 0.004 wt. %; AO-80 0.0024 wt. %; Hitec-580 0.004 wt. %. The results of studies are presented in Table 2.

Table 2

Results of testing the hydrotreated fraction of jet fuel according to KMKO

Indices	Fraction with additives		
	Agidol-1	AO-80	Hitec-580
Compatibility with resins, %	0.54	0.43	0.58
Microbiological phase	absence		
Carbon number, carbon factor, NACA factor	313.412	313.412	313.412
Opacity index SVI	281.92	281.92	281.92
Luminometernumber	59.5	59.5	59.5
Refraction index	1.4426	1.4426	1.4423
Mechanical admixtures, wt. %	absence		

Then we studied the influence of Agidol-1 (0.004 wt. %) and AO-80 (0.0024 wt. %) on the properties of hydrotreated fraction of jet fuel. The results are presented in Table 3.

The influence of Hitec-580 (0.004 wt. %)) on the properties of hydrotreated fraction of jet fuel is shown in Table 4.

At the last stage of research we compared the samples with different additives to evaluate the efficiency of additives and their influence on the quality performance of commercial aviation fuel. The samples contain the following mixture of additives:

– antiwear additive Hitec-580 and antioxidant Agidol-1;

– antiwear additive Hitec-580 and antioxidant AO-80.

The research results are presented in Table 5.

Table 3

Properties of hydrotreated fraction of jet fuel with additives Agidol-1 (0.004 wt. %) and AO-80 (0.0024 wt. %)

No.	Indices	Experimental results		Standard values
		Hydrotreated fraction with Agidol-1	Hydrotreated fraction with AO-80	RT (GSTU 320.00149943. 007–97)
1	*2*	*3*	*4*	*5*
1	Acidity, mg KOH per 100 cm^{3}of fuel	0.184	0.18	No more than 0.7
2	Acidnumber, mg KOH per 1 gof fuel	0.046	0.046	-
3	Existentgum content, mg per 100 cm^{3}of fuel	1.22	1.08	No more than 4
4	Corrosiveness to copper strip at 100 °C for 3 hours	stand the test	stand the test	stand the test
5	Thermal oxidative stability under static conditions at 150 °C			
	weight content of deposit, mg per 100 cm^3 of fuel	1.64	1.6	No more than 6

Table 3 continue

1	*2*	*3*	*4*	*5*
6	Water soluble acids and alkali	absence	absence	absence
7	Mechanical admixtures and water	absence	absence	absence
8	Thermal oxidative stability JFTOT at the control temperature below 260 °C			
	a) differential pressure of filter, kPa	0	0	-
	b) color of deposits over tube according to the color scale (in the absence of non-typical deposits), points	1	1	-
9	High-temperature corrosion, mass loss during test, g/m^2, at 120 ºC			
	for copper	0.47	0.44	No more than 3.0
	for bronze	0.42	0.38	No more than 2.5
10	Compatibility with resins, %	0.54	0.43	-
11	Specific electric conductivity, pS/m			
	- without antistatic additive at 20 °C	3	3	10

Table 4

The influence of on the Properties of hydrotreated fraction of jet fuel with the additive Hitec-580 (0.004 wt. %)

No.	Indices	Experimental results	Standard values
		Hydrotreated fraction with AO-80	RT (GSTU 320.00149943. 007–97)
1	Weight part of total sulfur, %	0.002	No more than 0.25
2	Kinematic viscosity, mm^2/s		
	– at 20 ºC	1.54	No less than 1.25
	– at minus 40 ºC	6.9	No more than 16
	– at minus 20 ºC	-	-
3	Mechanical admixtures and water	absence	absence
4	Mechanical admixtures, % according to GOST 10577	absence	0.0003
5	Antiwear properties under sliding friction at the device UPS-01		
	- antiwear properties criterion, %	132	No less than 95
	- wear spot diameter, mm	-	-

Table 5

Properties of hydrotreated fraction of jet fuel with the mixture of additives

No	Indices	Samples	
		Fraction + Hitec-580 (0.003 wt. %) + Agidol-1 (0.003 wt. %)	Fraction + Hitec-580 (0.003 wt. %) + AO-80 (17 mg/dm^3)
1	*2*	*3*	*4*
1	Density, kg/m^3		
	- at 20 ºC	789	789
2	Fractional composition, °C		
	initial boiling point	147.2	146.7
	10 %	172.5	171.1
	50 %	189.4	188.4
	90 %	214.4	212.2
	98 %	239.8	227.2
3	Kinematic viscosity, mm^2/s		
	- at 20 ºC	1.57	1.59

Table 5 continue

1	*2*	*3*	*4*
	- at minus 40 ºC	6.95	6.95
4	Low heat value, kJ/kg	43363.84	43363.84
5	Acidity, mg KOH per 100 cm^3 of fuel	0.38	0.4
6	Acid number, mg KOH per 1 g of fuel	0.062	0.063
7	Flash point, closed-cup, ºC	51	48
6	Chilling point, °C	minus 60.5	minus 61
7	Thermal oxidative stability under static conditions at 150 °C		
	weight content of deposit, mg per 100 cm^3 of fuel	1.6	1.48
8	Weight content of aromatic hydrocarbons, %	17.5	17.5
9	Existentgum content, mg per 100 $cm^3$of fuel	1.65	1.25
10	Weight content of total sulfur, %	0.0015	0.0012
11	Corrosiveness to copper strip at 100 ºC for 3 hours	stands the test	stands the test
12	Water soluble acids and alkali	absence	absence
13	Mechanical admixtures and water	absence	absence
14	Reaction with water, points, - state of interface	1	1
15	Specific electric conductivity, pS/m		
	- without antistatic additive at 20 °C	2.4	2.8
16	Thermal oxidative stability JFTOT at the control temperature below 260 °C		
	a) differential pressure of filter, kPa	0	0
	b) color of deposits over tube according to the color scale (in the absence of non-typical deposits), points	1	1
17	Antiwear properties under sliding friction at the device UPS-01		
	antiwear properties criterion, %	137	134
18	High-temperature corrosion, mass loss during test, g/m^2, at 120 ºC		
	for copper	19.2	31.2
	for bronze	0.92	2.0
19	Compatibility with resins, %	0.58	0.59
20	Microbiological phase	absence	absence
21	Carbon number, carbon factor, NACA factor	310.213	309.51
22	Opacity index SVI	283.17	278.23
23	Luminometernumber	59.48	59.48
24	Refraction index	1.4425	1.4425
25	Mechanical admixtures, wt. %	absence	absence
26	Content of antioxidant, wt. %	0.003	0.002

The experimental results show that introduction of Agidol-1 in amount of 0.004 wt. % does not significantly affect the properties of the hydrotreated fraction of jet fuel. At the same time, if we compare the samples with different amount of Agidol-1, we observed the decrease in the existent gum content. This value is 1.25 mg per 100 cm^3 of fuel (for Agidol-1 in amount of 0.003 wt. %) versus 1.22 mg per 100 cm^3 of fuel (for Agidol-1 in amount of 0.004 wt. %). Moreover, a slight decrease in the corrosive effect of the fuel with 0.004 wt. % of Agidol-1 was observed as well.

Antiwear properties of jet fuels were determined by a set of physico-chemical indices, in particular: the kinematic viscosity at 20 °C and minus 40 °C, the mass fraction of total sulfur, the content of mechanical admixtures and water, antiwear properties under sliding friction at the device UPS-01. For all of these parameters, the samples with antiwear additive Hitec-580 in various concentrations fully meet the requirements of the regulatory document for jet fuel (GSTU 320.00149943.007–97 «Fuel for jet engines «PT» . Specifications»).

The introduction of AO-80 in amount of 0.0024 mg/l shows a positive effect on the properties of the fuel fraction, which characterizes its chemical and thermal oxidative stability. These samples fully meet the requirements of the regulatory document for jet fuel (GSTU 320.00149943.007–97 «Fuel for jet engines «PT». Specifications»).

The additive AO-80 has a positive effect on thermal oxidative stability of fuel under static conditions. So, the weight content of the formed deposit was 1.6 mg per 100 cm^3 of fuel. It should be noted that existent gum content in the samples with AO-80 significantly decreased and amounted to 1.0 and 1.08 per 100 m^3 of fuel. This indicates the efficiency of AO-80.

The additive AO-80 has also a positive influence on corrosion properties of fuel. There is a significant decrease in the corrosive effect on both copper and bronze of the fuel with a minimum content of additive to compare with the sample with the maximum concentration of AO-80.

The experimental results of hydrotreated fraction of jet fuel with a mixture of additives showed ambiguous effect on the quality parameters of the fraction. It should be noted that the use of antiwear and antioxidant additives in the mixture does not have a negative effect on the quality parameters. The positive influence is observed relative to the antiwear properties. Thus, the antiwear properties criterion for the sample + Hitec-580 + Agidol-1 increased in comparison with the sample + Hitec-580 + AO-80. Such values as existent gum content and thermal oxidative stability under static and dynamic conditions had not essential differences. The difference was within the limits of the error. A slight increase in acidity (acid number) of the samples was observed. However, their numerical values were within the limits defined by the normative documentation.

We observed a significant loss in the sample mass during the experiments indicating the corrosive effect of the samples on copper and bronze compared with the samples with antioxidant additives only. In general, the results show the need for more detailed studies of the influence of the complex application of application packages on the properties of fuels for air jet engines.

A comparative study of the hydrotreated fraction of jet fuel with antioxidants and Hitec-580 was carried out. The efficiency of additives and their influence on the quality of commercial aviation fuel were evaluated.

The results show the effectiveness of the antiwear additive Hitec-580 in the maximal amount recommended by the manufacturer. The antioxidant Agidol-1 exibits low antioxidative effect but it does not have a negative effect on the quality of commercial jet fuel, which meets the requirements of regulatory document GSTU 320.00149943.007–97 «Fuel for jet engines «PT». Specifications».

The antioxidant AO-80 is effective as an inhibitor of oxidation. It also does not have a negative effect on the quality of commercial jet fuel, which meets the requirements of regulatory document GSTU 320.00149943.007–97 «Fuel for jet engines «PT». Specifications».

It is recommended to conduct more detailed studies on the complex influence of the additives on the properties of jet fuels, in particular in the conditions of long-term storage, as well as studies on the possibility of expanding the range of antiwear and antioxidant additives for jet fuels.

РЕФЕРАТ

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ВПЛИВ АНТИОКСИДАНТІВ І ПРОТИЗНОШУВАЛЬНИХ ДОДАТКІВ НА ВЛАСТИВОСТІ ПАЛИВ ДЛЯ РЕАКТИВНИХ ЛІТАКІВ

Стаття присвячена вивченню впливу протиокиснювальних та протизношувальних додатків на реактивне паливо. До гідроочищеної фракції палива для повітряно-реактивних двигунів додавали протиокиснювальні додатки Агідол-1, АО-80 та протизношувальний додаток Хайтек-580 у концентраціях, рекомендованих виробником. Встановлено, що додавання цих присадок, як окремо, так і в комплексі, покращує фізико-хімічні властивості товарного палива для паливно-реактивних двигунів, не чинить на нього негативного впливу, а його показники відповідають вимогам нормативних документів.

Ключові слова: реактивне паливо, термоокиснювальна стабільність, протиокиснювальні додатки, протозношувальні додатки

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ВЛИЯНИЕ АНТИОКСИДАНТОВ И ПРОТИВОЗНИСНЫХ ПРИСАДОК НА СВОЙСТВА ТОПЛИВ ДЛЯ РЕАКТИВНЫХ САМОЛЕТОВ

Статья посвящена изучению влияния противокислительных и противоизносных добавок на реактивное топливо. Во фракцию топлива для воздушно-реактивних двигателей гидроочищенного добавляли противокислительны добавки Агидол-1, АО-80 и противоизносную добавку Хайтек-580 в концентрациях, рекомендованных производителем. Установлено, что добавление этих присадок, как отдельно так и в комплексе, улучшает физико-химические свойства товарного топлива для топливно-реактивных двигателей, не оказывает на него негативного влияния, а его показатели соответствуют требованиям нормативных документов.

Ключевые слова: реактивное топливо, термоокислительная стабильность, противокислительные добавки, противоизносные добавки

ABSTRACT

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INFLUENCE OF ANTIOXIDANTS AND ANTIWEAR ADDITIVES ON JET FUEL PROPERTIES

The article is devoted to the study of antioxidants and antiwear additives influence on reactive fuels. The antioxidants Agidol-1, AO-80 and antiwear Hitec-580 were added to the hydrotreated fuel fraction for air-jet engines in the concentrations recommended by the manufacturer. It was established that the addition of these additives, both individually and in combination, improves the physical and chemical properties of commercial fuel for fuel-jet engines, does not affect it, and its properties meet the requirements of normative documents.

Key words: reactive fuel, thermal oxidative stability, antioxidant additives, antiwear additives.

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2.7 NITROGEN OXIDE AND DISPERSE PARTICLES EMISSION REDUCTION IN DIESEL ENGINES

Georgy Kuharyonok, Denis Kapsky, Vitaly Berezun

Constant toughening of requirements for diesels has directed the development of the world engine manufacturing to improving ecological indeces. The major difficulty for diesel engine-building is nitrogen oxide (NOx) and particles mater (PM) emission reduction. Their level limit is determined by the requirements of technical guidelines. Concerning available at the moment technologies, the strategy of emission reduction (ER) is conditioned by the compromise between the degree of diesel design complexity and fume cleaning efficiency [1, 2, 3].

Among the factors considered above the following parameters are worth mentioning: the injection pressure, the fuel injection advance angle and the exhaust fume recycle rate for reasons of the major influence on fume emission and the fuel-economic indicator. At the same time the effective value range shift of varying parameters is determined by the basic diesel engine design parameters. The use of injection systems allows to control flexibly the injection pressure and the fuel injection advance angle without making the engine design too complex. Together with the use of the exhaust gas recirculation (EGR) system the injection systems allow to coordinate design parameters and engine-on mode specifications.

The improving potential of diesel engine operating cycle is currently not exhausted: it is the main means of attaining up-to-date regulated markers, which makes the research of the fume emission reduction potential by means of improving engine workflows relevant and requested.

The most difficult task for diesel engines is to meet the requirements of NO_x and PM emission reduction [3].

The purpose of the research is to reduce the so called “unrefined” NOx and PM emission by means of choosing design and adjustment parameters of diesel engines workflows taking into account the priority of fuel economy.

A test facility for complex research of diesels workflows and NO_x and PM emission estimation has been worked out (Fig.1). Its peculiar features are the following: automation of measurement and data smoothing processes, on-line monitoring of the eye diagram changes, the beginning of injection and injection duration, recycle rate control of CO_2 concentration in engine exhaust of the inlet gas.

The test facility meets all the international UNO requirements (Rules №№ 24, 49, 96).An investigating methodology has been developed. According to it, for the efficient use of time and labor costs reduction the sequence of parameter changes Pinj, Θ and ρegr in providing an operating mode speed and torque = const was defined by the saturated plan of the experiment, which allows to express the acquired results in terms of quadric regression equations. The required engine power was compensated for changing the quantity of the injection rate. For engine trend monitoring in order to reject misleading tests data while carrying out experimental research the verification of fuel-economic and ecological figures was provided on the chosen in advance control point with the equal fuel-injection equipment alignments and the degree of EGR.

The reproducibility of measurements was provided by systematic equipment calibration and check-out.

Configuration parameters study has been carried out with account for ecological performance improvement and corrected car economy (ge) on the basis of a produced by Minsk Engine Plant 90 kilowatt turbocharged diesel (Д-245 production number) which is equipped with the electronic fuel injection system. The following characteristics have been investigated: the shape of the combustion chamber, angular placement of the spray sparger, its configuration and the quantity of its nozzle holes, swirl ratio of inlet ports of the engine cylinder head (ECH), gas distribution phases and the way of exhaust gas recirculation (EGR) organization [4]. As a result, regulated EGR contoured by high pressure with the chill of circulated exhaust gas (EG) has been chosen. The developed elements of the configuration are in Fig. 2.

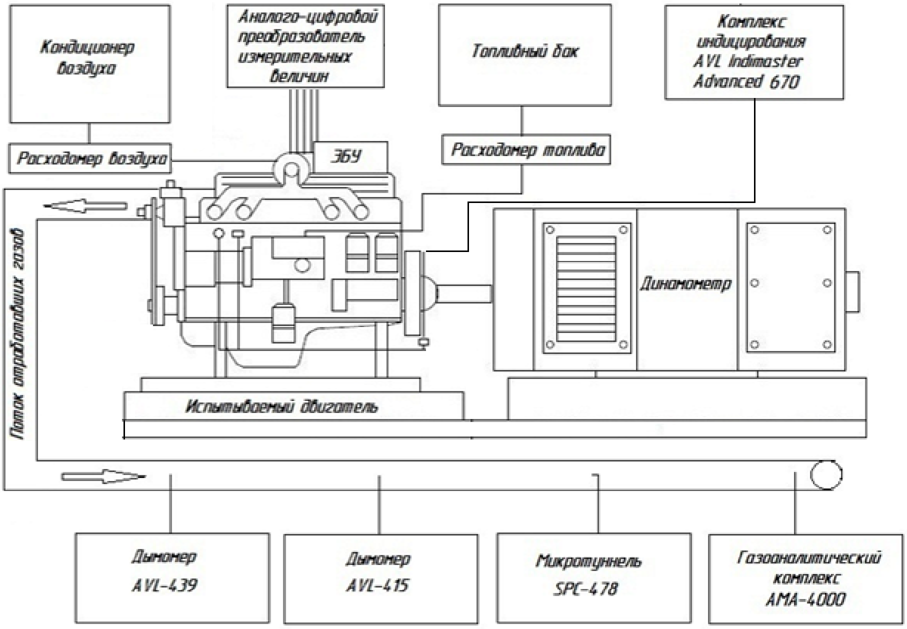

Fig. 1. Test facility lay-out

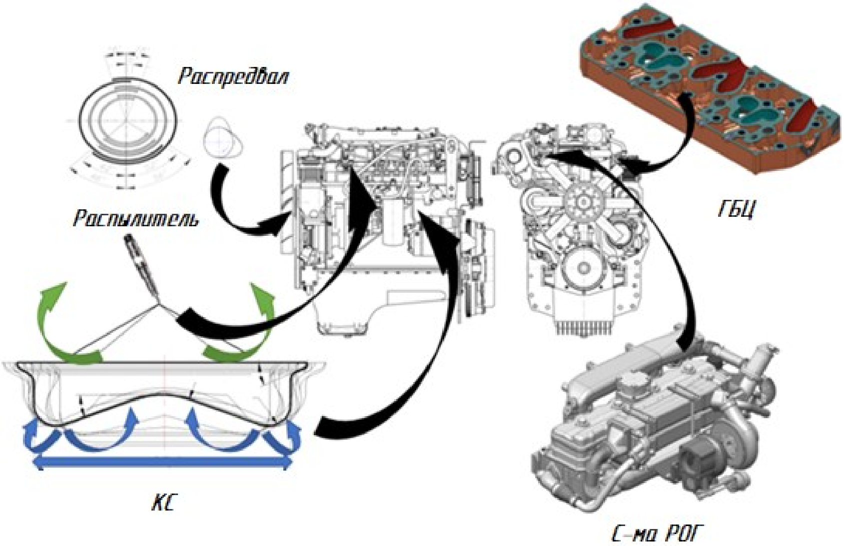

Fig. 2. Developed elements of the study object configuration

It has been revealed that the adjustment parameters Pinj, Θ and ρegr, which are changing in the engine's working process, play a crucial role in the working process organization that provides upholding ecological safety standards.

In order to conduct calculated analyses an integrated mathematical model of the diesel with ERG system working process has been created. It is based on the first law of thermodynamics and includes N. Razleitsev's analysis technique of the fuel combustion process with updated coefficients, deduced empirical dependence for calculations of disperse particles emission and the temperature of the exhaust gas after the turbocharger [4].

For mathematical model verification the calculation data for the nominal rating was compared with the experimental data.

Conformance checks of the indicator diagram (ID) design form by Fisher's criterion have been performed [5], which is the quotient obtained when the variance estimate of inadequacy S_D is divided by the variance estimate of the single observation error S_e:

$$F = \frac{S_D / \varphi_n}{S_e / \varphi_d},$$

where φ_n – number of degrees of freedom of random quantity numerator F; φ_d – number of degrees of freedom of random quantity denominator F.

The observed value $F = 1{,}08 < F\text{cr} = 1{,}16$ for statement performance probability $Pb = 0{,}95$ provides support for the model adequacy.

Dispersion numbers of the effective marker in examining the calculation sufficiency NOx, PM и Tr' do not drop lower than 94 %. It testifies to the high statistical significance of characteristic curve for its calculation.

The calculation algorithm was implemented in programming environment Delphi.

As a result, three means of the workflow organization have been singled out which influence NOx and RM emission in different ways. These means are determined by the type of ID that are shown in Fig. 3.

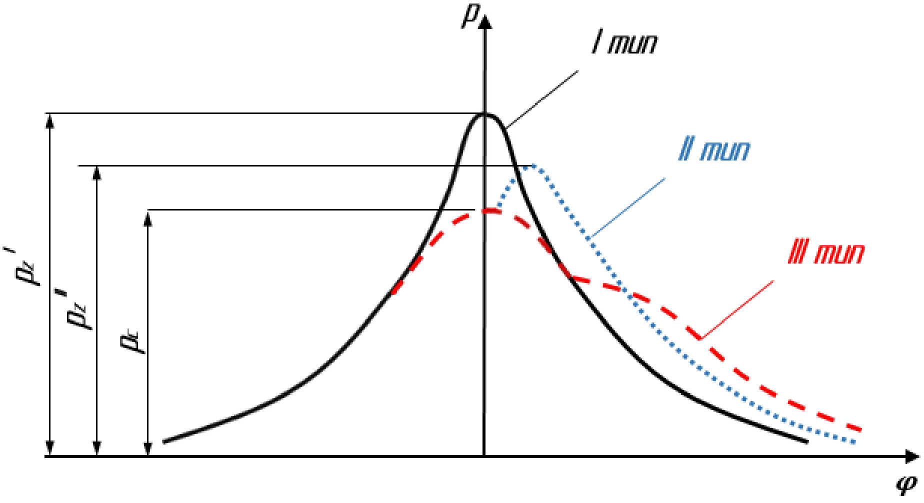

Fig. 3. Indicator diagrams

The first type (I type) is a one-humped ID depicting the ratio of peak combustion pressure to compressive pressure pz/pc>1; II type is a double-humped ID depicting pz/pc>1 and III type is a double-humped ID depicting pz/pc≤1 (with an indistinct peak pz).

Calculated analyses of PM and NOx emission adjustment parameters according to the saturated plan of the experiment for each NRSC (Non-Road Transient Steady-state Cycle) ecological cycle mode have been conducted. The margin limits of the variation range have been chosen according to the working processes in the area of the ID (three types). The variation range of pinj and ρegr has been limited by the fuel consumption rate of the initial related type stage along with the correlated ecological parameters. As an additional restricting parameter the exhaust gas temperature after the turbocharger (Tr') has been taken, which has been restricted with account of the study subject technical specifications. The margin limits of the adjustment parameters allow to define the minimization area ge as well.

In order to choose the fuel supply parameters and the exhaust fume recycle rate the simulation data has been analyzed as well as the obtained regressional dependence with regard of the ID type. Taking into consideration generally accepted emission reduction strategies for each peak of NRSC cycle target-oriented approaches to solving the problems have been searched for. For the peak of the ecological cycle H-100 substantiation of combustion process parameters data is in Fig. 4. The data analysis has been performed in the following three directions:

1. Minimization g_e (g_{emin});
2. PM minimization (PM_{min});
3. NO_x minimization ($NO_{x\ min}$).

Parameter selection has been conducted with the help of an imbedded program module «finding solutions» from the Microsoft Excel Table, where a principle of non-linear optimization is laid down.

For the first direction the following parameters have been chosen: p_{inj} = 160 mPas, θ = 10 degrees и ρ_{egr} = 0,12 if emitted NO_x= 6,07 g/kWh, PM = 0,04 g/kWh and g_e = 214,2 g/kWh.

While calculating the whole body of data the results of the search for NOx and PM minimization determine nonrational parameters from the point of view of fuel-economic figures. It shows itself in the choice of extreme settings of the working process in the range under consideration.

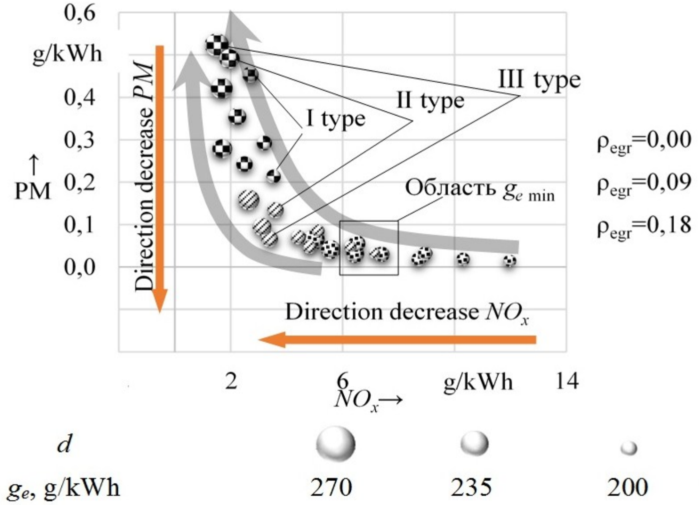

Fig. 4. PM-NOx diagram for nominal conditions

Consequently, for the 2nd and 3rd directions the solutions have been searched for in limiting fuel consumption in relation to the data of the 1st direction ($g_{e\ min}$). To minimize PM the search for solutions was made in the following two ways: NO_x increasing and NO_x decreasing by means of imposing an additional boundary condition. The simulated result of the three directions of the emission reduction strategy for the cycle H-100 is depicted in. As percentage in figure 5 fuel consumption variation is expressed.

In the proposed variant of decision making organization the parameters of fuel consumption degradation tend to organize the working process with the initial stage of the indicator diagram and a transition from type I to type III. This is reflected in the fact of θ decrease while Pinj is maintained at the upper variation limit. The difference in NO_x and PM minimization consists only in the fact that in the former case ρegr is in the value range of 0,16, but in the latter case it approximates 0.

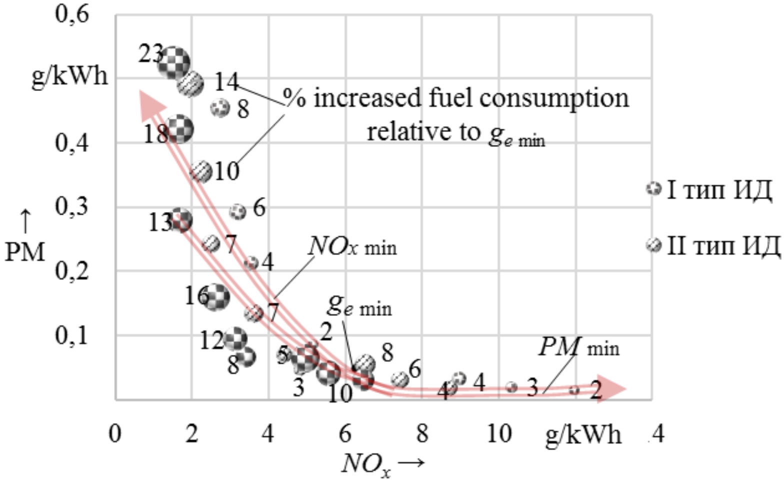

Fig. 5. Dimensions of ecological indices improvement for nominal operation conditions

In the range of obtained values the study of diesel emission reduction strategies has been carried out. For their estimation the following characteristics have been singled out:

Δg_e – fuel consumption change in regard of the basic cycle, defined by workflow management adjustment parameters which provide ge minimization at all toxicity level;

ΔT_{avr} – average toxicity level temperature change in regard of the basic cycle;

C_{PM}, C_{NOx} – desired degree of PM and NO_x clean-up system conversion in order to meet Stage 4 regulations. The degree is defined as difference quotient between the values of «raw» and normable diesel emission reduction to the value of «raw» emission.

Five stages of workflows calculation have been identified with account for fuel consumption with load increase, toxicity level factor weight and the presence of the EGR system (Table 1).

At the first stage to compose the basic toxicity level for each mode the workflow settings have been chosen which provide ge minimization. The summary NO_x and PM emission indicators have been 8,1 g/kWh and 0,031 g/kWh respectively. At the same time the exhaust gas temperature according to the toxicity level constitutes 647 K.

At the 2nd and 3rd stages a PM reduction strategy has been fulfilled involving the use of EGR system and its excluding. As a result, for the engine configuration without the EGR system the cycle with NO_x and PM of 13,1 g/kWh and 0,014 g/kWh has been obtained respectively. It allows to meet PM Stage 4 regulations without the use of the EGR system. Herewith, Δg_e is 2,4 %, but the ΔT_{avr} increase is 4o. For the engine configuration without the EGR system NO_x and PM emission constitutes 5,1 g/kWh and 0,089 g/kWh respectively, Δg_e is 10,9 % and the ΔT_{avr} increase is 54o.

Table 1

NOx and PM emission reduction strategies data

Calculation stage	NO_x, g/kWh	PM, g/kWh	Δg_e, %	ΔT_{avr},^{o}	C_{PM}	C_{NOx}	EGR
1	8,1	0,031	-	-	0,20	0,95	+
2	5,1	0,089	10,9	54	0,70	0,92	+
3	***13,1***	***0,014***	***2,4***	***4***	**-**	***0,97***	**-**
4	***7,7***	***0,025***	***2,4***	***4***	**-**	***0,95***	+
5	2,5	0,265	12,0	81	0,91	0,83	+

At the 4th calculation stage the strategy of meeting PM reduction within the framework of Stage 4 regulations was considered with the opportunity to reduce NOx by using the EGR system. The PM value of 0,025 g/kWh within a cycle has been successful with the NOx emission of 7,7 g/kWh and with the ΔTavr increase of 4o together with the Δge increase of 2,4 %.

At the 5th calculation stage a NOx reduction strategy has been fulfilled. The cycle obtained provided NOx and PM with 2,5 g/kWh and 0,265 g/kWh respectively, Δg_e has increased by 12 % and ΔT_{avr} – by 81o.

The choice of the emission reduction strategies was made with regard of fuel consumption and the reduction of engine configuration elements. Especially appealing are the strategies within the framework of PM Stage 4 regulations (variants 3 and 4).

РЕФЕРАТ

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ЗНИЖЕННЯ ВИКИДІВ ОКСИДІВ АЗОТУ ТА ДИСПЕРСНИХ ЧАСТИНОК ДИЗЕЛЯ

Виконано оцінку напрямів зниження викидів NO_x і PM через розгляд варіантів організації робочого процесу з урахуванням пріоритету паливної економічності при зростанні навантаження, вагових факторів циклу токсичності, комплектації двигуна, а також необхідної для досягнення цільового ступеню екологічної безпеки ступеня конверсії системи очищення ОГ і зміни середньої температури ОГ циклу токсичності.

Визначено параметри подачі палива і ступеня РОГ, що дозволили реалізувати в електронному блоці дизеля алгоритм управління, що забезпечує протікання робочого процесу в межах виконання норм Stage 4 по РМ без застосування сажевих фільтрів.

Ключові слова: дизель, параметри подачі палива, рециркуляція відпрацьованих газів, оксиди азоту, дисперсні частинки.

РЕФЕРАТ

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СНИЖЕНИЕ ВЫБРОСОВ ОКСИДОВ АЗОТА И ДИСПЕРСНЫХ ЧАСТИЦ ДИЗЕЛЯ

Проведена оценка направлений снижения выбросов NO_x и PM путем рассмотрения вариантов организации рабочего процесса с учетом приоритета топливной экономичности при росте нагрузки, весовых факторов цикла токсичности, комплектации двигателя, а также необходимой для достижения целевой ступени экологической безопасности степени конверсии системы очистки ОГ и изменения средней температуры ОГ цикла токсичности.

Определены параметры топливоподачи и степени РОГ, позволившие реализовать в электронном блоке дизеля алгоритм управления, обеспечивающий протекание рабочего процесса в границах выполнения норм Stage 4 по PM без применения сажевых фильтров.

Ключевые слова: дизель, параметры топливоподачи, рециркуляция отработавших газов, оксиды азота, дисперсные частицы.

ABSTRACT

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NITROGEN OXIDE AND DISPERSE PARTICLES EMISSION REDUCTION IN DIESEL ENGINES

The paper focuses on the directions of the strategy to reduce emissions of NOx and PM. They were assessed by considering options for organizing the workflow taking into account the priority of fuel economy with increasing load, toxic cycle weight factors, engine configuration, as well as the degree of conversion of the exhaust gas cleaning system and average temperature required to achieve the target environmental safety level Exhaust cycle toxicity.

The fuel supply parameters and the degree of EGR are determined, which allowed to implement a control algorithm in the electronic block of a diesel engine that ensures the flow of the working process within the limits of the fulfillment of Stage 4 standards according to the RM without the use of particulate filters.

Key words: diesel, fuel supply parameters, exhaust gas recirculation, nitrogen oxides, particles mater.

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2.8 MODIFICATION OF DIESEL FUEL COMPOSITION WITH METHYL ESTERS OF FATTY ACIDS FROM NON-EDIBLE FATS

Elena Shevchenko, Valeriia Kameneva, Alyona Shkekina

The demand for oil will be growing by 1 % per year until 2035, all over the world. As a result, instead of the current 84.5 million barrels per day, the global market will need 111.7 million barrels a day. Oil consumption will reach 106 million barrels a day in 2030. This is in line with the forecast of the International Energy Agency.

Forecasts show that the existing energy efficiency policy and the role of alternative fuels with high energy prices will curb the growth of energy consumption and ensure the transition to renewable energy sources.

Solution of the modern environmental problems requires the search for alternative sources of raw materials and energy. It is related not only to the need to reduce pollution of the environment, but also the importance of the transition from exhaustible raw materials to the increased use of renewable resources. Work in this direction has been conducted around the world for a long time. Oil crops are the most important source of renewable raw materials among modern bioresources, because vegetable oils could be used to produce fuels and lubricants as an alternative to petroleum raw materials. The renewability of the raw materials causes the expediency of expanding the use of vegetable oils in technology at present. In addition, the products derived from vegetable oils have less reliable as compared with the synthetic products, which are biodegradable [2].

An important fact is that the use of fats and fatty waste is possibly not only in the production of lubricants, but also in the production of fuels – gasoline, diesel, boiler houses. This makes it possible to use machines and mechanisms that work only on products of plant origin.

At present, Ukraine has a shortage of oil fuels (oil and gas condensate production is below 4 million tons, lacking more than 10 million tons), while production of biofuels from vegetable oils (rapeseed, sunflower, etc.) is relatively cheap process. Therefore, this is a promising area for research. Fuels of vegetable origin from rapeseed oil (a mixture of rapeseed oil fatty acid methyl esters) and glycerol are produced by methanolysis. Currently, more than 1.5 million tons of biofuels are produced in Europe (Germany, France, Austria, etc.).

Biodiesel can be used in diesel engines without constructional changes or swap. Fuel consumption is increased by 10 % when the engine is running on biodiesel (methyl esters of fatty acids are oxygen-fueled). The emission of harmful substances in the exhaust gases is reduced by 25–50 %. Therefore, this type of fuel can be used in environmentally sensitive areas (city zone, recreation area, etc.) [1].

Biofuels of the first generation are made according to the traditional technologies of sugar, starch, vegetable oil and animal fat. The main sources of raw materials are seeds or fruits. For example, vegetable oils are obtained by pressing seeds of sunflower. The resulting oil can be used to produce biodiesel. The starch is obtained from wheat. After transformation of starch, bioethanol is produced. But such sources of raw material are important in the food chain of people and animals. In addition, many first-generation biofuels are investment intensive and cannot compete with fossil fuels by value (for example, oil). Some first-generation fuels slightly reduce greenhouse gas emissions. Emissions from the production and transportation of the first-generation fuels often exceed emissions from the use of conventional fossil fuels [3].

The main task of biofuel technology of the second generation is to increase the amount of biofuel made of residual non-food parts of plants remaining after the removal of the food part, such as stems, leaves, husk. Non-food plants (millet, jatropha) and industrial waste, such as wood chips, peel and pulp from fruit pressing, etc., can also be used for the production of the second generation fuels.

The second generation biofuels technologies are designed to extract useful substances for the production of fuels using wood biomass. Wood biomass contains useful sugars in cellulose and lignin. All plants contain cellulose and lignin.They are complex carbohydrates (molecules based on sugar).Lignocellulosic ethanol is obtained by separating sugar molecules from cellulose, using enzymes, steam heating and other pretreatments.Ethanol can be obtained from sugar base using fermentation as well as in the processes of the first processing. The by-product of this process is lignin, which can be used to generate energy. Obtaining ethanol from lignin and cellulose reduces greenhouse gas emissions by 90 % compared with petroleum [3].

The first and second generation biofuels use existing technologies for the production of alcohol and vegetable oils. While the third generation of biofuels uses new technologies with photosynthetic algae. These algae use energy of light to absorb carbon dioxide from the air and produce organic compounds. Microalgae have very small size about 1, 2, 3, 10 micrometers. They are able to produce a lot of lipids inside their cells. Lipids can be isolated and transformed into biofuels. Microalgae grow up very quickly, do not occupy land areas, and are technologically processed.

Algae can be used to produce motor fuels that are very similar to the traditional ones. The microalgae have the following benefits:

- high yield;
- ability to develop in water, not on the ground, which can be used for other food crops;
- ability to absorb large amount of carbon dioxide; and
- low use water for cultivation.

The paths for biomass conversion into biofuels of the first, second and third generations are shown in Fig. 1.

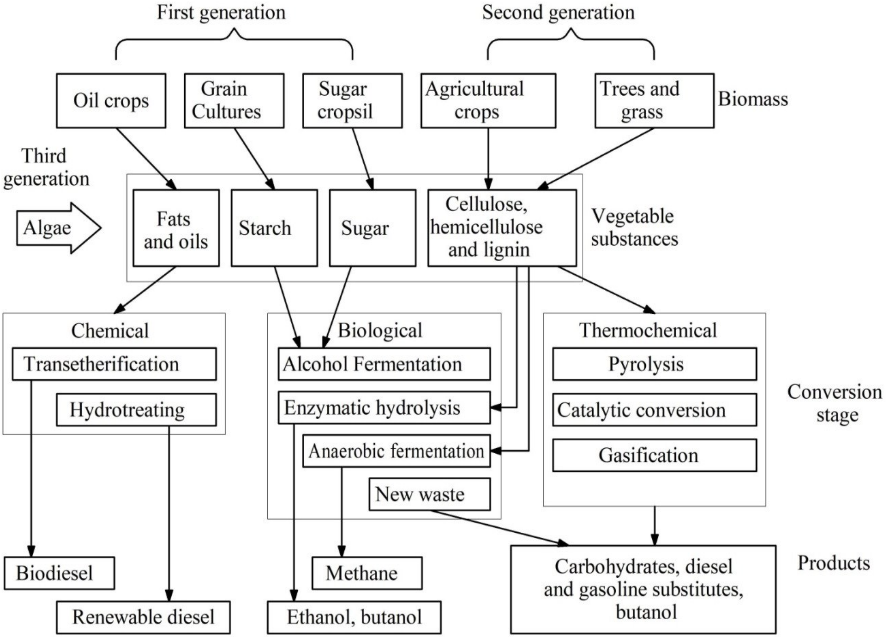

Fig. 1. Ways of biomass conversion for biofuels of the first, second and third generations [4].

At first, microalgae should be grown. Then this biomass should be collected.The collected algae can be immediately sent for recycling. The hydrocracking process will take place and the fraction of bio-oil will be separated at high pressure and temperature. This bio-oil can be purified by conventional petroleum distilleries. There is another option. First, the separated microalgal biomass fraction can be isolated and then recycled into biofuels by chemical methods. So, there is a range of technologies.

Microalgae provide an opportunity to get by order of magnitude more biofuels as compared with conventional crops. The agricultural crops grow for a long time, and microalgae grow in 2 weeks.

There is no algae fuel in Ukraine due to the absence of strains. Algae strains that can be used in the industry are costly. But such algae can be a promising source of raw materials for the production of biodiesel fuel. Data indicate that 1 hectare of land can give 446 liters of soybean oil or 2690 liters of palm oil, while the same area of the water surface can yield about 90.000 liters of biodiesel. The development of the third-generation biofuels production is an important task for Ukraine.

The development of alternative energy sources and the production of biofuels are topical in our time due to the energy crisis. Biofuel production from microalgae has a number of significant advantages over the production of biofuels from oilseeds and rape. But now the project for obtaining biofuels from algae is only at the stage of experimental development.

The fourth generation of biofuels is a technology using photosynthetic cyanobacteria. Bacteria produce the final product using CO_2 and sunlight. This method greatly increases the system performance. The photosynthetic cell can be genetically modified for ethanol production. The surface of water in a special reactor, where the cyanobacteria live, is heated by sunlight. The alcohol evaporates from the surface of the water and is collected by condensation. This is a very interesting process without intermediate stages of biomass collection and processing. By now, such technology is under development in the USA.

The fifth generation of biofuels is now being developed. Electric biosynthesis is the basis of this process. There are microbes that can consume electricity from the electrode in solution. These microbes perform very high energy conversion efficiency, potentially. Some microorganisms are able to use up to 80 % of the electrons obtained from the electrode for the synthesis of organic compounds. The processes of obtaining biofuels of the fifth generation do not affect agricultural areas and drinking water. The use of electric biosynthesis may increase the production of food and biofuels [4].

The National standard of Ukraine 4840:2007 «Diesel fuel of high quality. Specifications» limits the content of methyl esters of fatty acids by not more than 5 %. Sunflower and rapeseed oils are traditional sources of triglycerides in Ukraine. The production of biofuels from this raw material is limited by its high price (sunflower oil of the 1st grade is 22 UAH / kg, rapeseed oil is up to 18 UAH / kg), and is now not economically profitable. In addition, large agricultural areas should be used to grow these crops. It is more rational to use sunflower oil as a food product, and it is better to import rapeseed oil. Non-standard vegetable oils (such as worked or dark sunflower oil) can be used to synthesize biofuels.

A significant amount of technical animal fat is available in Ukraine. Non-food animal fats are of lower value than high quality vegetable oils. For example, if the fats do not meet the standards of color, transparency, contain impurities, etc. they can be used for FAME synthesis. This is a mixture of pork-beef fat, chicken fat and fish oil, they are meat-processing residues. Approximate price of such fats: pork beef – 10 grn, chicken – 12 and fish – 6 grn per kilogram.

Technical pork-beef fat is burned. Chicken and fish oils are partly used as additives to animal feed. The rest, which is most of the chicken and fish oil, can go for FAME. Ukrainian enterprises receive about 1000 tons of chicken fat per month.

The advantages of using technical fats and oils are: availability throughout the year, independence from the weather conditions, safe process of transesterification. The production of fuel or fuel components from waste companies can reduce the self-cost of products. Also, the use of biofuels can increase the level of energy independence of the country.

We used chicken fat, fish oil, pork beef fat and palm oil, sunflower oil and soybean oil as raw material for the synthesis of fatty acid methyl esters. Such a wide range is due to the following factors: sunflower oil and soybean oil are best studied and widespread; palm oil and technical fish oil are the cheapest; pork-beef fat and chicken fat are undocumented industrial waste. The processing of technical animals of low-fat fats is not only an additional source of raw materials for the synthesis of the MES, but also a partial solution to the problem of waste recycling in the food industry.

All samples of the FAME were synthesized by specialists at the Department of Chemical Technology of High-Molecular Compounds, and the study of the physical-chemical properties of the FAME was carried out at the Department of Chemical Technology of Fuels at the Test Laboratory of Petroleum Products at the Ukrainian State Chemical-Technological University.

The transesterification reaction allows obtaining products close to diesel fuel according to physical and chemical and operational characteristics. But methyl esters of fatty acids are unsuitable as an additive to fuels for a number of indicators, although this possibility is considered in some cases. We have investigated samples of products derived from Ukrainian raw materials in comparison with diesel fuel (Table 1).

Table 1

Properties of fatty acid methyl esters from fats and oils

Property	Standard EN 590	Diesel Class C	Fatty acid methyl esters (FAME)					
			Chicken fat	Fish fat	Sunflower oil	Soy oil	Palm oil	Tallow (pig & beef)
1.Distillation recovered at 250 °C, %V/V	65	49	–	–	6	–	–	–
350 °C, %V/V	85	87	100	100	75	100	100	100
95 % V/V recovered at, °C	360	360	–	–	360	–	–	–
2.Boiling range, °C	-	180–360	298–340	324–348	302–360	259–348	290–350	318–350
3.Cetane no. min.	51	51	54	56	53	54	52	53
4.Density at 15 °C, kg/m^3	820–845	825	899	896	899	892	889	-
5.Kinematic viscosity at 40°C,mm^2/s	2,0–4,5	3,5	8.32	6.58	5.4	6.68	7.19	7.12
6.Flash point, closed cup °C, min.	≥55	55	159	142	154	151	169	165
7.Pour point,°C	-	-14	-3	-5	-7	-3	5	6
8.Cloud point,°C	-	-4	7	0	0	2	15	21
9.CFPP,°C	-5/-20	-8	2	-4	-1	-1	9	20
10.Acid no., mg KOH/g,	-	-	2,1	2,0	0,029	2,2	0,75	0,75
11.Sulphur content, mg/kg	≤10	10	9	2	0	0	0	0
12.Ash content, % m/m	≤0,01	0,01	0	0,006	0,029	0,016	0,05	0,015
13.Iodine Value, g I_2/100 g	-	-	89,1	91,6	101,7	96,9	60,0	60

Significant deviations exist in such properties as: fractional composition, viscosity, density, acid number, iodine value, low-temperature properties. But some of these indicators fit into the norms, as biodiesel is used only as an additive to fuel. First of all, it refers to the viscosity (Fig. 2) and density (Table 1, Fig. 3).

Table 2

Analysis of viscosity-temperature dependence of the biodiesel fuel samples

Fatty acid methyl esters (FAME)	Kinematic viscosity, mm^2/s at, °C									
	10	20	30	40	50	60	70	80	90	100
Fish fat	15,6	11,4	8,67	6,33	5,1	4,43	3,76	3,22	2,82	2,46
Soy oil	12,36	8,63	6,71	5,42	4,4	3,81	3,04	2,62	2,27	2,0
Palm oil	-	-	-	7,28	5,8	4,73	3,95	3,31	2,85	2,51
Chicken fat	-	-	-	8,95	7,03	5,6	4,65	3,85	3,29	2,95
Sunflower oil	15,62	11,25	8,69	6,32	5,05	4,24	3,81	3,21	2,77	2,42

Graphs of viscosity-temperature dependence are built according to the data of Table 2.

The excess of these indicators will not greatly affect the processes of mixture formation and combustion, due to the fact that biodiesel is a strong surfactant.

The low-temperature properties of mixed fuels are unsatisfactory. This limits their use only in warm seasons. Numerous attempts to lower pour points and filterability with depressor additives made it possible to establish that there are polyalkyl methacrylate additives in a concentration of up to 1 % or copolymers of ethylene with vinyl acetate. However, the effect of these additives is individual and applies only to the studied samples. On the other hand, this indicates the possibility and selection of effective depressors.

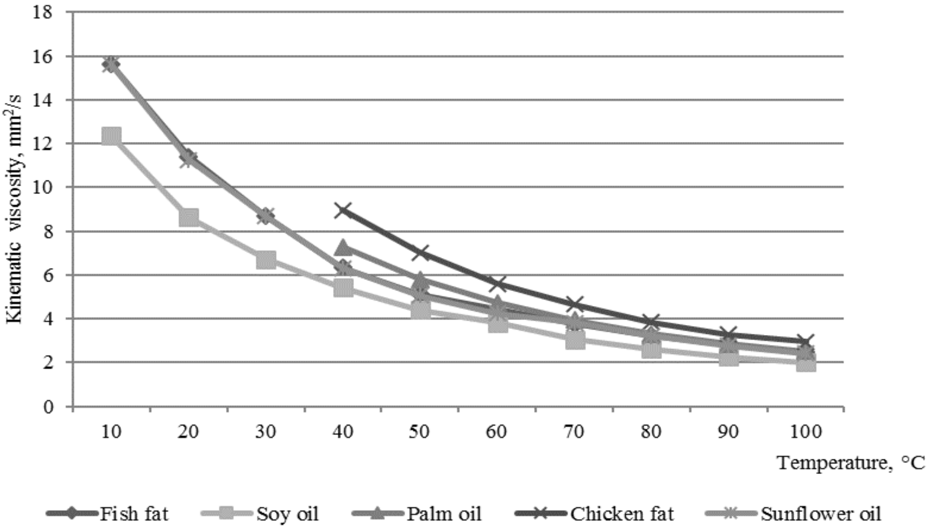

Fig. 2. Viscosity-temperature dependence of biodiesel fuel on the basis fats and oils

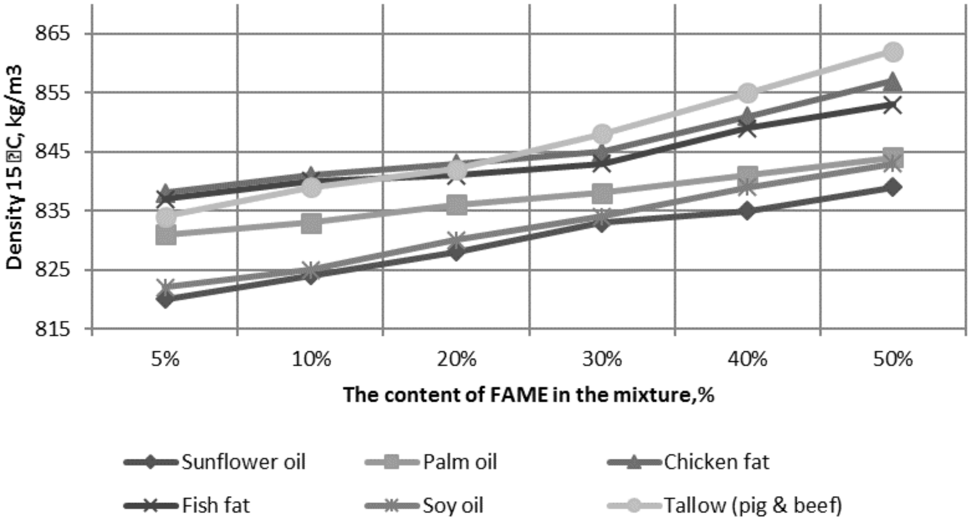

Fig. 3. Density dependence of biodiesel fuel on the basis fats and oils

A high iodine number depends on the fatty acid composition of biodiesel, more precisely, on the amount of unsaturated esters. This can adversely affect the thermal-oxidative stability of the mixed fuel.

The fatty acid composition of biodiesel was determined with chromato-aspirometer on the HP 6890 chromatograph with a flame ionization detector and a HP-INNOWax capillary column. $l = 30$ m, $d = 0.53$ mm, $h = 1$ µm, Conditions: -injector temperature is 220 °C, detector temperature is 275 °C, hydrogen flow rate – 30 ml/min, air flow rate – 300 ml/min, Helium flow rate – 10 ml/min; Sample volume – 1 µl. The results of the analysis are presented in Table.

Table 3

Typical fatty acid (FA) groups in fatty acid methyl esters from fats and oils

Property	Fatty acid methyl esters (FAME)					
	Chicken fat	Fish fat	Sunflower oil	Soy oil	Palm oil	Tallow (pig & beef)
Myristic acid, C_{14-0}	-	9,1	-	0,06	3,03	5,05
Palmitic acid, $C_{16:0}$	17,8	21,2	5,8	9,96	34,74	29,4
Palmitoleic acid, $C_{16:1}$	4,7	9,2	0,2	0,06	0,41	2,0
Stearic acid $C_{18:0}$	5,2	7,5	3,4	6,61	4,5	16,7
Oleic acid $C_{18:1}$	37,9	24,9	69,2	25,6	40,5	38,0
Linoleic acid $C_{18:2}$	33,4	3,4	19,6	51,16	16,4	6,8
Linolenic acid $C_{18:3}$	0,4	1,3	0,5	6,4	0,02	0,5
Eicosanoic acid $C_{20:0}$	0,4	9,2	0,5	-	-	0,15
Behenic acid $C_{22:0}$	-	13,0	0,4	-	-	0,55
Others	0,2	1,2	0,4	0,15	0,4	0,85

Oxidative stability was determined by three methods.

Method EN 14112 is Rancimat test. According to this method, a stream of air is passed through the sample at a given temperature. The vapors that are released as a result of the oxidation of the sample pass into the flask with distilled water together with the air. There is an electrode in the flask that measures the electrical conductivity. The end of the induction period comes at the time when the electrical conductivity begins to increase rapidly. This is due to the fact that oxidation products begin to flow intensively into water and dissociate. This method allows determining the role of radical-chain reactions in the course of oxidative processes in the sample.

Method EN ISO 12205. The method involves oxidation of the sample at the temperature of 95° C for 16 hours. At the same time, oxygen is passed through the sample. The sample is cooled and filtered after oxidation to determine the amount of insoluble products. Resinous products are washed from the vessel and their quantity is also determined. The intensity of all processes is characterized with the total number of solid products and resinous products.

The third method is testing the samples is under native oxidation. For this, the biodiesel samples are kept in a glass dish in the dark for a year. The acid and peroxide numbers of the samples were determined every three months.

The results of the native oxidation of biodiesel samples are presented in tables 4 and 5. It should be noted that biodiesel is quite stable when stored under normal conditions. The increase in acid and peroxide numbers 1.2–2.0 times can be considered insignificant. The standards of the most countries regulate the acid value of biodiesel at the level of 0.5–0.8 mg KOH/g [5].

Table 4

Dynamics of the biodiesel acid number increase during one year of storage

Period of storage, months	Fatty acid methyl esters (FAME)					
	Fish fat	Chicken fat	Tallow (pig & beef)	Sunflower oil	Soy oil	Palm oil
0	0,30	0,25	0,22	0,23	0,15	0,31
3	0,31	0,29	0,27	0,26	0,31	0,37
6	0,34	0,32	0,30	0,31	0,26	0,40
9	0,36	0,35	0,31	0,33	0,28	0,42
12	0,37	0,38	0,32	0,34	0,31	0,45

Table 5

Dynamics of biodiesel peroxide number increase during one year of storage

Period of storage, months	Fatty acid methyl esters (FAME)					
	Fish fat	Chicken fat	Tallow (pig & beef)	Sunflower oil	Soy oil	Palm oil
0	15	17	10	22	6	18
3	16	23	13	23	7	31
6	17	32	17	24	8	25
9	19	39	21	27	9	28
12	19	40	21	27	10	30

However, biodiesel is actively oxidized with increasing temperature and in the presence of oxygen. The intensity of oxidation depends on the total amount of unsaturated compounds in biodiesel when tested according to EN-14112 (determination of the induction period) (Table 6). The number of isolated double bonds in the molecule did not matter.

Table 6

The dependence of biodiesel oxidation resistance on its fatty acid composition

Fatty acid methyl esters (FAME)	The total content of unsaturated hydrocarbons, %	The content of hydrocarbons with two bonds and more, %	Oxidation resistance at 110 °C, h
Fish fat	38,8	4,7	12
Tallow (pig & beef)	47,3	7,3	11
Palm oil	57,3	56,9	9
Chicken fat	76,4	33,8	8
Soy oil	79,2	57,6	6
Sunflower oil	89,5	20,1	7

Such dependence is not observed in the oxidation of biodiesel according to EN ISO 12205. This indicates that compounds prone to reaction seals without oxygen or with a very small amount of oxygen are present in the biodiesel. To know what processes occur during the oxidation of biodiesel and how to inhibit them, it is necessary to know the exact composition of biodiesel. Biodiesel may contain substances that slow down or accelerate oxidative processes. The schematic diagram of the compaction processes occurring in oil fuels is already known. Acidic oxidation products play an important role in these processes. They catalyze polymerization, polycondensation and polyesterification reactions. Their activity can be reduced by the addition of neutralizing compounds, in particular, amines. The effectiveness of some amines has been tested by us. It turned out that amines perform an inhibitory effect on the formation of sludge and tar. Alpha naphthylamine was the best of them. Some results are presented in Table 6. At the same time, the test was not conducted with «clean» biodiesel, but diesel fuel containing 7 % biodiesel.

Table 7

The results of the oxidation of a mixture of diesel fuel with 7 % biodiesel

Fuel Sample	Oxidative stability, g/m^3		
	Non-inhibited oxidation	Inhibited oxidation, additive, 0.06 %	
		Shielded phenol	Additive based on aromatic amine
diesel without biodiesel	4	-	-
diesel with biodiesel from:			
Chicken fat	35	6,5	4
Fish fat	45	7	5
Sunflower oil	55	8,3	6
Soy oil	30	5,8	4
Palm oil	14	3,5	4
Tallow (pig & beef)	4	-	-

Low-temperature properties. Depressor additives can reduce important parameters such as the pour point and the cold filter plugging point (CFPP), but practically do not affect the cloud point.

The use of depressant additives is an efficient way to improve the low-temperature properties of diesel and increase fuel resources.

We have also studied depressor additives based on copolymers of ethylene with vinyl acetate – CEVA-1, CEVA-2, CEVA-3. They differ in their usage for fuels with different fractional composition.

Data for FAME from sunflower oil are given as an example. These additives were tested in diesel, too. The results are presented in tables 8 and 9.

Table 8

Low-temperature indicators of diesel with additives

Property	Cloud point,°C	Pour point,°C	CFPP,°C
Diesel	3	-13	-4
+0,05 % CEVA -1	-2	-24	-12
+0,05 % CEVA -2	-3	-29	-17
+0,05 % CEVA -3	-4	-20	-9

Table 9

Low temperature indicators of sunflower oil intermediate with additives

Property	Cloud point,°C	Pour point,°C	CFPP,°C
FAME of Sunflower oil	1	-14	-6
+0,05 % CEVA -1	1	-16	-7
+0,05 % CEVA -2	-2	-18	-8
+0,05 % CEVA -3	1	-15	-6

The fractional composition of the methyl esters of fatty acids of sunflower oil has been taken into account for a more detailed study (Table 1). The influence of depressant additives on narrow fractions of diesel has been studied extensively. The results of the studies are presented in Table 10.

Table 10

Low temperature parameters of diesel fractions with additives

Property	Cloud point,°C	Pour point,°C	CFPP,°C
Fraction 180–220°C	-22	-33	-28
+0,05 % CEVA -1	-20	-38	-36
+0,05 % CEVA -2	-20	-39	-37
+0,05 % CEVA -3	-20	-34	-29
Fraction 220 - 260°C	-28	-31	-26
+0,05 % CEVA -1	-30	-33	-35
+0,05 % CEVA -2	-30	-39	-37
+0,05 % CEVA -3	-24	-32	-28
Fraction 260 - 300°C	-12	-22	-17
+0,05 % CEVA -1	-15	-36	-20
+0,05 % CEVA -2	-16	-37	-22
+0,05 % CEVA -3	-12	-23	-17
Fraction 300 - 360°C	4	-12	2
+0,05 % CEVA -1	1	-19	-3
+0,05 % CEVA -2	1	-20	-4
+0,05 % CEVA -3	4	-12	2

The research results have shown that depressor additives work the worst in the diesel fraction of 300–360°C. FAME of sunflower oil has exactly this fractional range.

The depression of pour point and CFPP with depressor additives are shown in diagrams (Fig. 4–5). Depressor additive CEVA-2 operates most effectively.

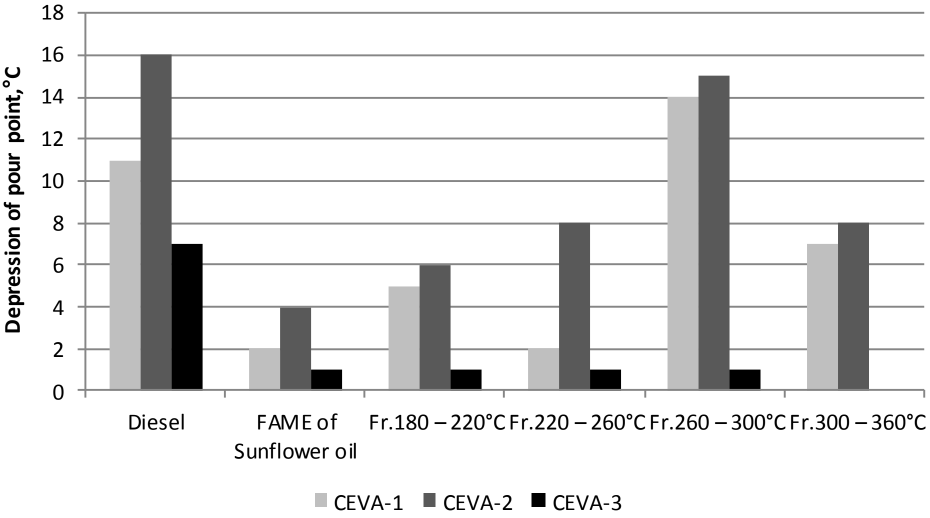

Fig. 4. Depression of pour point

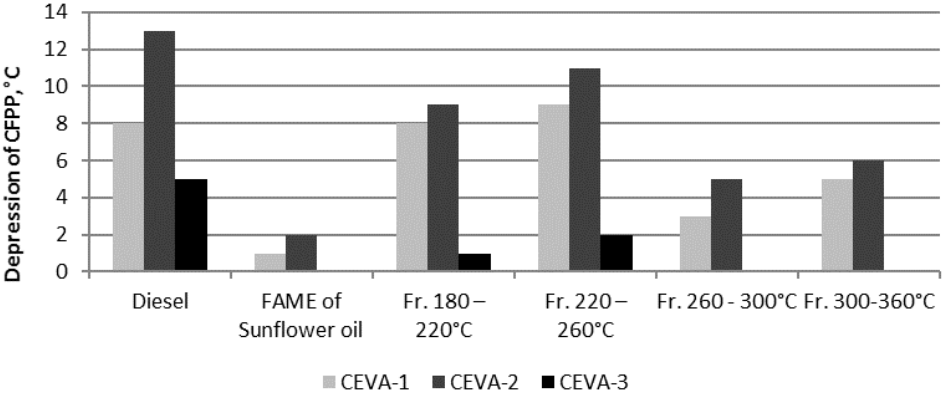

Fig. 5. Depression of CFPP

The content of methyl esters of fatty acids which is expedient to use in a mixture of diesel fuels does not exceed 30 % by weight. Such mixtures can be used in diesel engines without constructive changes.

Table 11

Low temperature properties of the diesel fuel mixture and FAME of sunflower oil

Property	Cloud point,°C	Pour point,°C	CFPP,°C
70 % Diesel +30 % FAME of Sunflower oil	3	-8	-4
+0,05 % CEVA -1	-1	-17	-13
+0,05 % CEVA -2	-1	-20	-16
+0,05 % CEVA -3	-1	-13	-9

Additive CEVA-2 reduces the pour point by 12 °C, and CFPP – by 9 °C. Low temperature properties of diesel fractions mixtures with FAME and depressor additive of CEVA-2 has been determined. The results are presented in Table 12.

Table 12

Low temperature properties of diesel fractions mixtures andFAME of sunflower oil

Property	Cloud point,°C	Pour point,°C	CFPP,°C
70 % fr.180–220 °C+30 % FAME of Sunflower oil	-15	-21	-17
+0,05 % CEVA -2	-19	-28	-23
70 % fr. 220–260 °C+30 % FAME of Sunflower oil	-12	-20	-18
+0,05 % CEVA -2	-15	-25	-22
70 % fr. 260–300 °C+30 % FAME of Sunflower oil	-8	-12	-11
+0,05 % CEVA -2	-10	-18	-15
70 % fr. 300–360 °C+30 % FAME of Sunflower oil	8	2	4
+0,05 % CEVA -2	6	-4	-1

Additive BEC-2 effectively operates in the mixtures of all fractions with FAME. Pour points are reduced by 5 ÷ 7 °C, and the CFPP are reduced by 4 ÷ 6 °C. In the fraction of 300–360 °C, the pour point is reduced by 6 °C, and CFPP – by 5 °C.

The low-temperature component (LTC) has been added to improve the low-temperature properties of the mixed fuel, together with other additives. The results obtained are shown in Table 13.

Table 13

Low temperature properties of the diesel mixture with FAME of sunflower oil and with the addition of low-temperature component (LTC)

Property	Cloud point,°C	Pour point,°C	CFPP,°C
70 % Diesel + 30 % (70 % FAME +30 % LTC)	-6	-16	-15
+0,05 % CEVA -1	-9	-29	-23
+0,05 % CEVA -2	-10	-32	-25
+0,05 % CEVA -3	-7	-16	-16

Introduction of the low-temperature component in the composition of diesel reduces the pour point by 8 °C, and CFPP – by 11 °C. When adding the CEVA-2 additive at the concentration of 0.05 %, the depression of the pour point and CFPP is by 24 °C and 21 °C, respectively. CFPP of fuel composition meets the requirements of the standard for winter diesel.

The combined effect of the low-temperature component and the depressant additive on the low-temperature properties of diesel fuel fractions with FAME has been studied. Data is given in Table 14.

Table 14

Low temperature indicators of the mixture of diesel fractions, FAME of sunflower oil with the low temperature component added

Property	Cloud point,°C	Pour point,°C	CFPP,°C
70 % fr. 180–220 °C +30 % (70 % FAME +30 % LTC)	-23	-28	-25
+0,05 % CEVA -2	-25	-39	-28
70 % fr. 220–260 °C +30 % (70 % FAME +30 % LTC)	-18	-27	-23
+0,05 % CEVA -2	-19	-37	-26
70 % fr. 260–300 °C +30 % (70 % FAME +30 % LTC)	-10	-18	-14
+0,05 % CEVA -2	-12	-25	-17
70 % fr. 300–360 °C +30 % (70 % FAME +30 % LTC)	5	-2	4
+0,05 % CEVA -2	3	-10	-3

The obtained results are presented in the form of diagrams, which illustrate depression of the pour point and the CFPP of mixed fuels with depressor additives and LTC.

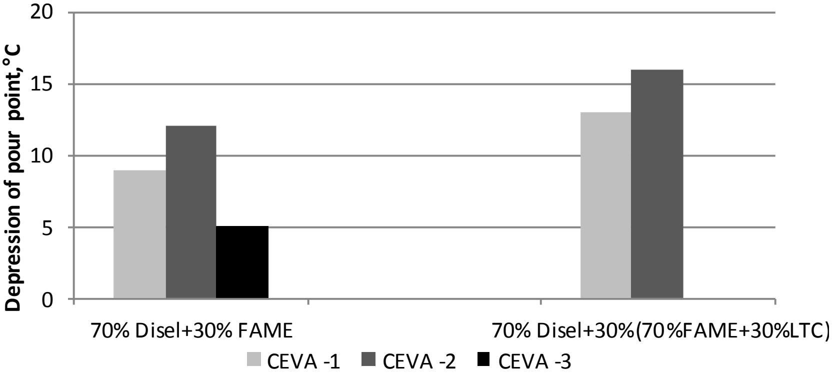

Fig. 6. Depression of pour point

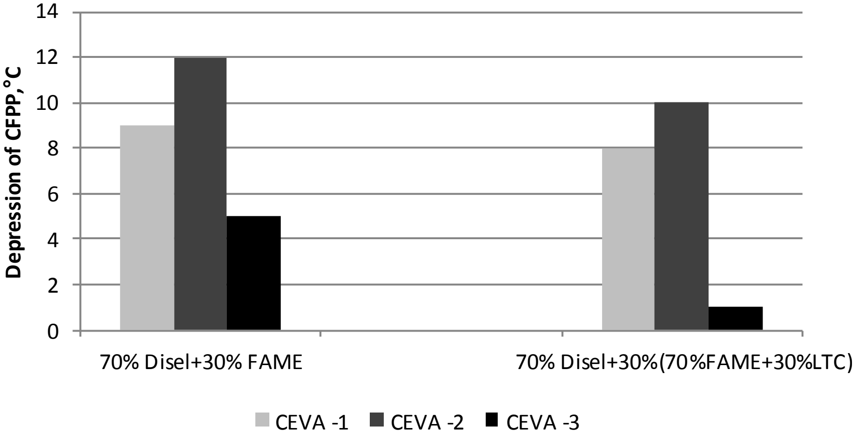

Fig. 7. Depression of CFPP

Based on the sample of FAME sunflower oil, it has been shown that up to 30 % FAME can be used in a diesel fuel composition at low temperatures at the presence of the low temperature component and the depressant additive based on ethylene vinyl acetate copolymers.

Combustion rate of diesel fuel. Data about cetane numbers (CN) of the FAME from various sources vary considerably, but the general opinion is that the values of the CN of fatty acid esters are higher than those of diesel fractions. The cetane numbers of the FAME samples have been determined (Table 1), and the values are in the range of 52–56 units.

Lubricity. It is well known that long-chain carboxylic acids and their derivatives have excellent lubricating properties. The effect of chicken fat based FAME additive on the average diameter of a diesel wear spot ($d_{\text{mean value}}$) is presented as an example at Fig.6. Tests have been conducted on a standard standHFRR [5]. The anti-wear properties of the fuel are brought to the normal (less than 460 microns) by adding 1–2 % FAME.

With further increase in concentration, $d_{\text{mean value}}$ value has become stabile at 200 microns.

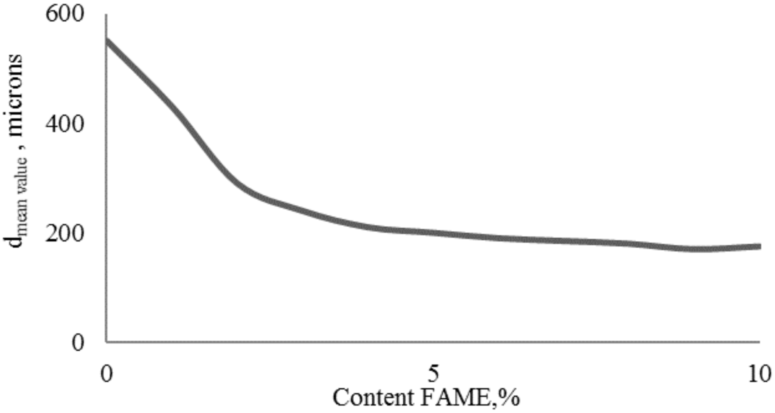

Fig. 8. Effect of chicken fat based FAME additive on the average wear spot diameter of diesel

Energy properties. Biodiesel, depending on the origin, contains from 10 to 14 % m/m oxygen. Accordingly, its calorific value is reduced by this value (Table 15). This will reduce the power reserve of the car. But the calorific value does not presumably affect the power characteristics of the engine, since the filling ratio of the cylinder will change due to the smaller air supply. However, there is a need to adjust the high pressure fuel pump.

Table 15

Calorific Valueof FAME

Property	Diesel	Fatty acid methyl esters (FAME)						
		Rape oil	Chicken fat	Fish fat	Palm oil	Soy oil	Sunflower oil	Tallow (pig & beef)
Sulfur content, % m/m	$1*10^{-4}$	0	$9*10^{-4}$	$2*10^{-4}$	0	0	0	0
Lower heating value, kJ/kg	42617	38088	38160	37017	38236	38206	38120	38098

Mixed diesel fuels containing methyl esters of fatty acids have the closest quality indicators to diesel fuel. Studies of the physical-chemical properties of the FAMEs suggest that its concentration in the mixed fuel can be increased up to 30 %. The obtained mixture is subject to the use of appropriate additives. The introduction of the maximum number of the FAME from different raw materials into diesel fuel is acceptable. The FAME has a positive effect on the environmental performance of the mixture, lubricity. This gives advantages and in addition increases the resource of diesel fuel in Ukraine.

РЕФЕРАТ

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МОДИФІКАЦІЯ СКЛАДУ ДИЗЕЛЬНОГО ПАЛИВА МЕТИЛОВИМИ ЕФІРАМИ ЖИРНИХ КИСЛОТ З НЕЇСТІВНИХ ЖИРІВ

Розглянуто сучасний стан технології отримання метилових ефірів жирних кислот (МЕЖК) з нехарчових жирів та олив, дано оцінку сировинної бази на Україні, обґрунтовано можливість переробки. Описано переваги і недоліки жировміщуючої сировини. Досліджено фізико-хімічні та екплуатаційні властивості МЕЖК з нехарчових жирів і олій. Обговорено властивості, що лімітують кількість альтернативного компонента в дизельному паливі на підставі його жирнокислотного складу, окисної стабільності, в'язкісно-температурних характеристик, низькотемпературних властивостей. Підібрано присадки, що покращують низькотемпературні і антиокислювальні властивості сумішей біодизеля з нафтовим паливом. Висловлено припущення про можливе збільшення концентрації МЕЖК в сумішевих паливах до 30 %.

Ключові слова: метилові естери жирних кислот, нехарчові жири.

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МОДИФИКАЦИЯ СОСТАВА ДИЗЕЛЬНОГО ТОПЛИВА МЕТИЛОВЫМИ ЭФИРАМИ ЖИРНЫХ КИСЛОТ ИЗ НЕПИЩЕВЫХ ЖИРОВ

Рассмотрено современное состояние технологии получения метиловых эфиров жирных кислот (МЭЖК) из непищевых жиров и масел, дана оценка сырьевой базы на Украине, обоснована возможность переработки. Описаны преимущества и недостатки жиросодержащего сырья. Исследованы физико-химические и экплуатационные свойства МЭЖК из непищевых жиров и масел. Обсуждены свойства лимитирующие количество альтернативногокомпонента в дизельном топливе на основании его жирнокислотного состава, окислительной стабильности, вязкостно – температурных характеристик, низкотемпературных свойств. Подобраны присадки, улучшающие низкотемпературные и антиокислительные свойства смесей биодизеля с нефтяным топливом. Высказано предположение о возможном увеличении концентрации МЭЖК в смесевых топливах до 30 %.

Ключевые слова: метиловые ефиры жирных кислот, непищевые жиры.

ABSTRACT

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MODIFICATION OF DIESEL FUEL COMPOSITION WITH METHYL ESTERS OF FATTY ACIDS FROM NON-EDIBLE FATS

The state of the art of producing fatty acid methyl esters (FAME) from non-edible fats and oils has been reviewed. Evaluation of the resource base in Ukraine is given. The possibility of processing is substantiated. The advantages and disadvantages of fat-containing raw materials are described. The physicochemical and operational properties of FAME from non-edible fats and oils have been investigated. The properties that limit the amount of the alternative component in diesel fuel have been discussed on the basis of the fatty acid composition of the alternative component, its oxidation stability, viscosity-temperature characteristics and low-temperature properties. Additives that improve the low-temperature and antioxidant properties of mixtures of FAME with oil supplements are selected. The possible increase in the concentration of FAME in mixed fuels up to 30 % has been assumed.

Key words: fatty acid methyl esters, non food fats.

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2.9 THE INFLUENCE OF OXYGEN CONCENTRATION ON THE FIRE SAFETY OF AIRCRAFTS FUEL SYSTEMS

Valeriy Yefymenko, Tetiana Kravchuk, Lidiya Kovshun, Natalya Atamanenko

The development of aviation and rocket-space techniques constantly sets new requirements for fuel and lubricant materials, since the quality of fuel and the technology of its preparing for refueling should ensure not only the keeping of physico-chemical indicators with its subsequent long-term storage, but also the chemmotological reliability of the fuel systems operation.

The complexity of ensuring an adequate level of fire safety is that aircrafts use a large amount of hydrocarbon fuels, which requires effective protection for trouble-free operation. A reactive fuels vapor can form explosive mixtures with air under the influence of external factors. They are capable to fire under the influence of the means of military impact, electric discharges, damaged electrical equipment, static electricity discharges or sources of ignition occurred in emergency situations. Thus, knowledge of the conditions for the formation of explosive fuel-air mixtures and the possibility of preventing their formation during operation will allow providing the safety of the fuel systems operation.

One of the possible ways of this problem solving is to remove the dissolved oxygen from fuel in fuel tanks and above fuel space by blowing with nitrogen. Such technology is used very limitedly only for military aviation and rocket techniques. The widespread implementation of this technology for the fuel preparation to refueling in an aircraft is restrained by high nitrogen outlay, high cost of its transportation and the need for additional special containers and equipment for its storage near fuel and lubricant warehouses.

That is why this study of the processes of air (oxygen) dissolution in fuels, the determination of its concentration in the above fuel space of aircraft's fuel tanks and the formation of fuel-air mixtures dangerous to ignition are relevant due to the necessity to provide the chemmotological reliability of aviation techniques fuel systems.

The analysis of fuel systems explosive safety showed that the possibility of ignition of a steam-air mixture of reactive fuels is determined by many factors: the presence of a large number of combustible hydrocarbons, the temperature of their ignition and self-ignition, the concentration and temperature limits of ignition. But the main and determining factor is the presence of air's oxygen which contacts with fuel vapor. When fuel is isolated from oxygen its ignition is impossible under any conditions.

The characteristic feature of fuel systems from the point of view of fire and explosion danger is the change in the fuel level both when stored in a tank in the fuel and lubricants warehouses and in the aircraft's tank during the flight. Fuel combustion takes place in the vapor phase. That is why the volume of the above fuel space increases with jet fuel use from a tank and this space is filled with air and the fire-explosion danger of fuel systems increases [1–4].

The certain correlation between the fuel vapor and oxygen concentration in the air is necessary for ignition the fuel-air mixture, as well as the temperature at which the oxidation reaction may proceed. Combustion of a fuel-air mixture is possible only in the boundaries limited by the upper and lower concentration limits of ignition. The upper concentration limit of ignition for most hydrocarbon fuels is 6–8 % vol., the lower one – 1,0–1,5 % vol. The non-flammability of very rich and very poor mixtures can be explained by the fact that the reaction rate is rapidly reduced because the heat loss into the environment is higher than the heat emission during the limited oxidation reaction because of oxygen or fuel vapor lack.

There are also temperature limits of ignition due to the dependence of fuel vapor concentration in the above fuel space on its partial pressure, which in turn depends on temperature.

Explosive mixtures formation is possible only at certain temperature intervals, which are limited by the lower and the upper temperatures of fuel ignition. The lower and the upper temperature limits of ignition form the temperature zone of fire-explosion danger.

The temperature limits of fire-explosion danger are not constant for fuels of a certain fraction composition, and vary depending on pressure, i.e., the flight altitude of the aircraft. Moreover, the temperature zone of the fire-explosion danger decreases and shifts towards lower values, because fuels evaporation increases in the result of atmospheric pressure decrease. This factor increases the risk of fuel tanks explosion when an aircraft climbs in altitude.

Foam is formed in the result of mechanical mixing of fuel in reservoirs and aircrafts tanks in dynamic conditions. This foam has a higher propensity to ignition due to higher solubility of oxygen in fuel compared with nitrogen, and its higher concentration in emitted from fuel gases. It has been established that the flame can spread over fuel-air foam at the lower temperature than the fuel flash point.

The dissolved air with increased oxygen content is emitted from fuel with atmospheric pressure decrease during aircraft climbing in altitude. According to this oxygen concentration in the above fuel space increases to 30–35 % vol., and this increases the fire-explosion danger of the fuel system.

Combustion of fuel-air mixtures is an explosion, i.e., it occurs with an instantaneous rate of change their physical and chemical composition, which is accompanied by the release of a large amount of energy. During this the flame spreading rate reaches 10–100 m/s, the temperature exceeds 1000 ºC, the pressure increases to 10 MPa, which leads to the complete destruction of the fuel system.

There are two possible ways to ignite the fuel-air mixture. The first one consists in the mixture heating to the temperature of self-ignition, which depends on the chemical composition of fuel and pressure. This occurs when the fuel gets on the heated surfaces of a fuel system or engine part. The second one is the ignition of the fuel-air mixture from the source of open flame inside the fuel tank, due to static electricity discharges, lightning discharges, and in military aviation due to defeat by military means.

It is taken to characterize fire danger of fuel mixtures by the flash point which is 10–15 °C lower than the lower temperature limit of ignition. Only the fuel-air mixture burns down at a temperature corresponding to the flash point, but the combustion process does not stabilize.

Fire and explosion in fuel tanks can occur only if three constituent conditions are present: fuel, oxidizer and sources of ignition. It is possible to cause the most effective influence only on the oxidizer concentration in the above fuel space. Reducing its concentration to 10–12 % vol. allows to exclude the possibility of fire-explosive mixture formation in the fuel tank, as well as to increase the chemical stability of fuel hydrocarbons.

Static electricity discharges, lightnings, defeat by military means, damage to the electric wire, engine surfaces heated to high temperatures can be sources of activation energy of fuel-air mixtures.

Fuels are dielectric liquids, but when pumped through the system and filtrated they can gain electrical charge. In this case, charges of static electricity are accumulated, the potential difference of which can reach the values of 3000 kV/m and be higher than the breakdown voltage of the phase separation surface of fuel-air.

The analysis of cases related to accumulation of static electricity in petroleum fuels showed the following causes of explosions and fires in %: transportation and pumping of fuel – 57; during pour in and pour out operations with fuel splashing – 16; increased fuel evaporation – 10; fuel pumping at an unacceptably high speed – 6;discharges on the service equipment shells – 6; permeation of dust and lightnings – 5.

Accumulation of electric charges of a dangerous magnitude is caused by the presence of organic impurities in fuels (sulfuric, nitrogeneous, oxygen-containing compounds and pitch), and non organic (water, mechanical impurities).

The minimum spark discharge energy, sufficient for the mixture ignition, should be 0,20–0,25 MJ. At the same time, the spark discharge is possible at a voltage of 300–330 V at some cases. Electrical discharges occur on sharp edges, protrusions of the sensors in the the tanks upper part.

A dangerous factor influencing flight safety is an of action external static electricity besides internal. It occurs on the aircraft's body as a result of its interaction with charged parts in the atmosphere – water drops, dust, ionization radiation.

Thunderstorm discharges are also very dangerous for fuel systems. Aircrafts are struck by lightning on average over every 2400 hours of flying at European Airlines. Mechanical and thermal damage can appear in the result of lightning striking, resulting in an flash and explosion of fuel vapor.

Military airplanes can be further affected by combat means, rocket fragments, inflammatory bullets.

It is impossible to completely exclude the possibility of formation of a ignition source of a fuel vapor in the above fuel space in the current conditions of aviation development. But we can reduce partially this influence by applying antistatic additives, grounding aggregates and pipelines, limiting the pumping and refueling speed.

Reducing the oxidant amount or fuel vapor in the above fuel space of fuel tanks or fuel vapors prevents the possibility of an explosive mixture formation and thereby the occurring of a fire and explosion.

Like any liquid, reactive fuels can dissolve gases, including oxygen contained in the air. The air and its gases permeate into the fuel in two ways: dissolving in the process of diffusion and when stirring. Accordingly, the maximum concentration of oxygen in the fuel is observed after its filtration.

The solubility of gases in liquids depends on partial pressure. As the pressure decreases, the solubility of gas in hydrocarbons also decreases, which causes its emission into the above fuel space. The solubility of oxygen, nitrogen and other gaseous air components is proportional to the partial pressure of each of them under these conditions. The solubility coefficient of oxygen in the jet fuel is almost twice higher than the nitrogen solubility coefficient. As a result, oxygen dissolves in fuel in a greater proportion than nitrogen compared with their ratio in the air. Therefore, the gas mixture emitted from fuel is more oxygen-rich than conventional air. The volume ratio of nitrogen to oxygen is 2.07:1 in it, while in the air it is 3.76:1.

Air with oxygen content 30 % vol. is emitted from fuel at the altitude 8000 m, therefore the explosion danger of the fuel system increases significantly. It also increases the fire-explosion danger limits of fuel-air mixtures.

The solubility of air in fuels decreases with temperature increase, especially during supersonic flights. The influence of temperature on gases solubility can be explained by the principle of Le Chatelier: with temperature increase the process that weakens its growth, that is, endothermic, intensifies. Gas emission from the solution is such process, the solubility decreases due to this process intensification.

The lower temperature limit of fire-explosion dangerous mixtures is a minimum fuel temperature at which a combustible mixture capable to ignite from external source of energy in a closed volume of the above fuel space may be formed. If the fuel temperature in a tank will decrease, the concentration of fuel vapor in the air will also decrease and the mixture will become non fire-explosion dangerous.

The upper temperature limit is the maximum temperature of fuel at which the mixture of fuel vapors with air still retains fire-explosion dangerous properties. With further rise in temperature, the mixture becomes oversaturated with fuel vapor and stays fire-explosion safe.

Concentration limits of the flash are limiting concentrations of fuel vapors in the air, at which the flashing of fuel vapor and air mixture and further spread of flame is possible.

The equipment for determination of the concentration and temperature limits of fire-explosion danger of fuel-air mixtures has been developed; its principal scheme is shown in Fig. 1.

The equipment consists of a chamber *1*, which has the heater *2* on its outer surface connected through an autotransformer *3* to a voltage of 220V of an alternating current. The chamber is protected from the environment by a heat-insulating material *4* to reduce the heat exchange. The chamber is closed with a cover and sealed with a gasket of gas-resistant rubber. The heating of the chamber is carried out by autotransformer *3*, and cooling – by blowing with liquefied nitrogen from the Dewear vessel. The top cover of the chamber is equipped with a thermocouple *19*, which sends a signal to the temperature recorder *20*. The ignition source of the vapor-air mixture is the spark discharge, which is formed between electrodes of the spark plug *8* by pressing on the push-button switch *9*. The ignition coil *10* is used as a high voltage source, the voltage on it is fed from the power supply unit *13*. The pressure impulse from the explosion of the vapor-air mixture is detected by the pressure sensor *15* and registered by the self-recording device *16*.

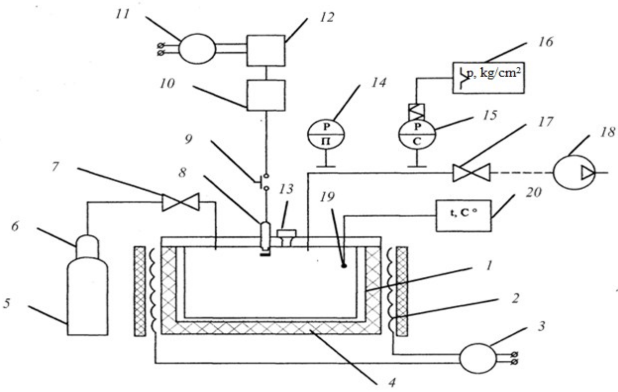


Fig. 1. The basic scheme of equipment for determination the temperature limits of the formation of flammable fuel-air mixtures: *1* – chamber; *2* – heating element; *3, 11* – autotransformer; *4* – heat-insulating material; *5* – cylinder with compressed air;*6* – reducer with high and low pressure manometers; *7, 17* – faucets; *8* – spark plug; *9* – push button switch; *10* – ignition coil; *12* – voltage stabilizer; *13* – sampler; *14* – manometer; *15* – pressure sensor; *16* – self-recording device; *18* – vacuum pump; *19* – thermocouple; *20* – temperature recorder

Accumulated after the explosion gases in the above fuel space are taken from the chamber by blowing air from the cylinder *5*, equipped with a reducer 6 with manometers of high and low pressure. In this case, faucets *7* and *17* are in the open position. Sampling from the above fuel space is carried out through a sampler *13*. Gases samples are analyzed by the chromatographic method for the determination of oxygen content in them.

The chromatographic method is used for determination the volumetric content of oxygen, nitrogen, and also products of fuel combustion.

A vacuum pump *18* is connected to the outlet nozzle of the faucet *12* for the study the temperature limits of the formation of combustible mixtures with aircraft climbing to the altitude. The dilution in the chamber is created depending on the flight altitude (by the international standard atmosphere) and is controlled by a monovacuummeter *14*.

Thus, it is possible to carry out investigation of the influence of oxygen concentration, neutral gases, flight altitude, concentration of fuel vapor on temperature and concentration limits of the formation of fire-explosive dangerous mixtures and the magnitude of a pressure impulse from their explosion with the help of the designed equipment.

Investigation of the influence of increased oxygen concentrations on the temperature limits of the formation of explosive mixtures was carried out by blowing the test chamber's above fuel space with oxygen, the influence of decreased concentrations – by blowing with nitrogen, with following chromatographic method for determination oxygen concentration in the above fuel space.

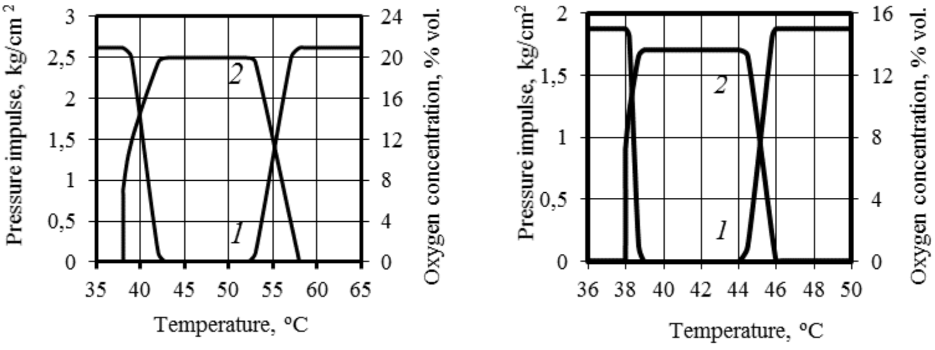
Explosive mixtures of fuel vapor and air can only be formed at certain temperature intervals and oxygen volume fraction of in the above fuel space. The study was carried out on fuels RT and Jet A-1 with constant oxygen content in the above fuel space equals to 21 %. The experimental data (Fig. 2*a*) shows, that the lower temperature limit for the formation of combustible mixtures for fuels coincides with their flash point and is 38 °C. These fuels have practically the same fractional composition, that is why, and their flash points are equal.

We can observe the decrease of oxygen concentration up to 12 % vol. and the impulse pressure increase up to 0,8 kg/cm^2. The pressure impulse increases with further heating due to increase the fuel vapor volume fraction, which takes part in an oxidation reaction. It can be explained by the further decrease of oxygen's residue concentration.

The maximum of the pressure impulse corresponds to the lowest concentration of residual oxygen in the above fuel space after the explosion, and it is stable for jet fuels at temperature intervals 43–52 °C. With further increase in temperature, the fuel concentration increases so much, that there in not enough oxygen to start the reaction of ignition of the fuel-air mixture. The upper temperature limit of the flash is 58 ^{o}C for fuels RT and Jet A-1.

Thus, the lower limit of formation of combustible mixtures for the most common reactive fuels is 38 ^{o}C, and the upper one is 58 ^{o}C. The lower and upper temperature limits of the explosion danger form a so-called, temperature zone of fire-explosion danger, which primarily depends on oxygen concentration in the above fuel space. The safe fuel temperature is 10–15 ^{o}C below the lower and higher the upper temperature limits of the flash due to the fact that intense evaporation and the evolving of dissolved gases from the fuel takes place at real flight conditions under vibrations and stirring.

The decrease of oxygen concentration in the above fuel space to 15 % vol. (Fig. 2*b*), which is achieved by blowing with neutral gas, leads to a slight shift of the flash start temperature towards lower values.



(*a*) (*b*)

Fig. 2. Dependence of the temperature limits of the formation of combustible mixtures and the pressure impulse from the initial oxygen concentration in the above fuel space of 21 % vol. (*a*) and 15 % vol. (*b*): *1* – oxygen concentration; *2* – pressure impulse

The temperature zone of explosive mixtures formation becomes even narrower and equals to 38–40 °C for the studied fuels with further reducing oxygen concentrations to 13 % vol. (Fig. 3).

The flash of fuel-air mixtures does not occur at oxygen concentration in the above fuel space less than 12 % vol.

It is necessary to mention that with change of oxygen concentration from 21 % vol. to 12 % vol. the lower limit of explosion danger at ground conditions varies on 1–3 °C, while the upper limit varies on 25–30 °C.

The determining factor in the flash process of fuel vapor is the flight altitude, which simultaneously affects two factors: the volume content of fuel vapor and oxygen concentration of in the above fuel space.

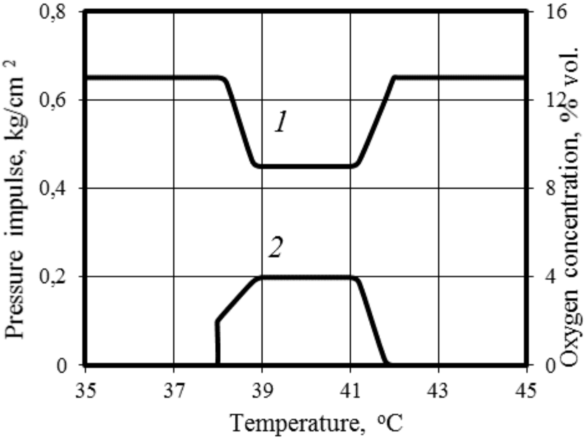


Fig. 3. Dependence of the temperature limits of combustible mixtures formation and the pressure impulse from the initial oxygen concentration in the above fuel space 13 % vol. for fuel RT, Jet A-1:
1 – concentration of oxygen; *2* – pressure impulse

When the aircraft climbs in altitude the temperature limits of combustible fuel-air mixtures formation of depend on the concentration of oxygen in the above fuel space. In ground conditions the minimum oxygen concentration at which an explosion is still possible is 12 % vol., than at an altitude of 5000 m is 15 % vol., and at an altitude of 10000 m is 17 % vol. An increase of oxygen concentration above these values extends the temperature zone of explosion danger.

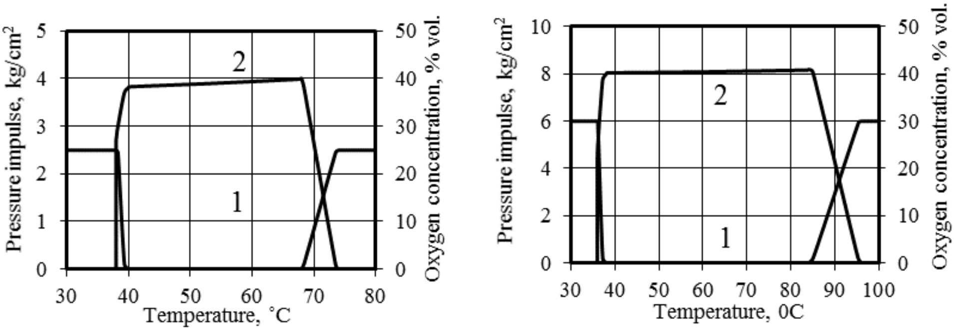
The lower temperature limit of explosion danger is slightly depends on changes in oxygen concentration at different altitudes; it can be explained by the lack of fuel vapor for oxygen excess, i.e., the mixture is poor. Therefore, the change in oxygen concentration of practically does not affect the lower temperature limit of explosion danger. The upper temperature limit greatly depends on oxygen concentration in the above fuel space; it can be explained by the high vapor content and the lack of oxygen. That is why even a slight change in oxygen concentration significantly affects the upper temperature limit of explosion danger.

The increase of oxygen concentration to 30 % vol. in the above fuel space, by its emission from fuel, practically does not affect the flash lower temperature limit. But the flash upper temperature limit is greatly expanded. So, when oxygen concentration is 21 % vol. in the above fuel space, it equals to 58 °C for the studied fuel, when concentration is 25 % vol. – 74 °C, and when 30 % vol. – 96 °C. The increase and expanding of the maximum pressure impulse range also takes place, and it can reach destructive values for the aircraft design.

It has been experimentally proved (Fig. 5) that with an aircraft climbing in altitude the explosion danger zone shifts towards lower temperature limits, due to increase of fuel evaporation in the result of atmospheric pressure reduction; that is why dangerous concentrations of fuel vapor are formed at lower temperatures.

Since the lower temperature limit of explosive mixtures formation is characterized by an excess of oxygen and a lack of fuel vapor, the flash temperature does not significantly depend on oxygen concentration and the fuel temperature, whereas the upper zone of explosion danger depends considerably on temperature at all flight altitudes.

Analysis of graphic dependencies shows that with increase the aircraft's flight altitude, the permissible concentration of oxygen in the abovefuel space in a fuel tank increases, if its explosion safety is provided. The maximum permissible concentration of oxygen in fuel tanks depending on the flight altitude, taking into account the guaranteed exception of fuel-air mixture flash (2 % vol. less than the minimum oxygen concentration for the formation of a combustible mixture) has the following values: in ground conditions (0 m) – 10 % vol.; 5 000 m – 12 % vol.; 10 000 m – 15 % vol; 15 000 m – 21 % vol.



(*a*) (*b*)

Fig. 4. Dependence of the temperature limits of combustible mixtures formation and the pressure impulse from oxygen initial concentration in the abovefuel space 25 % vol. (*a*) and 30 % vol. (*b*) for fuel RT, Jet A-1:
1 – oxygen concentration; *2* – pressure impulse

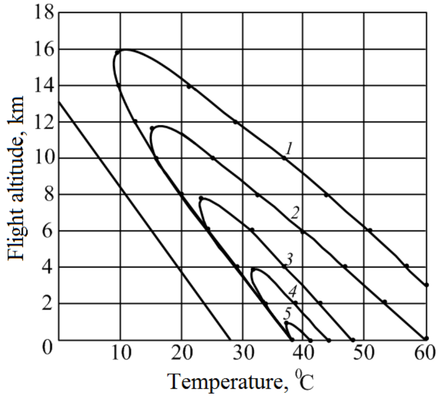


Fig. 5. Temperature limits of combustible mixtures formation depending on the flight altitude and oxygen concentration for fuel RT, Jet A-1: *1* – oxygen volume fraction 25 %; *2* – oxygen volume fraction 21 %; *3* – oxygen volume fraction 15 %; *4* – oxygen volume fraction 13 %; *5* – oxygen volume fraction 12 %

The obtained results allow to use neutral gas more purposefully and efficiently. There is no need for its use when flying at altitudes above 14 000 m.

The ground treatment of fuels to remove dissolved oxygen from them allows maintaining a high level of fire-explosion safety in different modes of the aircraft flight.

It is possible to conclude in the result of analysis the processes that occur with fuel-air mixtures in fuel tanks during the aircraft flight, that these mixtures are explosive only on separate stages of the flight.

Aircrafts' fuel tanks filled in with fuel RT or Jet A-1 will be explosive only if fuel temperature will be higher than 38–40 °C, i.e., the temperature of the flash point of fuel at oxygen concentration in the abovefuel spaceis 21 % vol. Such temperatures of fuel-air mixture can only be achieved in countries with hot climate, as the experience of operating aviation equipment shows.

With increasing flight altitude the fuel temperature does not change significantly in the first 30–40 minutes and its impact on the air solubility and the temperature limits of the fuel flash is not noticeable. External pressure is the main factor determining fire-explosion danger at this flight stage. The external pressure decrease causes emission of the diluted air from fuel, which leads to an increase of oxygen and fuel vapor concentrations in the above fuel space. It provides a shift of the temperature limits of combustible mixtures formation to the direction of lower values.

Vibrations and mixing of fuel in tanks, the formation of foam in dynamic conditions lead to expanding temperature limits of explosive mixtures due to the shift of lower temperature limit towards lower temperatures and despite the fuel temperature decrease, the lower concentration limit of explosive danger is reached. It is 0,6 % vol. for fuels RT and Jet A-1 at altitudes 4 000–5 000 m.

During the horizontal flight of a supersonic plane, the fuel temperature exceeds 100 °C in the fuel system, and sometimes can reach 135–200 °C. As practice shows, the dissolved air emits from fuel gradually when an aircraft climbs in altitude, and a sudden emission of a significant amount of dissolved gases takes place at altitudes greater than 8 000 m. This leads to increase of oxygen concentration in the above fuel space and to increase the fire-explosion danger of fuel tanks at the initial period of the horizontal flight. The vapor concentration increases due to the intense fuel evaporation, and fuel-air mixtures in fuel tanks become fire safe when it reaches 4,5 % vol.

The fuel temperature decreases with reducing the altitude of a supersonic plane, and the fuel space becomes again explosive at temperature 58 °C for fuels RT and Jet A-1, because it is in the zone of the upper temperature limit of the explosion danger.

Thus, the most dangerous parts of the flight are the climbing in an altitude with the initial period of the horizontal flight and the aircraft lowering from the point of view of the formation of an explosive concentration of fuel vapor with air in the above fuel space of fuel tanks. That is why one of the possible ways to protect fuel tanks from explosion may be the pre-flight fuel preparation in order to remove both dissolved oxygen and oxygen located in the above fuel space.

The process of fuel cooling in an aircraft tanks occurs during long term flights with a subsonic speed. The highest rate of fuel temperature decreasing (10–20 °C per hour) is observed in the first hours of a flight.

Then the cooling rate is reduced to 5 °C per hour, and the fuel temperature can decrease to minus 43 °C at an altitude of 10–12 km at environment temperatures minus 75 °C.

It is possible to conclude analyzing this data, that fire dangerous flight field is climbing an aircraft to altitude.

The concentrations of oxygen and nitrogen in the tank space above fuel during the flight of the aircraft are changed as a result of the emission of air dissolved in the fuel. Numerous tests had shown that the fuel in the Jet A-1 under normal conditions contains about 16 % of dissolved air, while oxygen concentration is about 5,25 % by volume and the nitrogen concentration – 10,75 % (V.) At aircraft altitude raising the dissolved air is released, and the oxygen concentration in the tank space above the fuel can theoretically reach 33 % (V.) via a lower solubility of oxygen in hydrocarbons of fuel compared to nitrogen.

Experimental tests regarding to the amount of dissolved gases in the fuel as a function of the altitude of the aircraft had shown that under static conditions at rate of climb close to the performance, there arises a significant disagreement between the amount of allocated dissolved gases and those were calculated according to Henry's law. During the experiment was observed the growth (Fig. 6) of gas emissions delay, and at the increase of the rate of climb this delay had grown too.

It should be noted that at actual flight real conditions, in presence of aircraft evolution and vibration, the delay of dissolved gases release from fuel while having a complex character generally decreases. There is an opportunity to determine theoretically the dependence of oxygen content in the formerly dissolved gases that were emitted depending on the ratio of the fuel volume and over fuel space volume as a function of aircraft climb altitude. In this case we assume that the temperature of fuel and gas is constant.

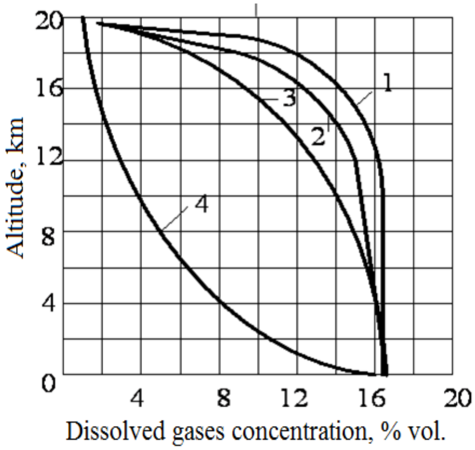


Fig. 6. Dependence of the dissolved air amount in the Jet A-1 fuel, altitude and aircraft rate of climb (Vy): *1* – Vy = 75 m/s; *2* – Vy = 45 m/s; *3* – Vy = 15 m/s; *4* – according the Henry's law

Then the amount of dissolved gases that are released when changing pressure according to Henry's law, is:

$$V_i = V_o \cdot (1 - P_f / P_o), \tag{1}$$

where V_o – initial volume of dissolved gas, m^3; P_o, P_f – the initial and final pressure, kPa.

At an aircraft climb in altitude the expanding of escaping gases takes place, the volume of which equals to:

$$V_i = V_o \cdot (P_o / P_f - 1) \tag{2}$$

Quantity of oxygen in the above fuel space in tank can be determined by the formula:

$$C \cdot V_t = 21 \cdot V' + 33 \cdot V'_t, \tag{3}$$

where C, 21, 33 – the oxygen concentration in the gas, % vol .; V_t – total above fuel space, m^3; V' – part of the air space of the tank, m^3; V'_t – part of above fuel space occupied by the gas released from the fuel, m^3.

Assuming that under normal conditions, the amount of air in the Jet A-1 fuel reaches 16 % , i.e. $V_o = 0.16\ V_f$ and $V' = V_i - V'_i$, and using equation (2) represented by formula (3), and after transformations we obtain the oxygen concentration in a mixture:

$$C = 21 + 1{,}92 \cdot V_i/Vt \cdot (P_0/P_f - 1), \tag{4}$$

Fig. 7. demonstrates the theoretical dependence of oxygen content in the above fuel space in the aircraft tank as a function of tank fuel filling in and of altitude. Oxygen concentration reaches 33 % vol. in the above fuel space at 70 % filling of the fuel tank with climbing in altitude of 10000 m.

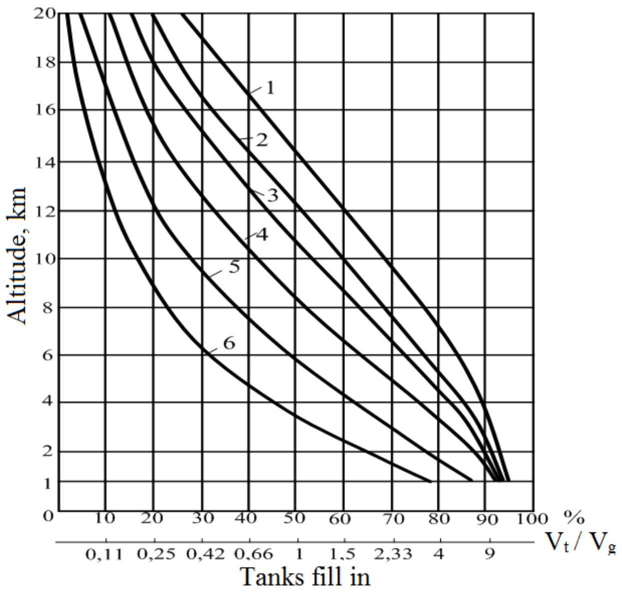


Fig. 7. Theoretical dependence of oxygen concentration in the above fuel space from the tank volume filled with fuel and altitude of an aircraft:
1 – O_2 – 33 %; *2* – O_2 – 29 %; *3* – O_2 – 27 %; *4* – O_2 – 25 %; *5* – O_2 – 23 %; *6* – O_2 – 22 %

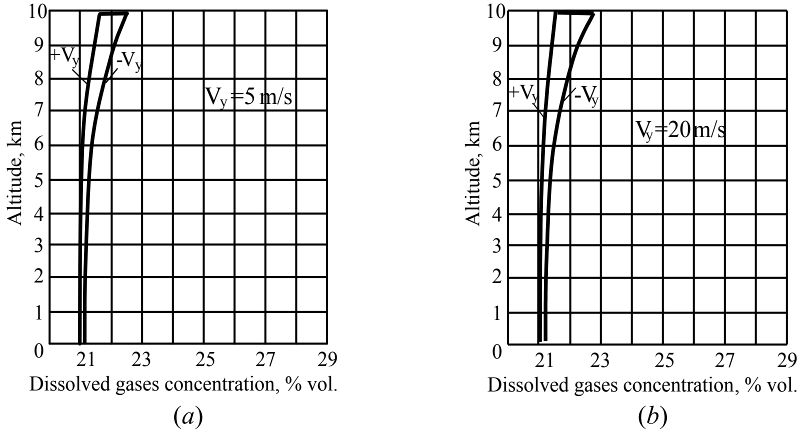
At 20 % the fuel tank filling (the ratio V_{gas}/V_{fuel} = 4) and at the climbing rate 5 m/s an increase of oxygen concentration occurs above 21 % vol. after altitude of 4000 m (Fig. 8*a*). This suggests that the release of dissolved air from the fuel does not occur immediately after take-off of the aircraft, but during the subsequent ambient pressure drop.

Further tests with various fuel tank filling and at different aircraft climbing rate also indicate an air release delay from the fuel at lift to the designed altitude. Oxygen concentration in the above fuel space increases to 21,7 % when reaching altitude 10000 m. Oxygen concentration increases to 22,3 % while maintaining the tank for 30 min at this altitude. Oxygen concentration is reduced in tanks at decreasing the aircraft altitude, a dilution of the gas mixture proceeds there in the result of the inflow of outside air into above fuel space. Oxygen concentration is leveled to 21 % vol. at reaching altitude of 4000 m.

Oxygen concentration in the above fuel space increases to 21,5 % from altitude 4000 m to 10000 m when the climbing rate is 20 m/s (Fig. 8*b*).

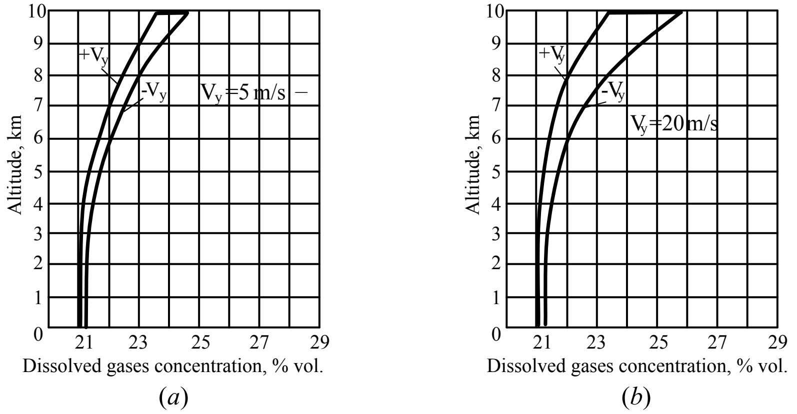
Some smaller amount of dissolved in the fuel air is released with the climbing rate increase, and when it reaches an altitude of 10000 meters, therefore occurs a smaller concentration of oxygen in the above fuel space. But when the tank is exposed to the altitude 10000 m, the oxygen concentration has been increased to 22,5 % vol.

Increase in the oxygen concentration up to 22,5 % occurs from altitude 4000 m to 10000 m (Fig. 9*a*) at 40 % filled fuel tank (the ratio $V_i/V_t = 3/2$) and the climbing rate 5 m/s. The further release of dissolved gases takes place when keeping tank at an altitude of 10 000 meters and in this case oxygen concentration increases to 24,3 % vol. Oxygen content is reduced to about 21,1 % in the result of reducing the altitude from 10000 meters to the ground level. A similar result was obtained with a chosen climbing rate of tank equal 20 m/s (Fig. 9*b*). However, oxygen concentration increases by a larger amount – from 22,2 to 24,3 % vol. at maintaining the tank at an altitude of 10000 meters.



(*a*) (*b*)

Fig. 8. Change of oxygen concentration in the above fuel space as the tank is risen to the altitude and at 20 % fuel tank filling

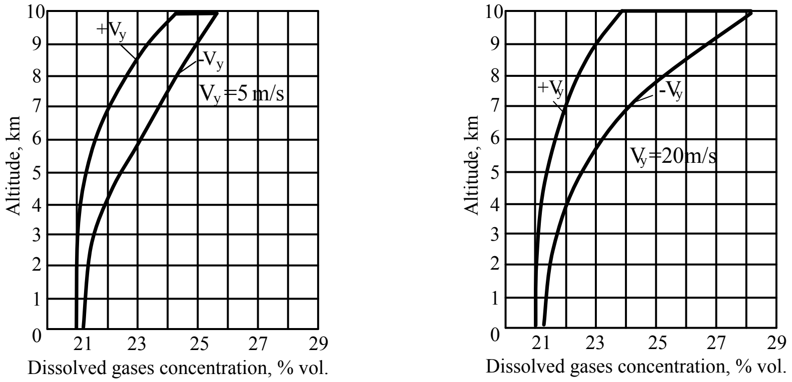


(*a*) (*b*)

Fig. 9. Change of oxygen concentration in the above fuel space as the tank is risen to the altitude and at 40 % fuel tank filling

Oxygen concentration increases to 24,3 % in the above fuel space for altitudes from 4000 m to 10000 m, at 70 % fuel tank filling and at the climbing rate 5 m/sec (Fig. 10). Oxygen concentration increases to 25,8 % vol. when maintaining the tank at altitude of 10000 m. Oxygen concentration is reduced to 21,3 % vol. (Fig. 10*a*) at aircraft descending. As the aircraft climbing rate 20 m/s while maintaining the fuel tank at an altitude 10000 m the oxygen content is increased from 23,8 % to 28 vol. (Fig. 10*b*).

It has been established that the temperature limits of the explosive fuel-air mixtures formation in aircrafts fuel tanks depend on oxygen volume fraction in the above fuel space. The pressure impulse increases from the explosion of fuel-air mixture, the lower temperature limit of the flash shifts towards lower temperatures and simultaneously the temperature range of explosive danger considerably expands with an increase of oxygen concentration, due to the evolving of dissolved air from fuel. There is no intense release of oxygen dissolved in fuel during the aircraft climbing in the altitude 3 000–4 000 m.



(*a*) (*b*)

Fig. 10. Change of oxygen concentration in the above fuel space as the aircraft tank is risen to the altitude and at 70 % fuel tank filling

It has been determined that temperature limits of combustible mixtures formation with increasing flight altitude are narrowed and shifted towards lower temperatures. The most dangerous flight conditions for subsonic airplanes are the fuel temperature from 12 to 74 ^{o}C and the flight altitude to 12 000 m. Explosive fuel vapor and air oxygen mixtures are formed in the above fuel space under these conditions.

It has been established that the flash does not occur in the ground conditions when oxygen concentration in the fuel-air mixture reaches 12 % vol. It has been determined that with the increase of the flight altitude, the temperature limit combustible mixtures formation is narrowed and shifted towards lower temperatures. The explosive area for subsonic aircrafts is 38–58 °C in the ground conditions, 29–44 °C at an altitude 5000 m and 13–36 °C at an altitude 10 000 m if oxygen concentration is 21 % vol.

It has been established that the maximum permissible concentration of oxygen in aircraft's fuel tanks increases depending on the flight altitude. Thus, it is 12 % vol. at ground conditions, 15 % vol. – at an altitude 5000 m, 17 % vol. – at an altitude 10000 m.

It has been determined that explosion of fuel-air mixture is not possible during flights at altitudes above 14 000 m.

Thus, at aircraft climbing at definite altitude in the above fuel space of tanks the increase of oxygen concentration takes place owing to the emission of gases dissolved in the fuel. The intensity and the magnitude of this increase depend on the degree of a fuel tank filling, on an altitude and a climbing rate.

Based on these studies, the staff of the National Aviation University had developed technical solutions that allow influencing the oxygen content in the above fuel space in the aircraft tanks that will increase fire-explosion safety and also the reliability of the fuel system.

РЕФЕРАТ

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ВПЛИВ КОНЦЕНТРАЦІЇ КИСНЮ НА ПОЖЕЖОБЕЗПЕЧНІСТЬ ПАЛИВНИХ СИСТЕМ ПОВІТРЯНИХ СУДЕН

Метою роботи є забезпечення пожежовибухобезпечності та поліпшення експлуатаційних показників якості реактивних палив.

Об'єктом дослідження є процеси розчинення повітря (кисню) в паливах, визначення його концентрації в надпаливному просторі паливних баків повітряних суден та утворення безпечних до

загоряння паливоповітряних сумішей. Ця проблема є актуальною з огляду необхідності забезпечення хіммотологічної надійності паливних систем авіаційної техніки.

Предметом дослідження є пожежовибухобезпечність реактивних палив РТ (Jet A-1) та її зв'язок з наявністю розчинених у них газів і газів, що знаходяться в надпаливному просторі паливних баків.

Визначені температурні межі утворення горючих паливно-повітряних сумішей залежно від висоти польоту повітряного судна, температури та зміни концентрації кисню в надпаливному просторі.

Ключові слова: реактивні палива, вміст кисню, паливо-повітряні суміші, пожежовибухобезпечність.

РЕФЕРАТ

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ВЛИЯНИЕ КОНЦЕНТРАЦИИ КИСЛОРОДА НА ПОЖАРОБЕЗОПАСНОСТЬ ТОПЛИВНЫХ СИСТЕМ ВОЗДУШНЫХ СУДОВ

Целью работы является обеспечение пожаровзрывобезопасности и улучшения эксплуатационных показателей качества реактивных топлив.

Объектом исследования являются процессы растворения воздуха (кислорода) в топливах, определение его концентрации в надтопливном пространстве топливных баков воздушных судов и образование безопасных к возгоранию топливовоздушных смесей. Эта проблема является актуальной ввиду необходимости обеспечения химмотологической надежности топливных систем авиационной техники.

Предметом исследования является пожаровзрывобезопасность реактивных топлив РТ (Jet A-1) и её связь с наличием растворенных в них газов и газов, находящихся в надтопливном пространстве топливных баков.

Определены температурные пределы образования горючих топливно-воздушных смесей в зависимости от высоты полета воздушного судна, температуры и изменения концентрации кислорода в надтопливном пространстве.

Ключевые слова: реактивные топлива, содержание кислорода, топливо-воздушные смеси, пожаровзрывобезопасность.

ABSTRACT

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THE INFLUENCE OF OXYGEN CONCENTRATION ON THE FIRE SAFETY OF AIRCRAFTS FUEL SYSTEMS

The aim of the work is to provide fire-explosion safety and to improve performance indicators of the jet fuels quality.

The object of the study is the processes of air (oxygen) dissolving in fuels, determination of its concentration in the above fuel space of fuel tanks and creation of safe to ignite fuel-air mixtures. This problem is relevant due to the need to ensure the chemmotological reliability of aircrafts fuel systems.

The subject of the study is fire-explosion safety of jet fuels RT (Jet A-1) and its connection with the presence of dissolved gases and gases in the above fuel space in fuel tanks.

It has been determined the temperature limits of the formation of combustible fuel-air mixtures depending on the aircraft's flight altitude, temperature and changes in oxygen concentration in the abovefuel space.

Key words: jet fuels, oxygen content, fuel-air mixtures, fire-explosion safety.

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2.10 IDENTIFICATION AND ASSESSMENT OF BIOLOGICAL RISK OF AVIATION FUEL SUPPLY

Iryna Shkilniuk[1]*, Sergii Boichenko*[1]*, Tetiana Kondratiuk*[3]*, Nataliia Shevchuk*[2]

Aviation fuel supply exists as much as aviation is more than a hundred years. Fuel is the blood of an aircraft. The mass of fueled jet fuel is up to 70 % of the maximum take-off weight of modern aircraft. The main link in all civil aviation activities is flight safety. The most important condition for ensuring the safety of flights is the use of aircraft in the range of expected operating conditions, taking into account operational limitations established in the norms of airworthiness.

Now ICAO is disturbed formed by the world tendency of entering of contaminated aviation fuel in airport. Many documents ICAO, IATA and Joint Inspection Group focuses on pollution fuels. ICAO issued a directive DOC 9977 «Guide to the supply of aviation fuel in civil aviation» and IATA issued EI/JIG STANDARD 1530 «Quality assurance requirements for the manufacture, storage and distribution of aviation fuels to airports». The essence of these documents is that all parties involved are jointly responsible for ensuring the quality, purity and possibility of quality control at every stage of production, supply and operation of aviation fuel.

Fuel and air machinery loss during operation are major aircraft losses for modern aircraft. The main factors and parameters that determine the indicated losses in operation are flight path, speed and altitude; equipment reliability; fuel conditioning.

The study of theoretical and practical aspects of risk, its analysis and assessment is becoming increasingly relevant, because the risk in today's economic environment has a significant impact on the results of enterprises.

The active study on microbial growth in the composition of petroleum fuels began in the USA during the creation of jet aircraft.

During the creation of jet aviation in the USA, began active study of questions connected with microorganisms' development in oil fuels. The work on this question in our country mainly was to determine fuels biostability in laboratory conditions. Purposeful researches of fuels biostability in operating conditions were not conducted practically [1].

In 1956, the United States Air Force recognized that its widely-used JP-4 fuels were microbial contaminated when Air Force B-47 and KC-97 flight operations were affected. Two years later, a B-52 crash was directly attributed to clogging of fuel system screens and filters by some form of fuel contamination. In that same year, the Wright Air Development Center determined that sludge accumulation in tanks used to store kerosene-type fuels was a common occurrence [2].

More instances of contamination and corrosion surfaced in the late 1950's and early 1960's and reached near epidemic proportions in storage tanks and aircraft fuel cells at various locations. At the beginning of 1962, approximately 52 governmental and non-governmental agencies were involved in various phases of research on microbiological contamination of fuels.

The modern world legislation raises the level of requirements for quality aviation fuels. In 2012, the International Civil Aviation Organization has developed directive 9977/AN 489

«Guidelines for the supply of aviation fuel for civil aviation», which focused on the clean air fuels, including microbiological contamination.

Air transport is a major consumer of high-quality fuels and lubricants. For large scale high oil consumption issue efficiency of aviation technology, economy and management of aviation fuel has an important public and economic value. The efficiency and reliability of the fuel system software greatly depends on the quality of aviation fuel. The largest number of failures and malfunctions elements of the fuel system, engine and aircraft related to fuel quality and purity.

A limited amount of oil resource, the introduction of ICAO and IATA standards, satisfaction of safety and operational safety requirements, economic indicators, financial profitability require a risk-based approach in aviation fuel supply [3].

The risk indicator is introduced for the quantitative characteristics of the safety of objects. Risk is a measure of danger. The analysis of the threats to sustainable aviation fuel supply is to identify all sources of threat and assess their impact on flight safety.

The process of performing risk analysis has traditionally consisted of the following consecutive procedures [4,5]:

– planning and organization of work;
– identification of risks;
– risk assessment;
– development of risk management recommendations.

The key stages in the risk analysis process are the identification of risks and their classification. At the risk identification stage, the risks that exist at different stages of the jet fuel cycle life were analyzed [5].

Stages of the fuel life cycle:

1) oil recovery stage;
2) oil refining stage;
3) stage of production of commodity jet fuel;
4) stage of jet fuel transportation;
5) jet fuel storage stage;
6) fuel use stage.

Specific aspects can be distinguished from the point of view of the chemmotological reliability. One of them is the purity of fuel, the presence or absence of mechanical impurities, water, microorganisms and other contaminants that should not be present in the fuel when shipped from production sites, but which can accumulate during transportation, storage, pumping and other operations.

There are many risks in the production of fuels, including the risk of microbiological contamination. The hydrocarbon component is the most dangerous raw material from this point of view. On the one hand, this is the basis of fuels, on the other is the source of potential infection of microbiological oil destructors.

Destruction of materials usually occurs under the influence of not a single group of microorganisms and an entire complex including bacteria and fungi. One group of microorganisms of its own activity prepares a substrate for another. The process is very complex and is due to a large number of factore. The substrate is of paramount importance, it forms the formation of such substrates new, functionally interconnected units, as a microbial association or biocenosis.

The biological risk factor can be defined as biological matter capable of self-replication and which can have a destruction effect on the fuel.

Microbes may be introduced into fuels as products cool in refinery tanks. Bacteria and fungi are carried along with dust particles and water droplets through tank vents. In seawater ballasted tanks, microbes are transported with the ballast. Vessel compartments ballasted with fresh, brackish, or seawater, all of which may contain substantial numbers of microbes, may easily become contaminated with the microbes transported with the ballast water [6].

Today it is known 200 species of microorganisms, including 30 families that can use hydrocarbons as sole source of carbon and energy (Fig. 1). These include bacteria, yeast and fungi.

Table 1

The main microorganisms, that cause biocontamination of fuels

Fungi	Acremonium sp. Altenaria altenarata Aspergillus sp. Aspergillus clavatus Aspergillus flavus Aspergillus fumigatos Aspergillus niger Cladosporium sp. Cladosporium cladosporoides Fusarium sp. Fusarium moniliforme Fusarium oxysporum Hormoconis resinae Monascus floridanus Paecilomyces variotii Penicillium sp. Penicillium cyclioium Rhinocladiella sp. Trihoderma viride Trichosporon sp.
Bacteria	Acitenobacter Alcaligehes Bacillus sp. Clostridium Sporogenes Flavobacterium difissum Micrococcus sp. Pseudomonas sp. Pseudomonas aeroginosa Serratia marcescens
Yeasts	Candida sp Candida famata Candida guilliermondii Candida lipolytica Rhodotorula sp.

Active development of the fuel and the fuel systems of microscopic fungi (*Hormoconis resinae*, his types. *Penicillium, Aspergillus fumigatus, Paecilomyces variotii,* etc.) recognized the most dangerous. Fungi form a dense mycelium, the accumulation of which not only clog pipelines and fuel filters, but also create numerous localized areas of corrosion on the surfaces of fuel systems. A most active destructor of aviation fuel until recently was recognized *Cladosporium resinae* (modern name *Hormoconis resinae* or *Amorphoteca resinae*) of microscopic fungi. This so-called «kerosene» fungi [7]. Today this group classified as fungi *Monascus floridanus*, which is inherent in the ability to develop rapidly in the aviation fuel [4]. Fungi have some morphological, physiological and genetic features, good with which they occupy the dominant position among organisms causing biological damage.

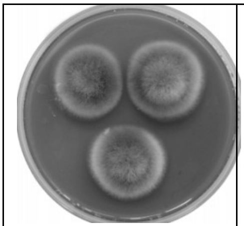
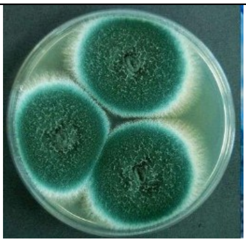
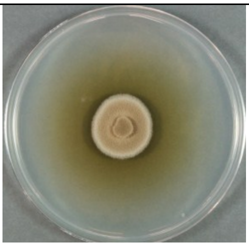
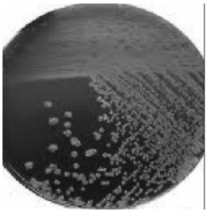
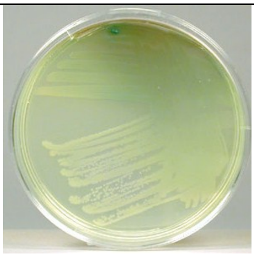
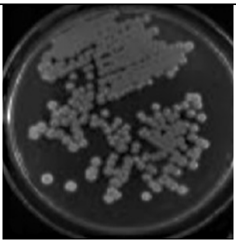
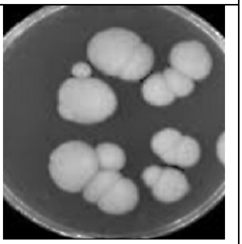
			
Monascus floridanus	Aspergillus fumigatos	Hormoconis resinae	Penicillium sp.
			
Acitenobacter	Pseudomonas aeroginosa	Rhodotorula sp	Candida sp

Fig 1. The main strains of microorganisms-petroleum product destroyers.

The first stable products of hydrocarbons oxidation are the primary alcohols. The next is usual biological conversion of alcohols to aldehydes and aldehyde to acid [8]. The general scheme of reactions:

$$R\text{-}CH_2\text{-}CH_3+[O] \rightarrow R\text{-}CH_2\text{-}CH_2OH\text{-}2H \rightarrow R\text{-}CH_2\text{-}CHO\text{-}2H+HOH \rightarrow R\text{-}CH_2\text{-}COOH.$$

Microorganisms have the selective ability related to various hydrocarbons, and this ability is determined not only by the difference in the structure of substance, and even the number of carbon atoms that are the part of their structure.

It is proved that microbial contamination of fuel is connected to microbiological enzymatic oxidation of hydrocarbons with formation of organic acids that have surface active properties. The speed and depth of the microbial oxidation of aviation fuel depend on their carbohydrate composition. Hydrocarbons with a linear structure of the molecules are destroyed faster than their branched isomers. Aliphatic hydrocarbons (paraffin's) are less biostable than aromatic. Therefore, fuels that contain mostly paraffin hydrocarbons can be destroyed by microorganisms faster than those containing more aromatic compounds. Cycloalkanes are more difficult to microbiologically destruction than alkanes, due to the presence of a cyclic structure that is heavier than oxidation. Strains that are capable of biodegradation of cyclic alkanes include bacteria of the genera *Cordonia, Xanthobacter*, and others. Seams that are capable of biodegradation of cycloalkanes have specific enzyme systems that are different from the enzyme systems used by microorganisms to oxidize non-cyclic alkanes.

The research of activity of growth of active and potential destructors spent in fuel by the value of the accumulation of biomass after a month of cultivation (Fig. 2). The greatest value of biomass is defined for the *Hormoconis resinae* isolated from the tank of the aircraft.

The ability to grow potential destructors for various hydrocarbons was studied. Micromycetes grow on all tested liquid hydrocarbons, except for hexane [9]. The tendency to increase in hydrocarbons with more long carbon chains (C_{10}–C_{17}) was observed in *Hormoconis resinae* and *Monascus floridanus*. The greatest importance of biomass increase in *Hormoconis resinae* was observed on heptadecane ($C_{17}H_{36}$), *Monascus floridanus* on hexadecan ($C_{16}H_{34}$).

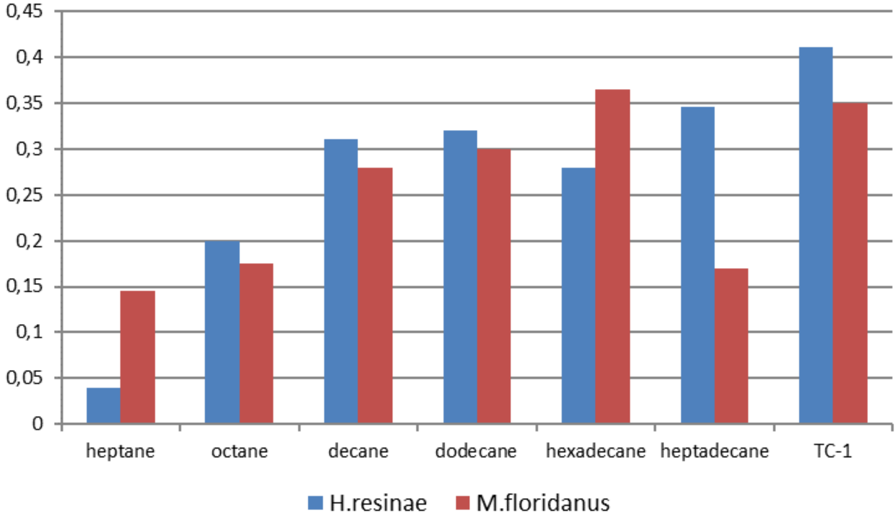


Fig. 2. Biomass of active destructors after a month growth in hydrocarbons

After arriving in fuel tanks, microorganisms may either stick to overhead surfaces or settle through the product. Some microbes will adhere to tank walls, whereas others will settle to the fuel/water interface (Fig. 3). Most growth and activity takes place where fuel and water meet. The tank bottom fuel/water interface is the most obvious fuel/water boundary. However, there is also a considerable area of fuel/water interface on the interior surface of tank-shells. Microorganisms require water for growth. Although bacteria and fungi can be present in the fuel phase, their growth and activity is restricted to the water phase of fuel systems. The water phase includes volumes ranging from trace (several μL) to bulk (>1 m^3) accumulations and water entrained within deposits that accumulate on system surfaces. Typically, fuel and system deterioration is caused by the net activity of complex microbial communities living within slimy layers called biofilms. Biofilms may be found on tank roofs, shells, at the fuel/water interface, and within bottom sludge/sediment [6].

The high temperature characteristic of distillation and other refinery processes sterilize refinery stocks used in fuel blending. However, conditions in refinery tankage, transport systems, terminal tankage, and users' system tankage may lead to microbial contamination and possible biodeterioration.

In refinery tankage, water can condense and coalesce as product cools. Tank vents draw moisture from the outside atmosphere and may allow precipitation to enter the tank.

Moreover, product withdrawal creates a partial vacuum that pulls pollen, dust, and other microbe-carrying particulates through tank vents. Consequently, refinery products tanks are the first stage of petroleum handling where significant microbial contamination can occur.

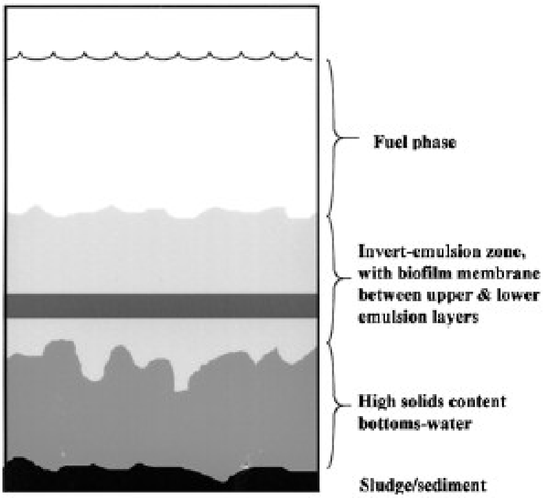


Fig. 3. Schematic of Fuel Tank Bottom Sample with Significant Microbial Contamination and Biodeterioration

In transport by means of tanker or pipeline, additional water may be introduced by condensation. In contrast to pipelines, condensate is not the major source of additional water. Rather, inadequate cargo compartment stripping, use of water as false bottoms to facilitate complete cargo discharge, and other incidental, intentional water use provide substantial water to fuel tanks. Biofilms can form on tanker or pipeline surfaces where they entrain water, inorganic particles, and nutrients to support growth. Such growth can slough off and be carried to terminal and end user tankage. In terminal tanks, turnover rates may be a week or longer, allowing particulates (including biofilm flocs) to settle into the sludge and sediment zone before product is drawn from the tank. As turnover rates increase, the likelihood of drawing biomass with fuel also increases, due to reduced settling times. Population densities of less than two million cells/mL will have no effect on fuel clarity. Consequently, contaminated fuel is rarely detected visually at the terminal rack.

The places of microbiological colonies development of on the fuel life cycle are established during the analysis of biological risk of aviation fuel supply. The places of microbiological colonies are presented in Fig. 4 [6].

Microbes require water as well as nutrients. Consequently, they concentrate at sites within fuel systems where water accumulates.

Water is essential for microorganisms’ growth and proliferation. Even negligible traces of water are sufficient to support microbial populations.

Nutrients are divided into macro-nutrients and micronutrients. Carbon, hydrogen, oxygen, nitrogen, sulfur, and phosphorus (CHONSP) comprise the macro-nutrients, and most of these are readily available in fuels. Only phosphorous is likely to be growth limiting in most fuel systems. A variety of elements, including calcium, sodium, potassium, iron, magnesium, manganese, copper, cobalt, nickel, and other metals, are required in trace quantities. None of these elements is limiting in fuel systems. Fuel systems that provide both the requisite water and nutrients will support microbial growth and proliferation.

The rate of microbial growth increases with increasing temperature within the physiological range (temperature range within which growth occurs) of a given microorganism. Microbes are generally classified into three groups, based on their temperature preferences/requirements. Some microbes require low temperatures (< 20 °C). Others thrive in superheated environments (> 100 °C). However, the physiological range of the microbes most commonly recovered from fuel tanks is 0 °C to 35 °C, with growth optimal between 25 °C and 35 °C.

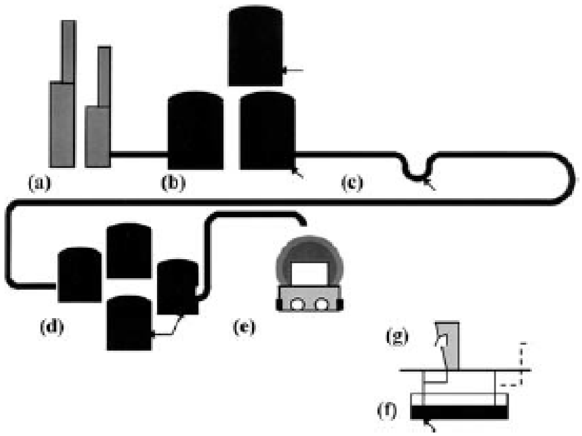


Fig. 4. Fuel supply scheme (arrows indicate sites where water and biologicals tend to accumulate): (*a*) refinery distillation towers, (*b*) refinery product tanks, (*c*) fuel transportation pipeline (low points in pipeline trap water), (*d*) distribution terminal tanks, (*e*) commercial dispensing rack and tank truck, (*f*) retail/fleet underground storage tank, (*g*) retail/fleet dispensing system.

The some strains of *Hormoconis resinae* are capable of developing in a fuel at a temperature of 50 °C and the strains of *Aspergillus fumigatus* survive in aviation kerosene up to 80 ºC. The growth of *Hormoconis resinae* in aviation fuel is fixed at a temperature of 28 ºC. The activity of mushrooms decreases with increasing or decreasing temperature (Table. 2).

Table 2

The growth of fungi in fuel at positive temperatures (in points)

Fungi	The time the manifestation of signs of growth, days	The temperature, ºC			
		9	18	28	36
Hormoconis resinae	7	0	0	0	0
	14	0	1	2	0
	21	1	2	3	1
Phialofora sp	7	0	0	2	0
	14	1	2	4	2
	21	2	2	4	3

0 – no signs of growth, 1 – turbidity of the water layer, the formation of precipitation, 2 – the appearance of large flakes in the water layer, 4 – the formation of small clots, 5 – the formation of large clots.

The risk of uncontrolled microbial contamination is generally greatest in tropical regions. However, in the absence of adequate housekeeping practices, microbial contamination problems can also occur in fuel systems located in cold climates.

Water pH is generally not a controlling factor in fuel systems. Most contaminant microbes can tolerate pH's ranging from 5.5 to 8.0. As with temperature, there are microbes that prefer acidic environments (some grow in the equivalent of 2N sulfuric acid) and others that grow in alkaline systems with pH > 11. Fuel tank bottom-water pH is usually between 6 and 9 [6,8].

As water activity tends to be greatest at interface zones, this is where microbes are most likely to establish communities, or biofilms. Numbers of microbes within biofilms are typically orders or magnitude greater than elsewhere in fuel systems. Biofilms can form on tank overheads, at the bulk-fuel, bottom-water interface, and on all system surfaces.

Using fuel hydrocarbon vapors as their carbon source, microorganisms can colonize tank overheads, where condensation provides the necessary water activity. Biofilms on overheads generally look like slimy stalactites.

Whereas a 1-mm thick biofilm on a tank wall may seem negligible, it is 100 times the thickness of most fungi, and 500 to 1000 times the longest dimension of most bacteria. This seemingly thin film provides a large reservoir for microbial activity. Within the biofilm micro-environment, conditions can be dramatically different from those in the bulk product.

Microorganisms consortia (communities) give the biofilm community characteristics that cannot be predicted from analysis of its individual members.

Microorganisms are able to consume hydrocarbons directly excrete waste products that other consortium members use as food. The net effect is a change in pH, oxidation-reduction (or redox) potential, water activity, and nutrient composition that has little resemblance to the environment outside the biofilm [6].

Microbes growing anaerobically produce low molecular weight organic acids (formate, acetate, lactate, pyruvate, and others). These acids accelerate the corrosion process by chemically etching the metal surface. There are data demonstrating that biofilm communities can deplasticize the polymers used in fiberglass synthesis. Such activity can result in catastrophic tank failure and is most likely to occur along the longitudinal centerline (the same place of the greatest frequency of MIC pinholes).

Biosurfactants facilitate water transport into the fuel phase and some fuel additive partitioning into the water phase. Other metabolites may accelerate fuel polymerization. Produced at concentrations that are difficult to detect against the complex chemistry of fuel components, these metabolites can have a significant deleterious effect on fuel stability. Although most of the change occurs within a few centimeters of the biofilm-fuel interface, product mixing can distribute metabolites throughout the fuel system.

More particularly after microbiological contamination of aviation fuels the following effects are observed in the presence of the above-mentioned favorable conditions [9]:

− *change in physical and chemical properties of fuels*, namely increasing of major physical-chemical parameters values as kinematic viscosity, refractive index, pH, content of actual resins and others. Also characteristic features are the formation of sediment, turbidity fuel and peculiar odor;

− *corrosion of storage tanks for aviation fuels.* Corrosion development of bottom part where accumulates water sludge, especially on verge of system distribution “fuel-water”, corrosive damage of aircraft tanks, corrosion of aircraft power constructions;

− *clogging and damage of fuel filters, pumps and fuel systems.* Sedimentation of mycelium and bacteria colonies at the inner walls of the fuel systems leads to clogging of pipelines, filters, pumps and fuel systems;

− *threat to the safety of aircrafts flights.* Changing the physical, chemical and exploitation properties of aviation fuels leads to early clogging of filters, pollution of regulating equipment, causing unstable operation of the fuel system, and therefore can cause failure of the engine, and even complete failure of the system, and as a consequences is appearance of accidents and emergency landings.

The changing the acidity of fuel is an important consequence of the proliferation of microorganisms (Fig.5). Acidity of fuel due to the presence of organic or inorganic acids or their derivatives. Therefore, the change in pH value of the fuel can indirectly determine the dynamics of microbial growth in fuel. The acidity of the fuel due to their content of organic acids and cidic compound. This quality index characterises the presence of the fuel products that provoke an increase in the rate of wear and corrosion of engine friction pairs and the air supply system, as well as corrosion of tanks, pipes and fittings. The metabolic products of microorganisms destructors fuels contain organic acids and increase the acidity of fuels.

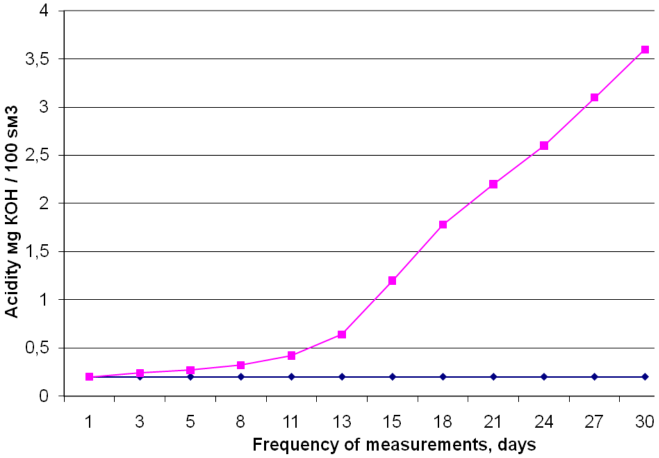


Fig. 5. Change jet fuel acidity under the influence of microbiological contamination

🟥 – research sample 🟦 – check sample

The aviation industry is experiencing increasing pressure from the public and environmentalists who say that the increase in traffic volume and number of aircraft operated by causing serious damage to the environment, besides aviation is one of the largest consumers of fuel and lubricants. Necessary to replace petroleum hydrocarbons alternative raw materials. Carbon biomass carbon cheaper oil. However, the conversion of the «cheap» carbon in the consumer goods while expensive. Before commissioning, the risk and the effect on reliability of equipment should be evaluated.

Biocomponents is a materials derived from the lipids of plants or animals, which can be used directly in existing combustion engines. In a base catalyzed process, triglycerides are broken down through the transesterification of the ester bond linking the glycerol backbone with the fatty acids. Through methanolysis, glycerol is substituted with a methyl group to produce single chain fatty acid methyl esters (FAME). FAME are structurally similar to petroleum alkanes and furthermore have suitable physical and chemical properties, which allows for use it in engines.

There are problems with biocomponents which need to be addressed before biocomponents become a fully viable alternative to fossil fuels. The problem is the higher propensity of biocomponents towards microbial contamination compared with petroleum hydrocarbon.

Biocomponents and petroleum hydrocarbons have similar calorific values, similar viscosities, similar densities and similar material compatibilities. However, despite these similarities, biocomponents with fuels are significantly more susceptible to bio-contamination. Studies have shown that biocomponent has a higher amount of microbial contamination, higher rate of microbial induced fuel degradation and higher rate of Microbial Induced Corrosion (MIC) of fuel system components compared to petroleum fuel. The high propensity for contamination of biofuels is likely due to several factors. The major issue deals with the hygroscopicity of biocomponent (i.e., it absorbs water from the atmosphere). Water may also occur as emulsions in biodfuel as a remnant of the transesterification process. Another factor is the higher bioavailability of biocomponent. Biofuels easily hydrolyzes to fatty acids by both chemical and microbial reactions. Fatty acids are important for every living organism and are easily incorporated into the tricarboxylic acid (TCA) cycle metabolism via β-oxidation. This bioavailability is a somewhat double-edged sword: while it makes use of biocomponent more difficult on a daily basis, biocomponent degrades in soil and water environments in a few days, diminishing the environmental impact of fuel spills.

Studies of microbiological stability of aviation fuels have been carried out in the laboratory of the Ukrainian Scientific-Research Center of Chemmotology and certification of fuel and technical liquids. Samples of fuels were submitted jet fuel «TC-1» and automobile gasoline A-95 (tabl. 3). The methyl ester of fatty acids of sunflower oil was selected as the bio-component jet fuel «TC-1». Gasoline A-95 has been selected as an alternative to leaded aviation gasoline. Ethanol was added in different concentrations to gasoline [9].

Table 3

List of samples

Number of samples	Samples
1	Jet fuel «TC-1»
2	Jet fuel «TC-1» + 10 % biocomponent
3	Jet fuel «TC-1» +20 % biocomponent
4	Jet fuel «TC-1» +30 % biocomponent
5	A-95
6	A-95+5 % ethanol
7	A-95+10 % ethanol
8	A-95+15 % ethanol
9	Biocomponent

The test specimens were infected colonies microorganisms and control samples are placed in a lit environment with ambient temperature 20–25 °C. The studies were conducted 2 weeks. Control of changes were made every week on visual and chemical methods. The acidity of fuel was chosen as the chemical method of control microbiological growths. The choice of rate is due to the mechanism of microbial degradation and metabolism products biodestruktors. The change of the value of the indicator will be judged on the impact biocontamination quality fuels, fuels and microbiological stability of the rate of growth of microorganisms.

The essence of the method lies in the titration of the acidic compounds of the test product with an alcoholic solution of potassium hydroxide in the presence of a color indicator. Acid number is expressed in mg KOH/100 cm^3. This is standart method [11]. Determination of the acid number performed in the semi-automatic titrator 702 SM Titrino Mettler Toledo.

Test results are presented in Fig. 6. The values on the vertical axis of the diagram of Fig. 1 is the acidity, expressed in mg of KOH/100 cm^3 of fuel.

Biocomponents such as the methyl ester of fatty acids of sunflower oil is subject to the same biodegradation by microorganisms like jet fuel.

Corrosive activity of aviation fuels is estimated by such indicators as acidity, tests on a copper plate, the content of water-soluble acids and alkalis, water content, sulfur content, etc. The test on a copper plate is a universal method for qualitative evaluation of corrosion activity of aviation motor fuels. Increased corrosion of fuels with microbiological contamination is confirmed by the results of experiments carried out in Test interactive laboratory «AviaTest» by the index of copper plate.

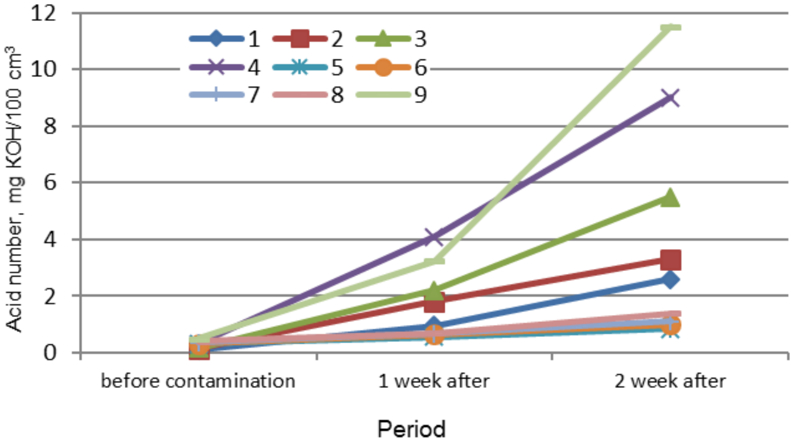


Fig. 6. The change of acidity of traditional and alternative fuels under the influence of microbiological contamination

The gist of the method is as follows. The prepared copper plate is immersed in a certain amount of sample, heated and kept at a temperature of 100 °C. for 3 hours. After this time, the plate is removed, washed and compared with standards of corrosion.

The list of samples and results of their tests is presented in Table 4.

Table 4

List of samples for research and test results

Sample	The test result
Clean fuel for jet engines «TC-1»	
Clean fuel for jet engines Jet A-1	
Fuel for jet engines «TC-1» with microbiological pollution	
Fuel for jet engines Jet A-1 with microbiological pollution	

The results of research have shown that fuel for jet engines with microbiological contamination has increased corrosion properties. The appearance of dark plaque and changes in color on the plates are very noticeable. The appearance of copper plates, which were kept in fuels for jet engines with signs of microbiological contamination, does not correspond to reference samples.

Corrosion occurs under the influence of the products of vital activity of microorganisms present in fuels. The fungi and many bacteria form ammonia, hydrogen sulfide, and various organic acids in the process of metabolism, most of which are characterized by high corrosive activity (Fig.

7, tabl. 5). In the course of its development, microorganisms destroy inhibitors that protect metal and stimulate its corrosion. Microorganisms are acceptors on the surface of metals. Corrosion of metal products, structures usually occurs in conditions of high humidity in the presence of contamination.

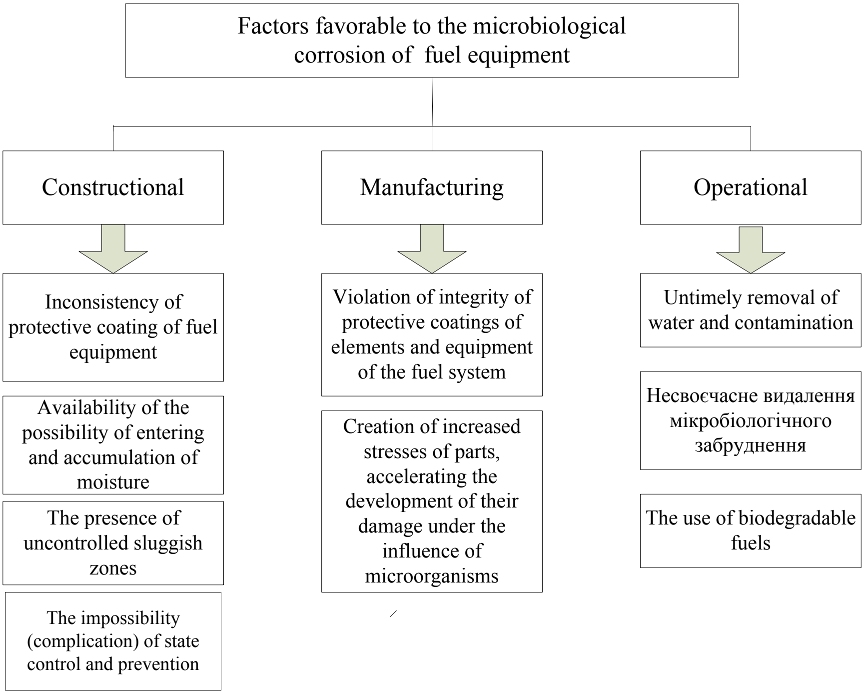


Fig. 7. The causes of microbiological corrosion.

The corrosion is one of the most dangerous types of metal destruction of aircraft structures. Over 50 % of all corrosion processes due to the influence of microorganisms. The causes of corrosion are analyzed. The effect of microbial contamination in aviation fuel on their corrosive properties are investigated and described in these materials. The conclusion that biocorrosion of the fuel system and aircraft structures is part of the problem fuel with microbiological contamination are made and justified in these materials.

There are many ways to prevent biological contamination of fuels. One of such method is the method of ultraviolet and electromagnetic radiation. Ultraviolet radiation causes the death of microorganisms. For this purpose the UV lamp was developed. During its development excluded the possibility of explosion and inflammation of fuels. The lamp can be mounted to the bottom of the fuel tank and move along it, as well as along the fuel line.

Possible installation of lamps during pumping fuel from one tank to another. Destruction of microorganisms is also possible by using electromagnetic radiation at a certain frequency radio waves [8]. Colonies of fungi and bacteria can be removed by filtration through a porous material, the pore size of which is not more than 2 microns. Possible way to protect the fuel through bacterial filters, filled with silver compounds (for example, cotton, glass, synthetic rubber).

To physical and mechanical methods of microbiological contamination control are also include centrifugation followed by agglomeration filtration, flotation, the use of ion-exchange resins, electro hydraulic deposition, ultrasonic control [6, 8].

The most effective way to protect the fuel from biological contamination at present is biocide additives that reduce activity of microorganisms in jet fuels and prevent biological corrosion of fuel tanks [1, 5].

Table 5

Potential consequences caused by microorganisms in aviation fuel systems

Risks	Principal Types of Microorganisms
Blockage of pipes, valves, filters	Fungi; polymer-producing bacteria
Increased water content	All
Sludge formation	All
Surfactant production	Fungi; and aerobic bacteria
Corrosion of storage tanks and lines	Fungi; and anaerobic bacteria
Production of suspended solids in the fuel	All
Breakdown of hydrocarbons	Fungi; and aerobic bacteria
Shortened filter life	All
Fouling injectors	Aerobic bacteria and fungi
Increased sulfur content of fuel	Sulfur-reducing bacteria (SRB)
Shortened life of engine parts	Undetermined
Penetration of protective tank	Fungi
Health problem	Endotoxing-producing bacteria, SRB

During the choosing of biocide additives there are the following requirements: they must not impair quality of fuels, characterized by prolonged action, detrimental effect on engine structural parts, fuel regulatory apparatus, reliability of filters and filter separators, to be toxic. Combustion products of these substances should not cause adverse effects on the environment [4].

Biocide additives may be soluble in fuels, and water cushion and destroy microorganisms in both phases [8].

Many biocide products have been tested abroad that meet the above requirements, there are the following: ethyleneglycol monometyl ether and Biofora F [8].

Ethyleneglycol monometyl ether – is anti water crystallization additive, with glycerol. However, it was found that glycerol actively contributes to the microorganisms, and without it ethyleneglycol monometyl ether reduces their growth. In addition to the fuel for air jet engines – 0.1–0.15 % by weight, substance concentrates in water up to 20 %, which not only prevents the formation of ice crystals, but also reproduction of microorganisms.

Biofor F after the penetration to oil product is concentrated in the free water. The mechanism of this substance action is also based on increasing of osmotic pressure. The effectiveness of the substance is in its lower concentrations in the water. This additive has the following drawback: when added to jet fuel is deposited on the blades of aircraft turbines and can cause them to corrosion due to increased acidity of water.

Long-term monitoring of fuel tanks coated with furan resins showed that microorganisms in these tanks is reduced [8].

There is well-known antiwater crystallization liquid “I-M”, which is a product of association ethyl cellosolve and methanol. Liquid “I-M” is designated for use as additives to the fuel for the air jet engines, refueled aircrafts of civil aviation to decrease the probability of icing aircrafts and helicopters filters at low temperatures. We researched bactericidal properties of the additive that caused by containing of methanol [10].

There are used biocides that have the active components – cellosolve, compounds of nickel, copper and other metals, heterocyclic compounds in quantities 0,0001–0,005 % [7].

Due to increasing the range of biocide additives, there were studied bactericidal activity of such compounds dimethyl-dialkil-ammonium chloride ($[R_2(CH_3)_2N]Cl$) and dimethyl-alkyl-benzyl-ammonium chloride ($[R(CH_3)_2NC_6H_5{-}CH_2]Cl$) for aviation fuels – gasoline and fuel «TC-1» for air jet engines [8].

During the study of these compounds has been established [8] that the amount of 0.05 % or more above mentioned additives reduce the growth of all microorganisms in the aviation gasoline and fuel «TC-1».

It was studied biocide activity of such compounds: zinc salts of synthetic fatty acids, mixed salts of zinc and mercury, acetic and oleic acids. With addition to jet fuel in concentrations of 0.05–0.1 %, they found sufficient activity, reducing the number of microorganisms on 75–85 %. The salts of higher carboxylic acids of chrome, copper and lead, and also naphthenate of iron, copper and chromium were low-toxic [8].

Taking into account problem actuality of protection from both fuels accumulation of static electricity, and from microbiological contamination, was obtained complex additive that has antibacterial and anti-static properties. Mixtures of bactericidal and anti-static additives of different composition were studied; both bactericidal components applicated dimethyl-dialkil-ammonium chloride [8]. Simultaneously, this additive is an effective anti-static additive in concentration of 0.003 %, increases conductivity and reduces oil electrification during their motion [8].

It is set that the antiwater-crystallization additive PFA-55MB has high bactericidal effect for jet engines. Addition to jet fuel in an amount of 0,05–0,15 % of PFA-55MB additive practically fully prevents development of microorganisms and corrosion of fuel tanks of jet engines. This additive is the most widespread abroad [9].

It was found that 8-hydroxyquinoline and disalicildenpropandiamin in addition to fuel for air jet engines brand «TC-1» in concentration 0,2 and 0,1 % diminished growth of microorganisms accordingly on 88 and 75 %. Primary amines of C_{12}–C_{15}, which was added to the fuel in an amount of 1 %, diminished growth of microorganisms on 95 %.

Special experiments reflected that active biocide additives in the water-fuels systems there can be substances that do not dissolve in fuel, but soluble in water. Thus, the complete destruction of microorganisms in the environment in fuel «TC-1» was observed when injected into the water phase one of the following substances: 0,04 % 1,2-diaminopropana or hexamethyldiamin, 0,12 % ethylendiamin, hydroxylamine of hydrochloric acid or methylamine tartrate, 0,16 % trimethylamine or *n*-butylamine.

Growth of microorganisms reducing on 98 % is observed when the content in the water phase 0,08 % *n*-butylamine, etylendyamina, hydroxylamine hydrochloride or methylamine oxalic acid.

Inhibition of microorganisms increasing by 70, 75 and 90 % was observed in environment of fuel «TC-1» when in the water phase added respectively 0,24 % chromium acetate, 0,16 % chromium nitrate, 0,16 % copper acetate [9,10].

There is also known multifunctional additive IPOD (isopropyloktadetsylamin).

Bacteria fungicidity of additive on the base of gas condensates was studied. Unlike the other additives, it obtained from hydrocarbon fractions (145–280) °C of gas condensates. Adding of the additive in amount of 0,1 % destroyed microorganisms within 10–15 days on 100 %.

Synthesized additive has not only antibacterial, but also antioxidant and anti-corrosion properties. The additive addition to final concentration of 0,1 % prevents sediments in fuel on 80 % [5].

Katon FP 1.5 of the company ROHM AND HAAS (U.S.A.) is one of the highly effective biocides that used worldwide for various fuels. In the nomenclature of the International Union of Theoretical and Applied Chemistry, an active component of Katon FP 1.5 is defined as 5-chloro-2-methyl-4-isotyazolin-3-one.

Today many foreign companies producing biocide additives to petroleum products, such as: «Bang and Bonsomer», «THOR», «ROHM AND HAAS» and others [8].

The authors conducted research on the efficiency of modern biocide additives (applications) of mentioned above foreign manufacturers. The research was conducted by the method of diffusion zone, which is testing the microbiological stability of jet fuel protected by antimicrobial additives with different concentrations in the Petri dish on nutrient dry agar for cultivation of microorganisms. Zones diameter of growth absence characterized the degree of test fuel stability.

It was used a mixture of aerobic bacteria (*Pseudomonas, Bacterium, Mycobacterium*) as a test cultures, allocated from the affected oil.

The research results of biological stability of aviation fuel RT, protected by biocide additives with the method of diffusion zone are shown in Table 6 and Fig. 7.

Table 6

Results of the experiment by the method of zonal diffusion

Additive name	Zone diameter, mm		
	Additive concentration in fuel RT		
	1 %	0,1 %	0,05 %
Formacide	0	11	10
KATHON	0	9	8
Grotan F10	0	7	5
Grotan OX	25	14	9
Grotan TK 6	0	7	6
ACTICIDE KL	0	10	6
ACTICIDE OX	16	27	13
ACTICIDE MV14	36	30	24
Pure fuel RT(control)	0	0	0

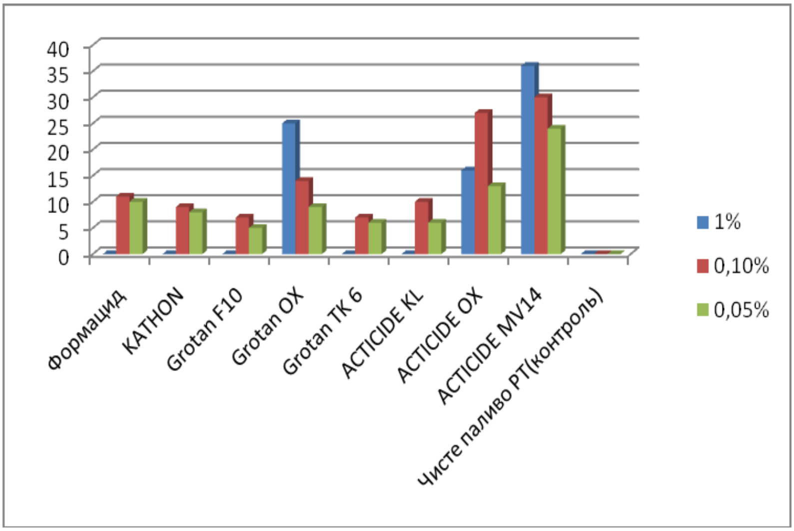


Fig. 8. Comparative distribution of research results of fuels biological stability, protected by biocide additives by diffusion zone method

So, this diagram represents that the best antimicrobial properties has the following additives: GROTAN OX, AKTICIDE OX, AKTICIDE MV14.

A host of problems will likely surface when uncontrolled microbial growth is allowed to develop. Microbial activity has been shown to cause degradation of fuel hydrocarbons. Flight safety also will likely be compromised, as well as increased maintenance and cost. Not all microorganisms, however, cause the same problems.

Assessment or analysis of risk is a process for identifying hazards, assessing the probability of an event and its consequences. The ratio of risk objects and risky events makes it possible to determine the link between the biological risk in the field of the use of aviation fuel with technogenic and economic risks. Technogenic risk is a complex indicator of reliability of elements of technical means of operation. It expresses the probability of an accident or disaster during the operation of machines and mechanisms, in particular vehicles, and the implementation of technological processes. The source of Technogenic risk is the violation of the rules of operation of technical systems, the untimely conduct of preventive inspections. Economic risk is determined by the ratio of benefits and harm that society receives from a particular activity.

The authors of this work identified and systematized the consequences and the risks of microbiological contamination of aviation fuel (Fig. 9) [12].

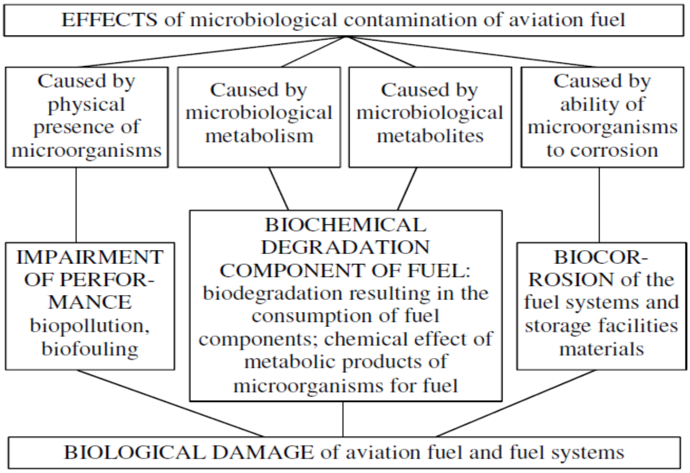


Fig. 9. The risks and consequences of microbial contamination of aviation fuels

Risk reduction is an action to reduce the likelihood of a negative event or mitigate the consequences of this event if it occurs.

A key factor is a multi-aspect approach to fuel hygiene to eliminate the inconveniences and costs associated with contamination of the fuel system. Each air operator should conduct his own risk assessment in order to determine the optimal regime.

An important component of this regime is the frequent checks of drainage systems, as well as regular testing and monitoring of microbiological contamination in the entire fuel system.

РЕФЕРАТ

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ІДЕНТИФІКАЦІЯ ТА ОЦІНКА БІОЛОГІЧНОГО РИЗИКУ ПОСТАЧАННЯ АВІАЦІЙНОГО ПАЛИВА

Основна увага в роботі приділена мікробіологічному забрудненню нафтопродуктів і паливних систем транспортних засобів і засобів експлуатації та зберігання. Обмежений обсяг нафтових ресурсів, впровадження стандартів ІКАО і IATA, дотримання вимог авіаційної безпеки та експлуатаційної безпеки, економічні показники, фінансова прибутковість вимагають заснованого на оцінці ризику до поставок авіаційного палива. У процесі дослідження були виявлені, оцінені і систематизовані ризики і наслідки мікробіологічного забруднення авіаційного палива, його вплив на якість палив і хіммотологічної надійність авіаційної техніки.

Ключові слова: авіаційне паливо, біологічний ризик, мікробіологічне забруднення, гриби, біоплівка,паливна система, кислотність, мікробіологічна корозія, біоцид.

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ИДЕНТИФИКАЦИЯ И ОЦЕНКА БИОЛОГИЧЕСКОГО РИСКА ПОДАЧИ АВИАЦИОННОГО ТОПЛИВА

Основное внимание в работе сфокусировано на микробиологическом загрязнении нефтепродуктов и топливных систем транспортных средств и средств эксплуатации и хранения. Ограниченный объем нефтяных ресурсов, внедрение стандартов ИКАО и ИАТА, соблюдение требований авиационной безопасности и эксплуатационной безопасности, экономические показатели, финансовая прибыльность требуют основанного на оценке риска подхода к поставкам авиационного топлива. В процессе исследования были выявлены, оценены и систематизированы риски и последствия микробиологического загрязнения авиационного топлива, его влияние на качество топлив и химмотологическую надежность авиационной техники.

Ключевые слова: авиационное топливо, биологический риск, микробиологическое загрязнение, грибы, биопленка,топливная система, кислотность, микробиологическая коррозия, биоцид.

ABSTRACT

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IDENTIFICATION AND ASSESSMENT OF BIOLOGICAL RISK OF AVIATION FUEL SUPPLY

The work is focused on microbial contamination of refined petroleum products and fuel systems of vehicles and means of operation and storage. A limited amount of oil resources, the introduction of ICAO and IATA standards, satisfaction of safety and operational safety requirements, economic indicators, financial profitability, require the risk-based approach in aviation fuel supply. The risks and consequences of aviation fuels microbiological contamination, impact of it on fuel quality and chemmotological reliability of the aviation engineering, have been identified, evaluated and systematized during research.

Key words: aviation fuel, biological risk, microbiological contamination, fungi, biofilm, fuel system, acidity, microbiological corrosion, biocide.

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Chapter 3

THE IMPACT OF AVIATION ON THE ENVIRONMENT AND THE DEVELOPMENT OF ECOLOGICAL LOGISTICS

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3.1 RELIABILITY OF MONITORING OF AVIATION INFLUENCE ON ENVIRONMENT

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Information support for environmental monitoring of aviation influence on ecosystems under the conditions of increasing requirements for the quality of environment and environmental standards is of particular importance. Only reliable and exhaustive information guarantees the efficiency of the tasks set for the system with minimal pressure on the environment and with minimal energy consumption. Moreover, it is also important to be able to predict situations in order to make managerial decisions in advance, which is impossible without effective monitoring system.

The main tasks of monitoring of aviation influence on environment are:

– collection of data that directly characterizes the state of the environment (types of contaminants, their concentration, migration, ability to concentrate – for example, precipitation to the bottom or exit to the surface, the ability to metamorphosis – for example: sublimation, metabolism, dissolution with the formation of new compounds, ability to self-decomposition, dependence on external influences, as well as data characterizing the conditions in which they were gathered);

– comparison of new collected data with relevant data collected at the same points during the previous data acquisition cycle in order to detect the dynamics of pollution and factors that could affect the state of the indicators;

– analysis of the reliability of the monitoring data (evaluation of the methods used to characterize the data, and the means of data determination – measuring instruments, evaluation algorithms, etc.);

– placement of data evaluated from the point of view of reliability, in the data bank indicating the coordinates of the place of receipt of data, dates and all related information;

– analysis of data relevant to this system at certain time intervals and taking into account external factors in order to predict state changes;

– elaboration of recommendations for measures aimed at stabilizing or improving the state of system or improving efficiency of purification process [1–3].

The aviation technical systems are sets of elements of a certain material nature, which are in the relationship. In each of these relations there is a certain variable, the set of its states, and the set of mathematical properties defined on this variable. It is known that if there is a finite sequence of relations that allow a predetermined element of the set $x_1 \in X$, then such a sequence of relations is an effective identification process.

A system is considered to be observable if it can be determined by a certain multiple experiment, when the inputs of the system that is in an unknown state are fed into the set of inputs and then the corresponding output values are observed. The observation channel forms a measuring system that includes measurement devices and procedures that determine the rules for using devices under different conditions.

The aviation technical system's effect on environment as a system that is exposed to external influences, some of them are poorly controlled or not defined (since assumptions about the properties of this usually avoid some of the essentially important components, less formal objects are taken into account than is necessary, etc.), is observed only in a limited number of points, can be regarded as an open system, for which there is a characteristic presence of at least one element of a set for which there is no effective identification process, and a decision regarding the state of the system accepts the conditions of uncertainty. Uncertainty arises also in those cases where the conditions of the technological process are evaluated within the area of the monitoring channel or at the boundary that divide the two specific states. By the way, the monitoring zones of the monitoring channels do not have clear boundaries, and the results of observation near these fuzzy, blurred boundaries can be characterized only by degrees of membership, and not by clearly defined functions.

In both cases, the uncertainty of the results of the observation leads to unreliability of the assessments of the state of the process. Such a falsehood is characterized by the value inverse to the membership function. That is, the inverse relationship between the degrees of affiliation of an element to a given set from a certain base variable and the rules used or metrics [3]:

$$\mathrm{d(xm,\ xr)} = \left\{ (\mathrm{n} - 1)^{-1} \sum_{i=1}^{n} (x_{mi} - x_{ri})^2 \right\}^{1/2} \tag{1}$$

which evaluates the degree of proximity of model estimates (predictions) of signal values (state parameters) x_m, or their distributions to the real values of these signals x_r. Here, under model estimates, we understand not only the results of the actual modeling (mathematical or physical), but also the data of measurements using the usual (non-standard) means. Results of measurements using means at the output of which the quality of information is guaranteed are considered as real (true).

This corresponds to situations for which the «usual Euclidian distance» as the criterion of proximity (or discrepancy) is justified:

– the observations are mutually independent and may have the same dispersion;

– the components of the observation vector are homogeneous in their physical content and they are equally important in terms of their use during identification;

– the sign space coincides with the geometric space and the notion of proximity of objects of observation coincides with the notion of geometric proximity in this space.

In practice, it is often more convenient to use a value that is a reverse metrics, a complement of a metrics, with the reliability (*TW*), and for a quantitative assessment of reliability, which is usually considered in the range [0, 1], use the relative metrics

$$D\mathrm{r(xm,\ xr)} = \frac{d(x_m, x_r)}{d_{\max}(x_m, x_r)}, \tag{2}$$

where $d_{max}(x_m, x_r) \geq d(x_m, x_r)$ is the metrics value in which the causal relationship between x_m and x_r is not detected or insufficient to make responsible decisions [3].

The size of this metrics depends on the number of states of variables, on the measure by which the restrictions on the variables are set, and on a number of other factors. Considering the following generalized expression for d_{max}:

$$d_{\max}\mathrm{(xm,\ xr)} = 2 \cdot \partial \cdot \xi_{\max}(\mathrm{x_{mi}} \cdot \mathrm{x_{ri}}) \tag{3}$$

where $\delta > 1$ is a certain proportionality factor which takes into account the degree of fuzziness of the observation channel data and which depends on its own characteristics of the channel and the degree of clarity of representations about the properties and behavior of the object (process); ξ_{max} is the maximum permissible value of the relative error of the simulation (forecast) or the permissible error of the integral estimates.

In the cases considered, authenticity is presented as an addition to the unit, i.e.:

$$TW = 1 - dr\,(x_m \cdot x_r) \tag{4}$$

As a characteristic of reliability, one can also use the functions of modeling estimates for the true value, for example:

$$TW = \exp\,[-(x_r - x_m) \cdot 2] \cdot \partial - 2 \tag{5}$$

where δ is fuzzy of the data, which should not exceed the measurement error by more than 1–2 orders [3].

Reliability is not the only characteristic of the quality of information. Information is characterized by the following properties:

– value, which is expressed in the form of increasing the probability of achieving the goal set, after receiving this information;

– inactivity, that is, inequality of influence on the final result of the joint use of several information and the consistent use of the same information separately;

– non-commutatively, that is, the dependence of influence on the final result of the order, which uses a series of information;

– non-consistency, that is, the difference of results in the consistent use of a number of information, irrespective of the results, when part of this series is used sequentially in part, and part – as a result of the joint use;

– completeness, that is, the degree of reflection of the real object (process) in the message;

– reliability, that is, the degree of conformity of the models used or the data taken and the errors of their determination by the true value.

However, from all the properties listed above, authenticity – is the most important, since it directly affects the value of information and the ability to achieve the goal that is directly related to the effectiveness of the information system.

As reliable can be considered those data that have successfully passed the procedure of critical analysis and generalization of the results of measurements and / or calculations, taking into account known regularities that include the estimation of errors. Reliability can be considered in terms of formally technical (no hidden occasional errors) and socio-psychological or behavioral (lack of distortion due to improper interpretation or reluctance to open the truth). Distinguish also engineering reliability, that is, deterministic confidence in the truth of information, and statistical reliability, that is, reliability, which follows from statistical conclusions.

Errors leading to a reduction in reliability can be classified into three categories:

– which do not directly lead to a decrease in the quality of the system's operation, but may, under adverse conditions or combination of such conditions, or in the presence of other similar errors, lower the quality of the functioning of the information system;

– which lead to a slight decrease in quality under normal conditions or to a significant one – under adverse conditions;

– which lead to a sharp deterioration in quality.

Reliability is the function of the state of any system, to which one or another extent is affected by various factors: random obstacles and noises, environment conditions, aging processes that change the characteristics of the components of the system hardware, the degree of load (overload), the volume of prior knowledge of object or process, etc.

The nature of the errors that are present or periodically occurring in the process of functioning of the information system is different. There are several groups of errors that do not depend on technical parameters of system. The first ones include:

– methodological errors that are caused by the imperfection of mathematical models that underlie the functioning of the system: the inadequacy of the adopted model for a real object or process in statics or dynamics; lack of a priori information about the nature of the object, or about the processes taking place; fuzzy connections and functional dependencies; attempts to simplify models due to the technical impossibility or complexity of taking into account individual parameters; the impossibility of an objective justification for choosing an optimal model in the presence of a set of quasi-equivalent models;

– methodological ones, which are caused by the imperfection of the chosen methods of calculation, that is, the errors of numerical methods, approximation, errors, which are caused by a limited number of iterations, etc.;

– output, that is, errors which are caused by inaccuracy of the initial data, statistical fluctuations of processes and interactions, interferences and distortions in the communication channels, errors of the operator, limited redundancy of the information necessary for statistical processing, etc.

The second group has instrumental errors, which, in turn, are divided into component errors, structure, interface and processing.The errors of individual components and system nodes are due to the drift of their characteristics under the influence of external factors and aging processes, the unessential characteristics, the effect of noise and interference, and so on.Structural errors are characterized by the finiteness of the bit representation of real numbers due to the constraints due to the finiteness (for each particular system) of bits of processors, memory, channels, converters and peripheral equipment, which forces to refer to the procedures for representing numbers by a limited number of significant senior discharges and, accordingly, to rounding off or rejecting the rest (junior) digits.

Interface errors are due to the fact that, when docking various technical means with each other, the accuracy of the representation of data is limited by the possibility of means, which has the slightest accuracy, that is, the smallest bit. In addition, they include errors that arise due to time or phase shift, as well as during human interaction with the system (errors when entering data into the system using a keyboard, oral or written sentence, errors during the preparation of intermediate storage media etc).

Processing errors are the most branched class of error, which is characterized by noise and interference, temporary hardware failures and self-abandoned failures, distortion of information during conflict situations, violation of the sequence and (or) loss of particular pieces of data or their duplication, overflow of memory, overloading channels or processors, by cycling programs, etc. A separate group of processing errors consists of integral errors that are associated with the accumulation of errors in individual steps of multi-step processes of information processing, when as a result of a systematic (methodological) error caused by an unrealized data processing algorithm from step to step, information that is not significant is lost at one step, but it is important if it breaks up at a number of processing intervals. In addition, the accumulation of error is possible due to the systematic overflow of registers and other buffer storage devices, as well as (with the use of adaptive data sampling methods) due to the deviation of the true laws of the distribution of random events from those used as working hypotheses and the rejection of data with low (supposed) priority.

The third group includes project errors that are due to syntactic and semantic errors, made during application programming, system programming errors, system developer errors, operator errors due to fuzzy instructions, etc.

Methods for eliminating errors, and thus ways to ensure reliability, depend on the type of error, the requirements put forward to the system, the working conditions and the level of knowledge about processes and phenomena that can cause errors.

All this suggests that for the successful development and application of methods for improving observation and identifying the state of the process, it is necessary to research specific sources of unreliability of the process data, as well as sources of unreliability of the integral estimates of the state of environment.

Sources of unreliability of data on the status of environment include:

– data detectors (indicators in a form that is acceptable for display, communication with channels, storage and documentation);

– measuring networks (it is economically inexpedient, and sometimes physically impossible to perform measurements at any point in the system, so large areas remain uncontrolled, and data about their conditions is obtained by interpolation based on data obtained at separate points – nodes of the measuring network, and so the reliability of the data on the state of the process is the function of the density of the measurement network and selected interpolation procedures);

– the influence of external factors and time.

Existing methods for increasing the reliability of the results of observation and identification of states use mainly two approaches:

– passive, when using a number of design solutions that objectively contribute to increasing the reliability of data, but the evaluation of actual results either is not implemented or is not used to improve the quality of information promptly;

– active, when the actual state of the system and the actual results of data processing are evaluated continuously or periodically, and on the basis of these estimates, decisions are made to adjust the data, characteristics of the individual components of the systems, algorithms of their operation, or to decompose the systems in order to improve the quality and efficiency of their work.

Passive methods for improving observation and identification of system conditions are widely used in monitoring procedures. However, the lack of permanent control and prompt processing of the results obtained and the possibility of providing timely adequate corrective actions does not allow adapting such systems to changing operating conditions (internal and external), which reduces their effectiveness in the presence of strong obstacles, deviation of actual data (statistics) from calculation and degradation as separate components of systems and systems as a whole.

Using of an active approach, a huge role is played by control, all the variety of procedures of which can be reduced to three types: syntactic, semantic, and pragmatic [3, 4].

The task of syntactic control can be formulated as follows: collecting and evaluating information in order to decide on the legality (admissibility) of the state and structure of technical and software tools, as well as the format of individual elements of the message in general and in a particular situation in particular. The syntactic control has a formalized and, as a rule, deterministic character, and has the following varieties:

– a statement of the fact of exceeding the allowable waiting time;

– control of the number of words in the message;

– control of the length of the time interval between the words of the message;

– control of the form of pulse code;

– correctness of discharges of synchronization;

– number of digits in the data word;

– correctness of the address of the subscriber in one of the words of the message;

– parity control;

– control of the word (byte) of the state of the technical means.

The task of semantic control is the analysis of consistency, logics, consistency of data, that is, meaningful evaluation of control data, which may have the following varieties:

– output of data values received, permissible range;

– exceeding the permissible deviation from the average value in the redundant data set;

– unacceptable discrepancy between data received from functionally reserved devices;

– the presence of the record "1" in the control levels of the equipment of the built-in control.

Pragmatic control aims to identify the value, availability, timeliness of data, the impact of errors in individual data on the performance of the system as a whole, the economic efficiency of data.

The realization of control tasks (regardless of the type of control) is associated with decision-making processes. These procedures can be classified as follows:

– in accordance with the nature of the decision to be made (the only choice from a limited number of alternatives; a unified assessment of the continuous field of possible solutions; the combination of the first two);

– according to the nature of the observed quantity;

– depending on the length of the observation interval.

By the technique of implementation methods of verification of reliability can be divided into the following groups: accounting, mathematical, introducing redundancy, logical, combined. Accounting methods include the following procedures:

– an account with the release of a known control result;

– calculation of checksums;

– calculation of records;

– checksum summary;

– control format;

– cross-checking;

– control count of rows and columns of matrices.

Mathematical methods use the following procedures:

– mathematical modeling;

– substitution in the output equation of the found roots with the subsequent solution and evaluation of the results;

– introduction of additional links (including correlation);

– detection of trends and displacements in measurements;

– verification of limit values;

– interpolation of missing data, with the assumption that the data locally represent a polynomial of a certain odd degree;

– statistical forecasting;

– filtration.

Methods of introducing redundancy use both procedural and informational redundancy. Procedural redundancy implies either multiple consecutive (or simultaneous – with the use of different technical means) solution of the problem with the same source data and, accordingly, the same algorithm with subsequent comparison of results and decision on their reliability, or simultaneous solution of the problem using several different algorithms (equivalent or different in accuracy and time of implementation), as well as a comparison of the results and the assessment of their reliability.

Using of information redundancy involves the following control options:

– entering control digits into messages;

– plurality of data sources instead of one with the following evaluation;

– mediated data and a priori information;

– feedback (demand for additional data).

Logical methods include:

– meaningful checks (detection of those values that are logically incompatible with a priori knowledge about the plausible boundaries of the change of individual variables);

– control over deviations (detecting significant deviations that are characteristics of hardware failures; detecting deviations that reflect the spread of characteristics due to fluctuations in technological factors or the environmental impact; the detection of deviations that are a function of time, that is, due to the «aging» of technical means);

– control of the given sequence of data;

– control of «templates», that is, the justification of the use of members of a particular data array;

– time control of task decision;

– expert evaluation of the received data.

Combined methods are based on:

– selective validation by re-processing the output data to obtain the final result (including alternative algorithms);

– control examinations-tests (with verifications, i.e. pre-entered data);

– selective assessment of the reliability of the results with the help of special control evaluation programs;

– other procedures.

The methodology for organizing monitoring of environment involves the stages of determining the current field of pollution, associated factors and their impact on the spectrum and magnitude of pollution, the dynamics of pollution in comparison with past measurements, checking the relevance of trends in the trend of pollution, which take place, as well as decision making on reliability of monitoring data and forecasts [1, 5, 6].

The first stage of monitoring includes the development of a measuring network by presenting it in the form of a Peano curve, which ensures the continuity of monitoring of the studied territory and the absence of jumps between individual points of observation. After determining the structure of the measuring network, the volume of the samples (measurements) is optimized in order to exclude the possible influence of random obstacles. Determination of the range of pollution is carried out using methods of the theory of fractals.

The next step in the first stage is the use of hybrid monitoring methods, which is aimed to select from a plurality of relevant models (which are simultaneously used to predict the migration of pollution) one of the models whose Euclidean distance is the smallest relatively to the real measurement data performed at the time specified by the model. If we consider the metrics that characterize the distance between the curve of the point distribution during real measurement *(f^r)* and the curves obtained by modeling with the help of the model *mj* *(f^{mj})*, then the increment of information characterizing the degree of closeness *(f^r)* and *(f^{mj})*:

$$d[f^{(r)}, f^{(m)}] = \{(x_i^{(r)} - x_i^{(m)})\}^{1/2} \tag{6}$$

where *N* is the number of points at which the measurements are made $x^{(r)}$and $x^{(m)}$ and – respectively, the value actually determined by measurement and calculated using the model of the value of pollution at the *i*-th point.

At the same time, the smallest of the calculated metrics corresponds to the model that better describes the process of migration of pollution. That model satisfies the following equation:

$$\mathrm{opt} \cdot \mathrm{dj}[f^{(r)}, f^{(mj)}] = \min\{\mathrm{d2}[f^{(r)}, f^{(mi)}], \ldots, \mathrm{dj}[f^{(r)}, f^{(m2)}], \ldots, \mathrm{dk}[f^{(r)}, f^{(mk)}]\} \tag{7}$$

The first stage ends with the definition of the number and nomenclature and the absolute values of pollution that are not previously observed in this area, the boundaries of critical pollution, the development of the equidistant contamination (using one of the algorithms for the construction of fractal curves) [5–7] and the formation of the corresponding (source) file in bank of facts.

The second stage of monitoring is identification of correlations between concomitant and mediocre factors and actual monitoring data, as well as analysis of migration and metabolism of contaminants under specific conditions (taking into account such processes as transfer, gravity deposition, dissolution, deflation, chemical and biological processes, radioactive decay, etc.).

The associated environmental factors significantly affect the reliability of the detection of actual discharges of pollutants, the determination of the type and source of contamination, and, consequently, the ways of reducing the anthropogenic impact on the environment. In addition, taking into account the additional factors of the processes of migration and transformation of pollution in the environment determines the potential of the stability of the ecosystem, that is, its ability to self-purification and recovery.

Determining the dynamics of pollution is extremely important. It indicates the possibility of irreversible changes in the ecosystem, which may lead to its degradation.

The third stage of the monitoring is performed by calculating the metrics that characterizes the distance of the points of the current and previous measurement cycles (like in stage I), as well as the vector of changes (the last one is detected by determining the centers of the contours of the equinity of the current and previous measurement cycles). Detection of the dynamics of contamination ensures an early change in the methodology for the determination of pollutants and the replacement of measuring equipment, which is associated with a change in the range of measurements and the possible decrease in the sensitivity of the instruments.

The task of identifying the dynamics of the range of pollution is to analyze the observations and compare their results with each other by estimating the metrics.

The fourth stage of the environmental monitoring of pollutants involves (in the case of a deviation from the trend by the value of $\Delta x > 2\sigma$) the analysis of possible influences of external factors, which are presented in the format of monitoring data as concomitant or mediocre factors. If the deviation from the trend is not significant, and external factors take place and are characterized by significant amplitude, an analysis of the reasons for the invariance of the monitoring results is necessary.

The fifth stage of the monitoring is verification of the hypothesis of the monitoring results (including, if necessary, requesting additional information from the monitoring system and using the Bayesian theorem to correct the initial hypothesis), the overall assessment of the reliability of the data and the formulation of the decision on the correctness of the estimates and forecasts. The use of the Bayesian theorem allows determining, and subsequently clarifying, the probability of the validity of the accepted hypothesis of the data distribution in the conditions of uncertainty that exists during monitoring. According to this method, probability is calculated taking into account both previously known and new received information. The evaluation results with a mark of reliability are sent to the relevant fact file to replace the relevant output file (which is formed at stage I).

The consistent implementation of the above-mentioned stages of the evaluation of information ensures the reliability of the data obtained to make responsible decisions in environmental management [7, 8].

The analysis of the consequences of accidents and disasters at industrial sites associated with the release of significant masses of toxic substances into the environment, as well as measures aimed at minimizing its consequences, allows revealing the following:

– in case of an accident, the equipment for monitoring the state of the system or completely out of order (in any case directly to the location of the accident, where its data are particularly important), or does not reflect the current state of the system due to the discrepancy between the levels of parameters actually measured, the operating range of devices, which are used and are designed for normal or (at least) abnormal modes of objects;

– as a result of accidents, communication channels are completely or partially failed, which results in the fact that some of the information does not reach the decision makers (DM) in order to organize adequate measures aimed at minimizing the consequences of the accident;

– the measuring equipment remaining under working conditions, under extreme conditions that affect its performance, may indicate fuzzy or even ambiguous information in the presence of strong interference that may distort the actual picture and obstruct the work of the ATS;

– there are no technical and software tools (essentially expert systems) for operational forecasting (based on incomplete, incorrect, as well as indirect and concomitant data) possible (near and far) consequences of disasters and elaboration of alternative, appropriately evaluated measures for their minimization;

– the actions of personnel, deprived of operational reliable information on the magnitude of the accident or disaster and its possible consequences, in times of shortage of time and high psychological stress, as a rule, complicate the situation further.

As it is clear from the above, in all cases it is actually to say that DMs lack adequate information at the time they are most in need of it. At the same time, the importance of evaluated in terms of reliability of information in a similar situation, is large. After all, decision making is usually associated with enormous costs and moral shocks (in the event of unreasonable consequences of a reassessment of the degree of danger of the consequences of a catastrophe evacuation of a population from a threatened zone, a stoppage of the enterprise, etc.) or with victims and economic losses, as well as a loss of confidence in the authority's (under conditions of underestimation of the degree of danger and the rejection of timely radical measures).

But under normal conditions of functioning of aviation technical objects, as well as during natural processes, and under conditions of mutual influence of man-made and natural factors on an environment, there is a number of problems, there are certain changes, there is a violation of the balance of various factors in the limited territories or and on a global scale. In all of the above cases, monitoring of the state of the system and its dynamics and predicting the probable future problems (as well as their causes) is of utmost importance.

The monitoring process includes a set of procedures that can be attributed to the following types:

– determination (by direct or indirect physical measurements) of parameters characterizing the current state of the system (physical monitoring and biomonitoring);

– calculation (using mathematical models) of those state parameters that are not available (physically or in time) for physical monitoring procedures (model monitoring);

– analysis of the data of physical and model monitoring (in other words, hybrid monitoring data) from the point of view of their completeness (adequacy) and reliability with execution, if necessary, procedures for ensuring the adequacy and reliability of data (analytical monitoring);

– comparative analysis of relevant current and past hybrid monitoring data in order to identify trends in changing the state of the system and forecasting the consequences of these changes (predictive monitoring);

– decision-making based on predictive monitoring of measures aimed ultimately to minimize pollution at the environment and / or their impact on the ecosystem.

The monitoring problem has the next four aspects:

1. A thorough detection of the «natural» background of pollution (before the development of a new facility – a source of pollution, or in the case when previously such monitoring in this region was not performed at all) in order to further compare the background values of pollution with those that will occur as a consequence of functioning of this new object (or the further operation of the whole complex of objects in the region).

2. Periodic control of the status of an environment under conditions of normal operation of objects – sources of pollution in order to confirm objectively the safety for the population and the environment of controlled levels of pollution, as well as to identify abnormalities and trends of pollution, which need to be considered when evaluating the prospects for further development such facilities in the region.

3. Operational control over the development of the state of the system in abnormal and emergency situations with the purpose of assessing the extent of emissions or discharges of pollution and predicting their environmental consequences (taking into account hydrometeorological and other factors that influence the processes of the spread of pollution), as well as working out recommendations for further functioning of certain objects and (if necessary) the development of protective structures and the use of other means of environmental protection.

4. Post-accident control in order to clarify the patterns of distribution of pollution, to identify the effectiveness of measures to protect the area or to minimize the impact of pollution on

the environment, forecasting of the boundaries and terms of normalization of the environment.

Environment under influence of aviation technique systems is characterized by the presence of plural elements for which there is no effective identification process, and decisions on the state of the systems are made in uncertainty. The uncertainty of monitoring results leads to unreliable estimations of state of system.

For effective analysis of the state environment, justification of the purpose of collecting information, sampling points, frequency of updating of data, their nomenclature, and alternative variants of information provision should be provided.

The developed methodology of analysis of technogenic hazardous objects of aviation allows to analyze the sources, conditions and circumstances of emergencies and processes of their development, as well as to assess their environmental impact for adoption of management decisions in order to minimize environmental impacts.

Monitoring of environmental pollution includes definition of the structure of the measuring network, the range of the area and the density of pollution on the basis of the data measuring network and the corresponding algorithms of interpolation and smoothing, as well as determination of the dynamics of the range of pollution.

The above-mentioned approaches to increase the reliability of monitoring data ensure significant improvement of the functioning of information systems and facilitate the adoption of more substantiated decisions to minimize the consequences of man-made and natural disasters and accidents. However, their use in the absence of accepted patterns of dissemination of pollutants and characteristics of measuring equipment, making them sensitive to external influences and focused on precise input information, requires new, non-standard approaches, one of which is the interpretation of information used in the system in terms of theory fuzzy sets and the theory of possibilities that form the basis of intelligent information systems.

РЕФЕРАТ

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ДОСТОВІРНІСТЬ МОНІТОРИНГУ ВПЛИВУ АВІАЦІЇ НА ДОВКІЛЛЯ

Вплив системи авіаційної техніки на навколишнє середовище спостерігається в обмеженій кількості точок, для яких існує щонайменше один елемент з множини, для якого немає ефективного процесу ідентифікації, і рішення про стан системи допускає умови невизначеності. Для успішного розроблення та застосування методів покращення спостереження та визначення стану процесу необхідно вивчити конкретні джерела ненадійності даних процесу та інтегральних оцінок стану навколишнього середовища. Надійна методологія моніторингу включає визначення поточної сфери забруднення, пов'язаних з нею факторів та їх впливу на спектр і величину забруднення, динаміку забруднення порівняно з минулими вимірами, перевірки відповідності трендів, прийняття рішень щодо надійності даних моніторингу та прогнозів. Впровадження таких етапів гарантує достовірність отриманих даних для прийняття відповідальних рішень в екологічному менеджменті.

Ключові слова: екологічний менеджмент, моніторинг, надійність даних.

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ДОСТОВЕРНОСТЬ МОНИТОРИНГА ВЛИЯНИЯ АВИАЦИИ НА ОКРУЖАЮЩУЮ СРЕДУ

Воздействие системы авиационной техники на окружающую среду наблюдаемо в ограниченном количестве точек, для которых присутствует хотя бы один элемент из множества, для которого нет эффективного процесса идентификации, и решение о состоянии системы допускает условия неопределенности. Для успешной разработки и применения методов улучшения наблюдаемости и определения состояния процесса необходимо исследовать конкретные источники ненадежности данных процесса и интегральных оценок состояния окружающей среды. Надежная методология мониторинга включает определение текущей области загрязнения, связанных с ней факторов и их влияние на спектр и величину загрязнений, динамику загрязнения по сравнению с прошлыми измерениями, проверку актуальности трендов, принятие решений о достоверности данных мониторинга и прогнозов. Внедрение указанных этапов обеспечивает достоверность данных, полученных для принятия ответственных решений в экологическом менеджменте.

Ключевые слова: экологический менеджмент, мониторинг, надежность данных.

ABSTRACT

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RELIABILITY OF MONITORING OF AVIATION INFLUENCE ON ENVIRONMENT

Aviation technique systems effect on environment is observed in a limited number of points, for which there is a presence of at least one element of a set for which there is no effective identification process, and a decision regarding state of system accepts conditions of uncertainty. For successful development and application of methods for improving observation and identifying state of process, it is necessary to research specific sources of unreliability of process data and of integral estimates of state of environment. Methodology for monitoring includes determining current field of pollution, associated factors and their impact on spectrum and magnitude of pollution, dynamics of pollution in comparison with past measurements, checking relevance of trends, decision making on reliability of monitoring data and forecasts. Implementation of such stages ensures reliability of data obtained to make responsible decisions in environmental management.

Key words: environmental management, monitoring, data reliability.

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3.2 AVIATION INDUSTRY OF XXI CENTURY: DEVELOPMENT AND NECESSITY OR SERIOUS THREATS FOR NATURAL ECOSYSTEMS

Iryna Novakovska, Natalia Belousova, Natalia Ishchenko, Liliia Skrypnyk, Valerii Frolov

At this stage scientific and technological progress, which reaches unprecedented levels is characterized by the continuous creation of new and improved existing technologies and means of production. In turn the aviation industry is the realization of new achievements and achievements in the practical aspect of application. There are the developments of new equipment, both on-board and on-board; creation of powerful engines; updating fleet of aircraft, as well as designing new types. But along with such positive achievements at the first glance, aviation transport remains a large source of harmful factors for the environment, the first of which is usually in the vicinity of large cities, and the latter, in turn, within large citiesTherefore, the current situation leads to the necessary, development and implementation of a comprehensive environmental safety program in aviation transport.

Most recently, experts and specialists in the field of the aviation industry have concluded that the using of passenger flight services as well as freight aircraft services have been much more efficient from an economic point of view than the using of automobile transport.So, in general, a passanger jet needs 100 times more fuel for a flight than an automobile. But if you talk about fuel consumption for a trip to a particular distance, in this case, that the needs of the aircraft will be almost 2 times less than for the automobile transport.

Let's consider this situation on a concrete example. How will the amount of necessary fuel for the Boeing 747 passenger aircraft and the Honda Civic passenger car differ, in overcoming the distance from Chicago to London?

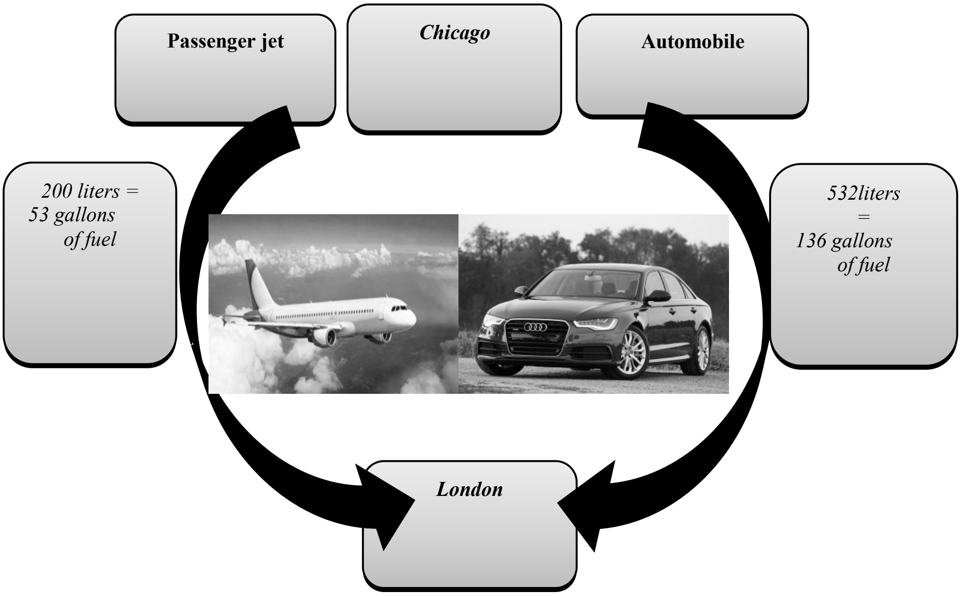

Fig. 1. Airplane and automobile movement relative to the same distance
with different costs of high-quality fuel

During the movement of the passanger jet 4 liters (1 gallon) of jet fuel are being burnt, and as a result 11 kg of carbon dioxide emissions are got into the environment, taking into account that the number of passengers might reach 200 people. At the same time, 4 liters (or 1 gallon) of gasoline, during an automobile trip, produce almost 10 kg of carbon dioxide emissions, taking into account the transportation of 4–6 passengers. As you can see, the difference in emissions during combustion of one and the same amount of fuel is practically absent. But let's take into account that in one passanger jet has more passenger seats and makes flights at greater distances in a shorter time than a car.And that information means that our natural ecosystems get more emissions from the automobile transport functioning than as a result of the aviation transport work.

For today, the expert`s observation proves once again that using of aviation industry is more efficient and more economical than an automobile industry.But at the same time production and using of both aircraft and automobile does not decrease, but increases with each passing day as a result of increase in consumer and industrial demand for modes of transport [1].

But is the situation with development and the benefits of the aviation industry so transparent as it seems?According to the article of the international magazine «The Guardian's», experts note that «.... aviation travel might not be a major source of carbon emissions, but it has become one of the fastest growing causes of global warming for many years, taking into account the fact that the industry annually increases by 5 %». At the same time, in the most populous country in the world, which today becomes one of the richest, hundreds millions of Chinese citizens might become the largest number of passenger traffic soon. According to the experts` conclusion of The Boeing Company, Chine`s flights will increase threefold by 2030.

Is the functioning of the aviation industry really such a serious imprint on the natural environment, including ecosystems and individual land territories? Of course, it is not news that frequent flights have caused serious damage to the environment, life and health of the population.But experts might not argue that the aircraft is more serious problem than the latter in the background of other modes of transport.

According to estimates of international experts and specialists, the aviation industry is produced 1.5–2 % of carbon dioxide (CO_2) emissions and other negative chemicals, hazardous compounds in the ratio to the 100 % world's emissions [3].

Official statistics from UK experts inform, that the aviation industry is responsible for releasing hazardous substances to the environment not only during passenger andfreight transportation, but also during various airport maintenanceactivities.

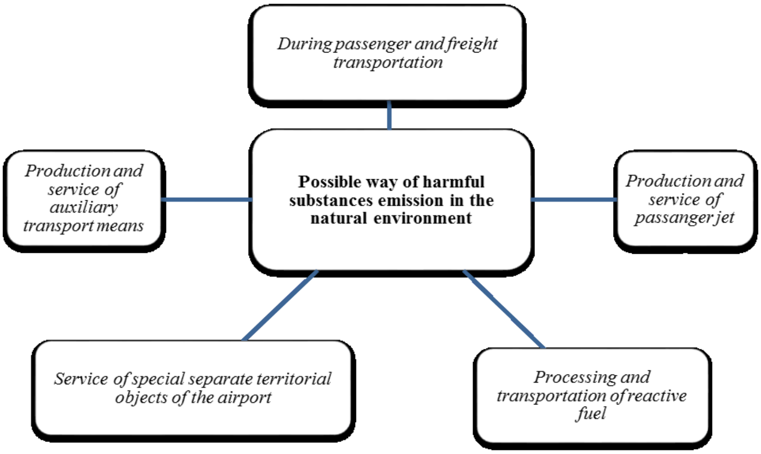

Fig. 2. Ways of harmful substances emission in the natural environments a result of aviation industry`s work

According to Fig. 2, there are different ways of harmful substances emission into the environment as a result of the aviation industry functioning. It is the cause of ever greater and more acute problems in preserving the integrity of natural ecosystems and global thermal balance, as well as the conservation of land and the preservation of soil fertility.Scientists, specialists and world-class experts are constantly working on the creation of new technologies, modern equipment. For today a lot of that things, which have been designed to reduce the impact of flights on the environment, have already been explored, tested and implemented [5].

Compared to more environmentally sustainable automobiles, where the technology of electric motors is fully justified and feasible, while energy-saving resources are enormous, the potential for ecologically balanced and clean flights looks quite transparent and limited.Some future studies in terms of efficiency, economy and environmental friendliness of the engines will be available in the coming decades, and larger passanger jet with a correspondingly larger number of seats will reduce the amount of harmful substances to the environment per passenger. But such transformations will not be related to working with the transformational potential of an electric automobile. After all, the electric motors engines might not produce enough energy to allow the aircraft to climb from the ground into airspace, which is the main problem in that situation. At present, there are special types of biological fuels (which are based on aviation fuel jet) as an alternative to conventional gas.

Now it's an indisputable fact that an alternative fuel option is a technically robust solution that will not require changes to the aircraft or the delivery of other fuels.In November 2009, the Councile of the International Civil Aviation Organization (ICAO) held the Conference on the Use of Alternative Fuels (CAAF) to demonstrate the most advanced production technologies. One of the main question, which was considered in the conference, was the issue of sustainable development, economic realization of production and infrastructure. Member States representatives of the ICAO Council agreed to develop, deploy and use sustainable alternative fuels to reduce atmospheric emissions.The main purpose of the Conference was the creation facilitate, on a global basis, and to promote the harmonization of initiatives that would encourage and support the sustainable development of alternative fuels for aviation [4].

The well-known Japanese scientist Keichi Okay, in his work and research, is considering and proposing the use of potential hydrogen alternative aviation fuels, fundamental combustion and aerodrome system concepts.

Radical efforts are needed to introduce low-toxic fuels, in order to achieve a significant reduction in CO_2 emissions. Using of hydrogen as a promising alternative fuel is based on the assumption of rapid realization, and its undeniable compatibility with the normal life of society.

World research activities related to hydrogen and fuel elements of its implementation, undoubtedly related to the preservation of the integrity of land-resource potential in a separate territory.

The technology of fuel cells attracts attention in more electric planes (MEA). Kaichi Okey is considering the potential of sub-commercial production using hydrogen fuel for other modes of transport.

As aviation fuel, hydrogen clearly has strong and weak sides.The predicted configuration of hydrogen fuel allows future use of subsonic aircraft, which is invariably a compromise solution.

Richard Altman is a Director of Commercial Airlines in the USA, Nate Brown is an Alternate Fuel Manager at the FAA's Environment and Energy Office, USA, Christine S. Lewis is an Environmental Biologist from Volpe; Lourdes K. Maurice is a Chief Scientific and Technical Advisor for Environmental Safety at the Office of the Federal Aviation Administration of England, explore the potential requirements for use and scale of fuel availability level [5].

Although, in spite of everything, the use of alternative fuels is not perfect solution at 100 % according to experts conclusions.After all, the production of biological fuels, which requires a large amount of organic materials, alcohol, wood, waste, might also cause environmentally unstable environment.

So, according to expert estimates at the world level, for the production of biological fuels will be needed almost 5 parts of all land plots on the Planet, which requires the cultivation of such special crops as flax, rape, corn and soybeansBut, this sphere of activity would have a fairly negative impact in order to ensure the work of all aviation industry.But again, we have two important question: will this situation be more serious for the problems of spatial planning and the development of world tricritories, or for the preservation of soil fertility and the protection of land from degradation processes?

Nevertheless, experts are inclined to believe that such a threat will be the same and serious for both parts of question.In this case, there is such a situation that one problem stems from another. These issues will be interconnected, and accordingly, the question of finding optimal, rational and effective decisions will be more serious.

The main important questions of land use development are solved by means of spatial planning prognostication and development processes. These processes are interconnected with main levers of economic growth, population life, protection and rational natural recourses use.

The questions of spatial (territorial) development are the main tool in realization of state policy in the field of effective regulation of land relations for all economically developed countries. That process functions at the national (federal), regional and local levels. State authorities solve many important land use tasks, in particular questions of environmental protection and rational land use.

Of course, the agricultural land necessary for the production of biological fuels will increase significantly due to the need to provide this product for the world aviation industry.As a result, solving of one serious problem would cause of other equally important problems of world significance. After all, during this period of time, the actual number of the earth's population will increase, again the problems in territorially located public settlements will grow, and consumer needs will increase, including the basic nutritional needs for maintaining the vital activity of the population.But we know that only land resources and their unique qualities can provide a normal level of human activity.

Another problem that arises from the provision of aviation industry's needs in the biological fuels production is the problem of reducing the level of soil fertility and the undeniable degradation of quantitative and qualitative characteristics of land resources as a result of the cultivation of technical cultures, for preservation the of natural ecosystems integrity.

Specialists in the field of agricultural activity have been studying the issue of maintaining soil fertility, holding rainwater events, preserving, re-cultivating unproductive and degraded lands for many years.According to expert estimates in the sphere of spatial planning, as well as territorial development and improvement of land resources, almost 15 % of the world's land area are degraded due to the influence of anthropogenic load. Of course, this part includes agricultural land on which the cultivation of biotech crops was carried out. Well-known fact that corn, rape, soybeans require a large amount of nutrients for sufficient development, and as a result, a high level of crop.But without proper measures, in particular crop rotation every 2 years, the fertile soil layer decreases and deteriorat of its quality.Restoration of such exceptional properties naturally takes decades.Of course, the latest technology allows to increase the fertility and high yield and artificial, in the form of organic and inorganic fertilizers. But, all the quantitative and qualitative characteristics of land resources do not change at the better way.

If you look at the situation on the passenger side, then we can conclude that the number of aviation transportation should be reduced, without flights for short distances.But will a modern person refuse such services? And the most important question, whether will all spheres of production, politics and socio-economic spheres of influence be able to abandon air transport forever?

About flights for short distances. Leading EUROCONTROL experts, in the course of constant research and development, argue that short-range flights result in more fuel combustion and, as a result, increase the quantitative emission of hazardous chemical compounds.

Also, none of the activity above-mentioned spheres would be able to refuse of the aviation industry services without changes or losses. As for the political and economic activities of the international community, this is primarily the loss of a number of international transport connections, a decline in the level of socio-economic activity. Of course, the picture of the political system would also have a different look.

Considering of the other modes transport functioning, the railway transport using allows significantly reduce carbon emissions – perhaps five to ten times compared to air transport. Nevertheless, railway transportation is much longer than the aircraft transportation, which is a problem for the modern man. In general, in a certain number of countries, the train uses diesel fuel rather than an electric motor, which, accordingly, causes significant releases of harmful chemicals substances in the environment, and in this case it might be argued that railway transport is more environmentally sustainable than the aviation transport. After all, the outdated model of a diesel train, which is traveling on large distances, might cause the same amount of harmful combustion products as an aircraft. Although in this case the train would not have such a serious impact on the preservation of the thermal balance as a passanger jet. And the last, the ticket for railway transport services might be more expensive than the ticket for aviation transport services .

The influence of harmful substances, that are formed as a result of fuel combustion, on climate processes and their changes is unquestionably difficult, but at the moment, however, is not completely understood. Emissions of carbon dioxide (CO_2) emissions are quite widespread in this area, but flat-air engines also create many other emissions and new chemically-hazardous compounds. There are nitrogen oxide, water vapor and carbon black. These emissions create conditions for the emergence of new dangerous climatic effects that only increase the negative impact on the environment. That effects depend from flight heights in the upper troposphere and lower stratosphere.

Table 1

Type of harmful substance, which are generated as a result of the aircraft engines` work and the effects of their impact

№ in order	Type of harmful chemicals substances	The name of the climatic effect, as a consequence impact	Short characteristics
1	*2*	*3*	*4*
1.	Carbone dioxide	Greenhouse effect	This substance has an enormous impact on climate change.Carbon dioxide is one of the greenhouse gases. It absorbs and holds infrared radiation from the Earth's surface, which contributes to temperature increase in on the planet eventually .This process is called the greenhouse effect. If that process has not happened, the Earth`s temperature would be about 30 °C below. The increase in the level of CO_2 in the Earth's atmosphere leads to an increase in the greenhouse effect, which can cause irreversible changes in the climate. Already, you might observe the melting of glaciers. For example, the level of famous Kilimanjaro snow cap has fallen over the past 100 years by 80 %

Table 1 continue

1	*2*	*3*	*4*
2.	Nitrous oxide	The formation of ozone, which is called greenhouse gas	This substance, like carbon dioxide, has the same effect as greenhouse gas. It causes reactions that destroy methane, which is another greenhouse gas from the atmosphere.
3.	Soot and water vapor	Contrails (condensed water paths)	The interconnection of these substances leads to the "contrails" during the flight of aircraft at high altitudes and at minus temperature. That concept means complex of the condensed water paths, or cirrus clouds.Of course, the research nature of this concept has not reached the unconditional, final conclusions yet. But the scientists believe that this effect is close to theconcept of greenhouse effect, especially at night, when the temperature of air is lowered.

So, the analysis of climatic effects (Table 1), which are formed as a result from the release of harmful chemicals substances as a consequence of the aircraft engines functioning, shows that the problems` level are huge and without proper measures the situation will not change for the better.According to data from world-class experts, the overall impact of the aviation transport industry work is almost twice the amount of carbon dioxide emissions according to possible maximum permissible level in the international norms and standards.But the exact values of these data always depend on the individual plane, local climate and time of day.

For an example, consider the features of an aviation flight between New York and California, and according to expert estimates, we get a number of dangerous harmful substances – greenhouse gases, which are equal to 20 % of the emissions generated as a result of the internal combustion engine of a single general automobile for the whole year.Currently, aviation industry accounts for 11 % of all world emissions.

According to the statistical reports, about 20,000 aircraft, which function around the world, are servered three billion passengers each year . Experts predict that by the year 2040 more than 50 planes may be in service, and they are expected to fly much more frequently.But there are several ways to make your plane travel a little green.

According to the World Bank, the average citizen of the United States of America in 2016 formed about 16.4 metric tons of carbon dioxide as a result of constant flights.According to some estimates, an aircraft, that crosses the distance from New York to San Francisco, throws about 0.9 metric tons of carbon dioxide per person.About one eighteenth of carbon emissions falls for an american per year.

According to the experts information of NASA organization 2010, about 25 % of the aircraft's emissions are due to landing and take-off and 2–4 % at the flight period.But, what can flight attendants and passengers make for decreasing harmful substances emissions in the atmosphere?

Table 2

Some interesting facts of local impact zone, that may be help to reduces amount of harmful substances in the natural environment

№ in order	Fact	Short characteristics
1.	Compensation for carbon dioxide emissions by transferring funds for additional planting of trees	Some amount of aviation companies (Delta, United and JetBlue) offer passengers compensation for carbon dioxide emissions to the environment by transferring funds for an additional planting of tree trees – the "green lungs of our Planet.It should be noted that such services are offered not only by airlines, but also by other organizations that deal with ecologically safe use and conservation of natural resources. The Sustainable Travel International organization, which specializes in the implementation and operation of the regulation program, compensation for losses and losses in all corners of the United States, offers the following options: 1) donations of $ 8.95 for the needs and functioning of the Texas Winery; 2) donations of $ 10.75 for the forest conservation program in Peru. Such actions will be able to compensate for almost 0.9 metric tons of carbon per passenger, who will fly from New York to San Francisco in July and in the opposite direction.
2.	Rules for lowering and increasing the window shades of an airplane during landing and take-off	Some rules on the aircraft, reducing and increasing window shades might help reduce emissions. How is it possible? «......When you land at a warm destination, stewardess may ask you to close the windows» as stated by Christine Busher, who is the Delta Air Lines director. According to him, this reduces the amount of required jet fuel used to cool the aircraft when it is on temporary parking site. That actions will be only a small fraction of which ones might be done to counter the entire amount of emissions as a result of aviation engines work. But that is an example, how aviation companies will be able to use fuel efficiently and economically.
3.	Use of a mixed fuel type for the passenger jet needs	Commercial airlines have been using biological fuels for a certain number of passenger flights since 2011.But at the same time biological fuel is mixed with traditional fuel oil in various quantities. Last year United Airlines started to use biological fuel for all its passenger flightsfrom Los Angeles. According to the company «United» informations, biofuels, which have been produced by AltAir Fuels, have reduced at least 60 percent of greenhouse gas emissions compared to conventional jet fuels. Other companies and the US government are working on the development of alternative biofuels for use in aircraft engineering. Recently, more than 190 countries have agreed to reduce carbon emissions from aviation travel by combining compensation and improving efficiency. According to the data and services of the airlines, the passenger is able to check the efficiency, quality and type of fuel, also other characteristics which are used by the particular airline.According to the report of the International Council for Clean Transport, Alaska Airlines and Spirit Airlines were the most efficient carriers in the United States in 2010. American Airlines and Allegiant Air were in the second part of the 15 largest airlines list in the world.

So, as the information analysis from Table 2 shows, even insignificant at first sight actions by the public and aviation staff might have a positive effect on the reduction of harmful influence and efficiency of the reactive fuel using.

If we consider more global methods of reducing the aviation activities impact , then a bright example of world experience is creation of the «green zones». It is the effective environmental decision-making on the territory of the airport and beyond. «Green zones»are included such actions:

− development, exploitation of technologies and equipment for control and reduction of harmful substances emissions and greenhouse gases;

− conservation and replenishment of green plantations in the airport and beyond;

− monitoring and forecasting of climate change;

− introduction of technological processes in the field of energy and resource saving and renewable energy [10].

The concept of «green zones» is widely used in the United States and European countries. They have developed a number of long-term programs and initiatives by 2025. Experts planne to develop new-generation planes with radically new technical and operational characteristics in accordance with the rules and requirements of these zones functioning.

Table 3

Example of functioning «green zone» in the world's airports

№ in order	Country	Airport name	Features of «green zone» implementation and functioning
1	*2*	*3*	*4*
1.	Thailand (Bangkok)	Suvarnabhumi International Airport	The green garden is situated on the ground floor of the airport, which is stylized to the sea, with swam boaton a on green waves , also with a small island «a house of spirits». The airport is similar to a tropical garden.
2.	South Korea (Seoul)	Incheon International Airport	The infrastructure of the airport has an energy-saving terminal, with a mini-city, which includes gardens, waterfalls, and greenareas. The latest energy-saving technologies have been used during the construction of the terminal. Optimization of natural ventilation has been made, lighting and large-scale installation of photocells.
3.	Maldives	Hanimadhoo airport	The air transport system is considered in the context of industrial infrastructure. For example, the infrastructure of the Hanimadhoo Airport (Maldives) is characterized by the efficient use of natural resources and the preservation of natural design. The roof of the airport is designed in the form of a shell on which solar panels are located. This feature ensures not only environmental friendliness, but also compliance with the surrounding landscape. At the aerodrome territory, which is located on the coast, remains untouched. Developers have introduced such high-performance solutions as rainwater and natural light regarding this territory
4.	Canada (Edmonton)	Edmonton International Airport	On the airport territory, Green over Gray company has created a vegetative installation in the form of a vertical green garden on a wall that occupies an area of 430 m2 and employs more than 32 plant species.This design solution reduces the amount of Carbone dioxide emissions, as well as increases the level of water use efficiency.
5.	England(East Midlands)	East Midlands Airport	The airport use swindt urbines, ground water sources for electricity generation, and water purification systems to reduce unwanted emissions into the atmosphere.In the future, it is planned to install an additional number of wind turbines, to develop programs of utilization and reuse of materials.The priority task for management is preservation unpolluted territory around the airport and establishment more environmentally friendly transport links between the city and the terminal.

Table 3 continue

1	*2*	*3*	*4*
6.	USA (Boston)	Logan .nternational Airport	In the United States, it was the first airport, that started to use environmentally friendly materials when handling premises, and has been awarded the LEED (Leadership in Energy & Environmental Design) Certificate of Conformity.In the design of the airport buildings, some factors have been taken into account. There were location, convenience of transport and the use of local building materials.The light is energy efficient, the roof has been made of a membrane that filters water and lets it onto those.
7.	USA (Wisconsin)	Stevens Point Airport	The airport uses solar energy and wind turbines to reduce the consumption of exhaustive natural resources.
8.	USA (Florida)	Northwest Florida Beaches Airport	The airport has been built on environmentally friendly materials, taking into account the site of construction, water indicators and flora, which is easily recover on the treated area.Lighting at this airport is energy efficient, and, among other things, it uses the maximum of daylight due to the special architecture of the building. Renewable energy sources are used for heating and cooling the building.
9.	USA (Denver, Colorado)	Denver International Airport	The Denver Airport project has been designed to make the building truly «green». Airport management has developeda special strategy, which allows gradually reducing harmful emissions to the atmosphere. The airport uses solar energy for heating and power supplies, processing materials.Taxi Park is equipped with electric cars and one of the greenest car parks in the world operates on its territory.
10.	Germany (Berlin)	Berlin Airport	Flughafen Berlin Brandenburg GmbH company has been elaborated strategy, which was called «Berlin Green Airport». Its purpose is to ensure the operation of the air handling unit in an energy efficient, resource-saving and environmentally sound manner.The environmental strategy definesthe main directions of work to wards the establishment of the «greenairport», settingnewstandardsforsustainableoperations.This is supported by its own system of environmental management, which controls all operational processes at the airport affecting the environment and climate.The management of environmental resources involves using of innovative storage technologies in order to increase transport volumes at lower resource costs.
11.	India (Keral)	Cochin International Airport Limited	Cochin International Airport has been the first Indian and the first world airport that has completely switched to solar energy.Also, the airport's activities will be projecting to reduce carbon emissions by 300 thousand tons for the next 25 years , which is equivalent to planting three million trees.

Consequently, we may conclude that the use of «green zones» for airports is a necessary innovative solution for the conservation, protection of natural resources and reduction of the negative impact on the integrity of the ecosystem.An important tool for ensuring the functioning of these zones is the formation of an effective system of environmental management, the introduction and harmonization of environmental policies, taking into account the specific conditions of operation.

As we see the danger from the work of the aviation industry is quite significant, but despite all the leading airline enterprises, international organizations in the field of conservation and environmental use of natural resources, including the International Civil Aviation Organization (ICAO), are investigating the balance between the environmental, social and economic consequences as a result of growth infrastructure capacity and work closely withmanagement bodies, environmental groups, various Planning and Forecasting Institutes, in order to achieve this balance and ensure fulfillment of their obligations to the public and to satisfyrequirements for international mobility.

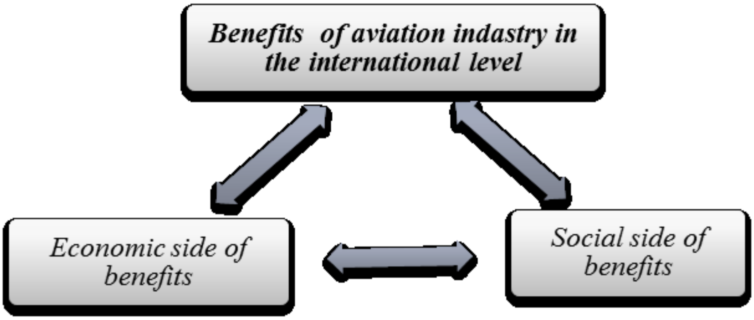

Fig. 2. Socio-economic benefits from the aviation industry

Let's consider the information in Fig.1 in more details.

Economic benefits as a result of aviation industry functioning:

- Aviation Transport is the single global transport network that makes it extremely important for world business and tourism. This sphere plays an important role in the issues of economic growth, especially in developing countries.
- It carries about 2 billion passengers annually and 40 % of inter-regional export of goods.
- According to the percentage ratio, 40 % of tourist trips are carried out by aviation transport.
- The aviation sector provides a total of 29 million jobs worldwide (through direct, indirect, induced and catalytic effects).
- The ratio of global economic consequences as a result of the aviation industry (direct, indirect, induced and catalytic) is estimated at $ 2.960 billion, equivalent to 8 % of the world's gross domestic product. On the whole, the world aviation networks are counted 900 airlines with 22,000 aircrafts.
- The world aviation sphere is served approximately 1,670 airports through a network of routes close to 2 million miles and operated through 160 air navigation service providers.
- It is a highly efficient user of natural, productive resources and infrastructure.
- It is equipped with high-quality technologies and the appropriate level of servicesin comparison with other modes of transport.
- It needs significant maintenance and infrastructure costs. Unlike other modes of transport, it provides a net contribution to the national budget through taxation.
- New generation aircraft (A380 & B787)focused on the efficiency and economy of the jet fuel using. So less than 3 liters falls per 100 passengers per 1 km, whichexceeds the efficiency of any modern compact car on the market.

Social benefits as a result of the aviation industry functioning:

- Provide a significant amount of social benefits.
- Improve quality of life, expanding the public's outlook as cultural and aesthetic qualities.
- Provides a wide range of places rest in all corners of the world and it is an accessible means of visiting friends and relatives living in separated places.

- Helps to improve life`s level and standards of living, reduce poverty, for example, through tourism services, which is offered by either country.
- Promotes sustainable development by expanding tourist and trade routes, which generates economic development, new workplace, increased taxation revenues.
- Facilitates the delivery of emergency and humanitarian assistance to either corner of the Planet, as well as the rapid delivery of medical supplies and organs for transplantation.

As a result of researches, analysis of the threats and benefits of the aviation industry, the public can see, that like any other transport systems, which ultimately depends on the availability of natural and productive resources, aviation might not be considered stable in the very long prospect. Due to the limited natural resources, this area is more realistic at a certain time to think what might we do to improve sustainability rather than to achieve future sustainable development.

Consumer demand for aviation transport services is steadily increasing, and if this demand is satisfied with all related benefits, then it is clear, the level of threat and hurmful impact grow (noise, pollution, climate change, risk, excessive use of resources, etc.).

Well, although it is impossible to make the development of the aviation industry stable in the very long term, nevertheless, some improvements in aviation stability remain real and priority:

- Flight safety;
- Efficient optimization of available power;
- Cooperation of international aviation organizations in order to achieve a common vision of a more stable development of aviation;
- Decision-making based on optimizing the balance between social, economic and environmental imperatives;
- Ensuring mobility needs in this way of meeting the stakeholders needs;
- Use of measures to minimize negative impacts and use of resources by creating, managing more efficient systems, equipment and technologies.;
- Raising the quality of citizens life;
- Investing in a number of research, education, education;
- Transparency and honesty in both the positive and negative aspects of the aviation industry;
- Avoiding controversial policies and regulations.

РЕФЕРАТ

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АВІАЦІЙНА ПРОМИСЛОВІСТЬ XXI СТОЛІТТЯ: РОЗВИТОК ТА НЕОБХІДНІСТЬ ЧИ СЕРЙОЗНІ ЗАГРОЗИ ДЛЯ ПРИРОДНИХ ЕКОСИСТЕМ

На сучасному етапі науково-технічного прогресу авіаційна галузь характеризується розробкою нового обладнання, створенням потужних двигунів, оновленням парку літаків, а також проектуванням нових видів. Та попри все авіаційний транспорт був і залишається масштабним джерелом впливу шкідливих факторів на навколишнє природне середовище. Тож сучасна ситуація призводить до необхідності розроблення та реалізації комплексної програми екологічної безпеки в авіатранспортній діяльності.

Яскравим прикладом світового досвіду щодо прийняття ефективних рішень екологізації середовища на території аеропорту та за його межам є створення так званих «зелених зон» та використання альтернативних видів палива (біологічного палива).

Ключові слова: авіаційний транспорт, вплив шкідливих речовин, розвиток, соціально-економічні переваги.

РЕФЕРАТ

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АВИАЦИОННАЯ ПРОМЫШЛЕННОСТЬ XXI ВЕКА: РАЗВИТИЕ И НЕОБХОДИМОСТЬ ИЛИ СЕРЬЕЗНЫЕ УГРОЗЫ ДЛЯ ПРИРОДНЫХ ЭКОСИСТЕМ

На современнномэтапе научно-технического прогресса, авиационная отрасль характеризуется разработкой нового оборудования, созданием мощных двигателей, обновлением парка самолетов, а также проектирование новых видов. И тем не менее авиационный транспорт был и остается масштабным источником воздействия вредных факторов на окружающую среду. Поэтому современная ситуация приводит к необходимости разработки и реализации комплексной программы экологической безопасности в авиатранспортной деятельности.

Ярким примером мирового опыта принятия эффективных решений экологизации среды на территории аэропорта и за его пределам является создание так называемых «зеленых зон» и использования альтернативных видов топлива (биологического топлива).

Ключевые слова: авиационный транспорт, влияние вредных веществ, развитие, социально-экономические преимущества.

ABSTRACT

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AVIATION INDUSTRY OF XXI CENTURY: DEVELOPMENT AND NECESSITY OR SERIOUS THREATS FOR NATURAL ECOSYSTEMS

At current stage scientific and technological progress, aviation industry is characterized of new equipment, creation of powerful engines, updating fleet of aircraft, as well as designing new types. But, for today, aviation transport remains a large source of harmful factors for the environment. Therefore, the current situation leads to the necessary, development and implementation of a comprehensive environmental safety program in aviation transport.

Now it's an indisputable fact that an alternative fuel option is a technically robust solution that will not require changes to the aircraft or the delivery of other fuels.

A striking example of the global experience in making effective environmental decisions is the creation of so-called "green zones" inside and outside to the airport.

Key words: aviation transport, influence of harmful substances, development, socio-economic advantages.

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3.3 ANALYSIS OF THE ENVIRONMENTAL PROPERTIES OF THE COMPONENTS OF TRADITIONAL AND ALTERNATIVE AVIATION GASOLINE

Sergii Boichenko, Iryna Shkilniuk, Lesia Pavliukh, Kateryna Babikova, Anna Iakovlieva, Roza Vinetskaya

Millions of years under the Earth's surface, oil, did not cause toxic effects on the environment, but people removed it from the bowels of the earth and intensively use for their purposes [1]. Oil, with benefits to person, raises the question the existence not only of people, but every living thing on Earth [2].

The toxicity of petroleum products and gases emitted is determined mainly by the hydrocarbons that are part of their composition. Heavy oil is more toxic than light, and the mixture of hydrocarbons is more toxic through separate components. Significantly increases the toxicity of petroleum products during the processing of sulfuric oil. The most harmful to the human body is the combination of hydrocarbons and hydrogen sulfide, the central nervous system and the brain are attacked.

High regulations on the ecological quality of fuel and lubricants require effective and informative methods for their evaluation. Nowadays, the most environmentally hazardous bioactive polycyclic arenes (PA) – a group of compounds with fused benzene rings. The most carcinogenic include the highest number of PA rings from 4 to 7. These compounds are damaging the immune system of humans and animals, can cause infertility (mostly men), cancer and other serious diseases [3]. Investigated and obvious facts of products' toxicity of oil refining, make it necessary to further study the toxicity of gasoline components.

The purposeof this article is analysis of the environmental properties of components of traditional and alternative aviation gasoline.

Object: background of the optimal component composition of gasoline in the context of their environmental characteristics.

Subject: component composition of traditional and alternative aviation gasoline.

Chemicals have the most hazardous impact on the environment. This include gaseous and aerosol pollutants of municipal origin. It also has negative effect on the atmosphere of carbon dioxide accumulation, the amount of which, unfortunately, moreover increase. This could lead increasing of annual average temperature on Earth in the near future. Pollution of the oceans continue with oil and its derivatives, which covered already 1/5 of the entire surface of the ocean. Such a situation may cause a gas and water exchange disruption between the atmosphere and the hydrosphere. Soil pollution by pesticides and excess of acidity can lead to collapse of ecosystem. All these processes can cause negative changes in the biosphere [4].

The main raw material for gasoline is oil. It is combustible minerals, a complex mixture of hydrocarbons of various classes with a small amount of organic, oxygen, sulfur and nitrogen compounds, which is thick oily liquid [4]. Component (chemical) composition of gasoline – a set of elements from which this kind of gasoline is formed.

Modern aviation gasoline is prepared by compounding of various components, the quality and content of which depends on the brand of gasoline and on the general balance of petroleum products produced at the plant. In industry, the most commonly used are butane-butylene fraction (90 % of *n*-butane, 2–4 % of isobutane and 5–8 % of pentane), technical isopentane (2-methylbutane) and various gas gaselines [5].

There are more than 1000 individual organic substances in the oil content, with different toxicity [6].

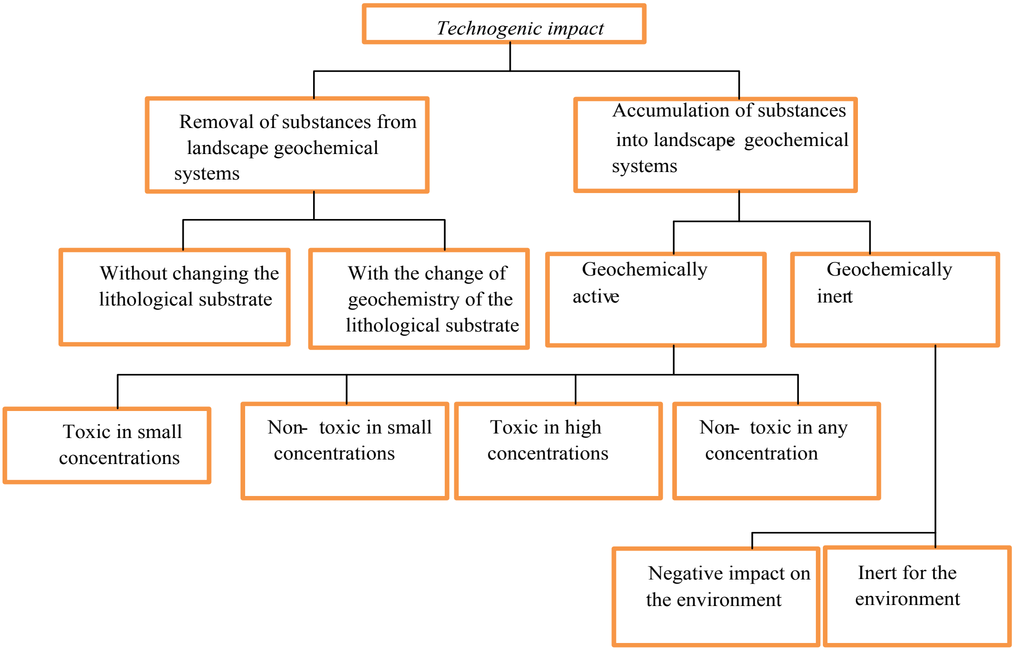


Fig. 1. Scheme of technogenic impact on the biosphere

Toxicity of petroleum products is determined by their hydrocarbon composition. Typically, the high-molcule-weight components are more toxic than low-molecule-weight, and the toxicity of a mixture of hydrocarbons is higher than the toxicity of its individual components. Most carcinogenic hydrocarbons are capable for bioaccumulation. Getting into the soil, the toxic components of oil can turn into even more toxic compounds, adsorb, concentrate and fall into the trophic chains, and get toxins into human body [7].

Light hydrocarbons have a local irritant effect, expressed neurotropic nature. Liquid carbohydrates with a number of hydrocarbon atoms from 5 to 16 have a narcotic and irritant effect, can cause prolonged excitation of the nervous system. When it exposed to the skin, oil causes dermatitis and eczema. All hydrocarbons have an effect on the cardiovascular system and on blood indices (lowering of hemoglobin and erythrocytes), as well as possible damage to the liver, disruption of the activity of the endocrine glands. Recognized carcinogenic action of a number of hydrocarbons [8].

One of the ways of getting gasoline is direct oil distillation [9].

In order to obtain high-quality gasoline, secondary (destructive) distillation of oil is carried out.

The main methods of destructive oil refining and the production of high-quality gasoline are:

- thermal cracking – processing of raw materials at temperatures of 450–500 °C and pressure of 2–5 MPa;
- catalytic cracking – flows at temperatures of 470–530 °C and a pressure of 70–370 MPa in the presence of a catalyst to produce the desired hydrocarbons;
- catalytic reforming is a process of upgrading low-quality gasoline by its catalytic processing under hydrogen pressure in the presence of a catalyst. As a result of catalytic reform, the high octane components of automotive gasoline are released;
- hydrocracking is a catalytic processing of petroleum fractions and residual products of distillation of oil (fuel oil, sludge) under hydrogen pressure to produce gasoline. The hydrocracking proceeds at a temperature of 260–450 °C and a pressure of 5–20 MPa in presence of catalysts;
- hydro-purification is carried out to improve the quality and stability of light distillates at a temperature of 250–420 °C and a pressure of 2–5 MPa in the presence of catalysts.

There are special cases when other hydrocarbon raw materials are used to produce gasoline. Possible flashing off gasoline fractions from semi-coking and coking resins (utilization of heavy residues of cracking in order to produce a distillate of a wide fractional composition) with additional purification. Gasolines are formed from synthesis-gas (coal gasification product, methane conversion) with the help of syntin-process method (Fischer-Tropsch synthesis).

Synthesis is used to produce individual hydrocarbons that have high anti-knock properties and are used as an additive to gasoline. The process is carried out in the presence of catalysts.

In gasoline, depending on the hydrocarbon composition of the raw materials and production technology, there can be more than 200 individual hydrocarbons of different structures [10].

Aviation fuels are middle-distilate oil fractions. They contain hydrocarbons of various classes, heteroatomic compounds and inorganic impurities.

Table 1

Basic classes of hydrocarbons that are part of aviation gasoline [11]

Class of hydrocarbons	Mass fraction of hydrocarbons, %
Alkanes (normal and isometric ctructure)	10–40
Cycloalkanes	20–60
Arenes	20–22

Table 1 continue

Class of hydrocarbons	Mass fraction of hydrocarbons, %
Monocyclic arenes	3–25
Bicyclic arenes	1–5

The most important properties of individual hydrocarbons, which determine their presence in the composition and the impact on the quality of gasoline, are boiling temperature and detonation stability (octane number). These properties, as well as density, maximum allowable concentrations (MAC), hazard class and flash temperature of some individual hydrocarbons of all classes that may be part of the gasoline components are presented in Table 2.

Environmental properties – combination of properties of fuel and lubricants appearing during interaction of the product with the environment and have a negative impact, namely during contact with the means of mechanization in conditions of storage, transportation, transfer and filtration, in contact with man, atmosphere, water, animal and plant world. Environmental characteristics (indicators) include toxicity, carcinogenic, fire hazard and explosion hazard, stability of product quality during storage, transportation, concentration of harmful substances in the exhaust gases of engines, MAC of harmful substances in the working area, the ability of the product to affect environmental pollution.

Flesh point is called the temperature to which it is necessary to heat the fuel, so that its vapor forms an explosive mixture with the air, flaring up when it is exposed to an open flame. The flash point, which is determined in a closed crucible, to some extent characterizes the degree of fuel fire hazard [10, 12]. Coefficient indicating the minimal temperature of a combustible substance, in which, under conditions of testing, a mixture of vapor or gases with air that can ignite in the air from the ignition source, but the velocity of their formation is still insufficient for subsequent combustion (in °C) is formed over its surface.

Table 2

Boiling temperature, octane number, density, maximum allowable concentrations, class of hazard and flash point of individual hydrocarbons that are in gasoline

Hydrocarbon	Hydrocarbon molecular structure	Boiling temperature °C [4,8]	Octane number		Density at a temperature of 20 °C, kg/m, [4, 8]	Maximum allowable concentrations, mg/m^3	Class of hazard	Flash point, °C
			Research method [1]	Motor method[2,3]				
1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
Paraffinic hydrocarbons								
Propane	C—C—C	-42	107,5	110	газ	200	-	472 (t of self ignition)
n-Butane	C—C—C—C	-0,6	93,6	92	600 (0 °C)	300	4	405 (t of self ignition)

Table 2 continue

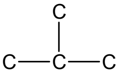
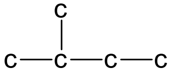
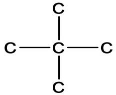
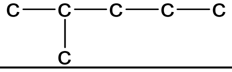
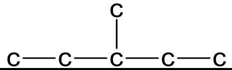
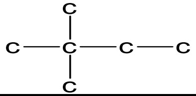
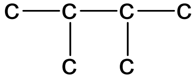
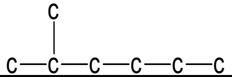
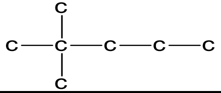
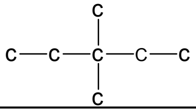
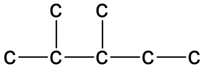
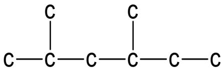
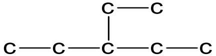
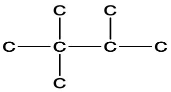
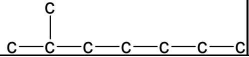
1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
2-Methylpropan (isobutane)		-11,7	101,1	99	600 (0 °C)	NA *	Combustion gas	
n-pentane	C—C—C—C—C	36	61,7	61	626	217	4	-49
2-Methylbutane (i-pentane)		28	92,3	89	620	NA *		<-51
2,2-Dimethylpropane		9,5	85,5	83	591	NA *		Non use
n-Hexane	C—C—C—C—C—C	63,7	24,8	25	659	60	4	-22
2-Methylpentane		60,3	73,4	73	660	NA *		-32
3-Methylpentane		63,3	74,5	75	664	NA *		-6
2,2–Dimethylbutane (neohexane)		49,7	91,8	96	649	0,02	3	-21,6
2,3–Dimethylbutane (diisopropyl)		58,7	101,7	95	662	0,07	3	-29
n-Heptane	C—C—C—C—C—C—C	98,4	0	0	684	200	4	-4
2–Methylhexane		90,1	42,4	45	678	NA *		-18
2,2-Dimethylpentane		79,2	92,8	94	674	0,06	2	-
3,3-Dimethylpentane		86,1	80,8	86	693	0,04	2	-
2,3-Dimethylpentane		89,1	91,1	89	695	0,008	1	-
2,4-Dimethylpentane		89,7	83,1	82	673	NA *		-
3-Ethylpentane		93,5	65,0	69	698	3	3	-32
2,2,3–Trimethylbutane (triptane)		80,9	105,7	101	690	NA *		-
n-Octane	C—C—C—C—C—C—C—C	125,7	<0	-22	702	10	3	13
2-Methylheptane		117,6	21,7	24	698	NA *		-32

Table 2 continue

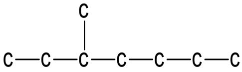
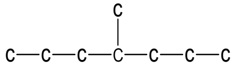
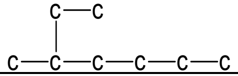
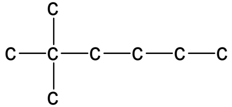
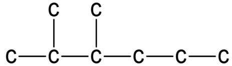
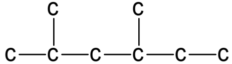
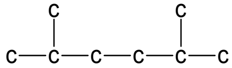
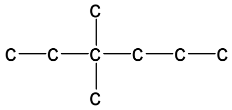
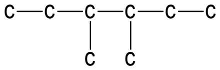
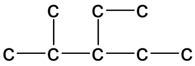
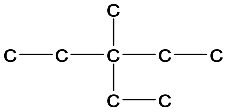
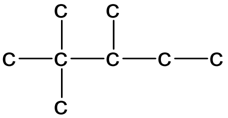
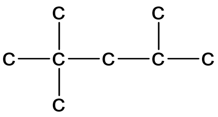
1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
3-Methylheptane		118,9	26,8	35	706	NA *		<-20
4-Methylheptane		117,7	26,7	39	705	NA *		-
3-Ethylhexane		118,5	32,5	52	714	NA *		136
2,2-Dimethylhexane		106,8	72,5	77	695	NA *		-
2,3-Dimethylhexane		113,9	71,3	78	712	NA *		-
2,4-Dimethylhexane		117,7	65,2	70	719	NA *		22
2,5-Dimethylhexane		109,1	55,5	54	694	NA *		26
3,3-Dimethylhexane		112,0	75,5	83	710	NA *		-
3,4-Dimethylhexane		117,7	76,3	85	719	NA *		31, 6
2–Methyl–3-ethylpentane		115,6	87,3	88	719	NA *		-
3–Methyl–3-ethylpentane		118,3	80,8	90	727	NA *		
2,2,3-Trimethylpentane		109,8	104,5	101	716	NA *		
2,2,4–Trimethylpentane (isooctane)		99,3	100,0	100	692	NA *		

Table 2 continue

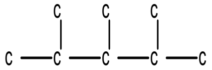
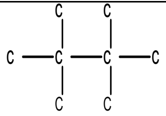
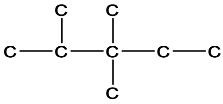
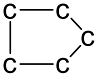
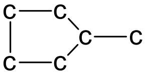
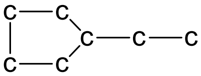
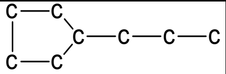
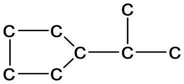
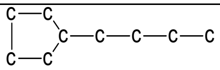
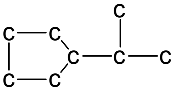
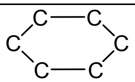
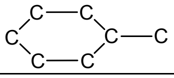
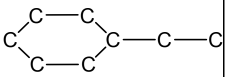
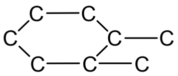
1	2	3	4	5	6	7	8	9
2,3,4-Trimepentane		113,5	101,3	96	719	NA *		
2,2,3,3-Tetramethyl-butane		106,3	103	-	-	NA *		
2,3,3-Trimethyl-pentane		114,8	102,9	99	726	NA *		
n-Nonane	C—C—C—C—C—C—C—C—C	150,8	-	36	718	NA *		
Cyclopentane		49,3	-	84	744	0,1		-
Methylcyclo-pentane		71,8	91,3	81	728	NA *		
Ethylcyclo-pentane		103,5	67,2	62	766	NA *		
n-Propylcyclo-pentane		130,9	31,2	28	776	NA *		
Isopropyl-cyclopentane		126,4	-	76	776	NA *		
n-Butylcyclo-pentane		156,6	0	-1	785	NA *		-
Isobutylcyclo-pentane		154,4	33,4	28	-	NA *		-
Cyclohexane		81,4	83,0	77	718	100		-
Methylcyclo-hexane		100,9	74,8	71	769	3,9-1,8		-18
Ethylcyclo-hexane		131,8	46,5	41	788	NA *	-	-6
Cys-1,2-Dimethylcyclo-hexane trans-		129,7 123,4	80,9	79 79	796 776	NA *		-

Table 2 continue

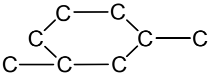
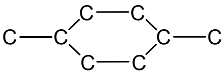
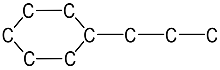
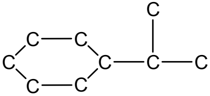
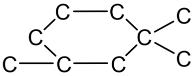
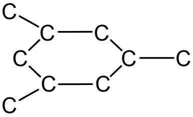
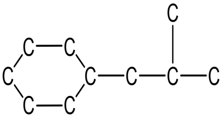
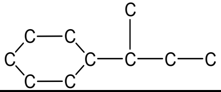
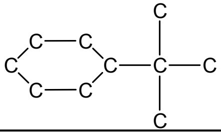
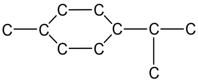
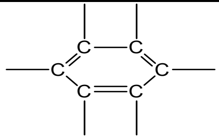
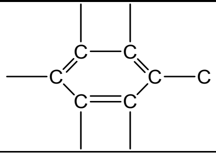
1	2	3	4	5	6	7	8	9
Cys-1,3-Dimethylcyclohexane trans-		120,1	69,3	71 64	766	NA *		9,4
Cys-1,4-Dimethylcyclohexane trans-		124,3	67,8	68 62	783	NA *		15,6
n-Propylcyclohexane		156,7	17,8	14	794	NA *		-
Isopropylcyclohexane		154,6	62,8	61	790	NA *		-
1,1,3–Trimethylcyclohexane		136,6	81,3	83	779	NA *		25,2
1,3,5–Trimethylcyclohexane		140,2	-	-	773	NA *		18,6
Isobutylcyclohexane		171,3	33,7	35	813	NA *		-
sec-Butyl cyclohexane		179,3	51,0	60	795	NA *		-
Tert-Butyl cyclohexane		171,6	98,5	91	810	NA *		40
1-Methyl 4-isopropyl cyclohexane		-	67,3	66	-	NA *		-
Aromatic hydrocarbons								
Benzol		80,1	113,0	108	879	15	2	-11
Toluene		110,6	115,7	102	867	50	3	4

Table 2 continue

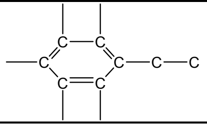
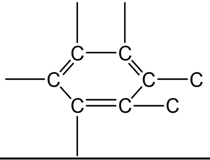
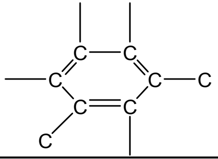
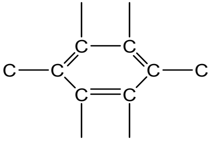
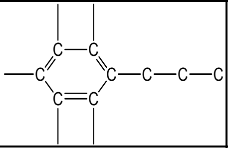
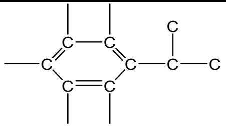
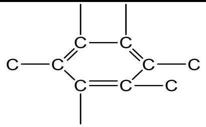
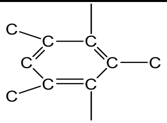
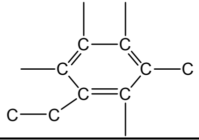
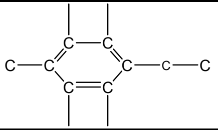
1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
Ethylbenzol		135,2	103,6	98	867	NA *		18
o-Xylol		144,4	-	100	880	NA *		32
m-Xylol		139,0	-	100	864	NA *		27
p-Xylol		138,3	-	100	861	NA *		27
n-Propylbenzene		159,0	105,1	99	862	Unidentified	-	23-60
Isopropylbenzene (Cumene)		152,4	108,0	99	862	0,014	4	31
1,2,4-Trimethyl-benzene		176,1	-	98	894	NA *		48
1,3,5,Trimethyl-benzene		164,7	-	114	865	NA *		50
1,3-Methyl-benzene		161,3	-	100	864	NA *		-
1,4,-Methyl-benzene		162,0	-	97	861	NA *		-

Table 2 continue

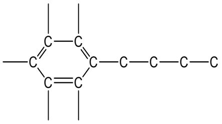
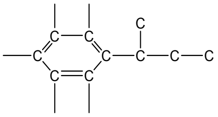
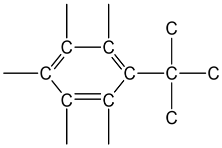
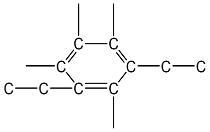
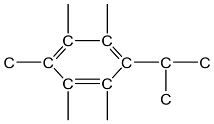
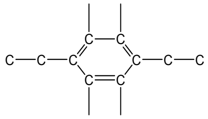
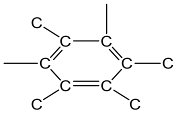
1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
n-Butylbenzene		183,3	-	96	860	NA *		-
sec-Butylbenzene		173,3	-	96	862	NA *		52
Tert-Butylbenzene		169,1	-	106	866	NA *		44
1,3-Diethylbenzene		181,3	-	-	864	NA *		-
1,4-Methyl-isopropylbenzene		177,2	-	98	857	NA *		-
1,4-Diethylbenzene		183,8	-	96	862	NA *		-
1,2,3,5-Tetramethylbenzene		198,2	-	102	891	NA *	62	
Olefinic hydrocarbons								
Propylene	C=C—C	-47,7	101,4	85	gas	NA *		23-61
1-Butene	C=C—C—C	-6,2	97,4	82	618 (0°C)	NA *		Combustion gas
2-Butene	C—C=C—C	3,7	99,6	86	645 (4°C)	NA *		-

Table 2 continue

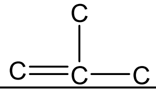
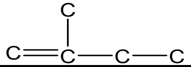
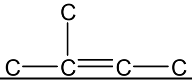
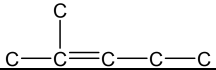
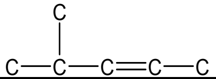
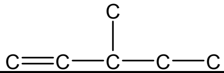
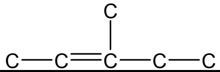
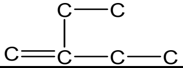
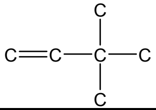
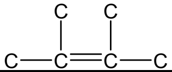
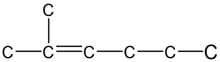
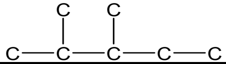
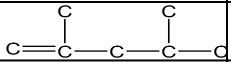
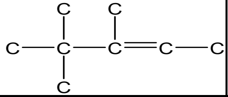
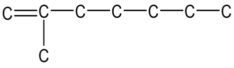
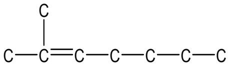
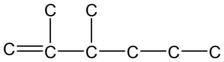
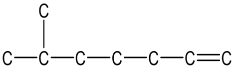
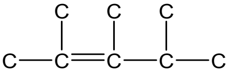
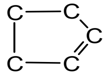
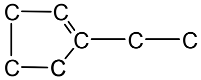
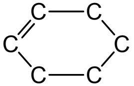
1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
2-Methylpropene		-7	101,5	88	gas	NA *		-76,1
1-Pentane	C═C—C—C—C	30,0	90,9	77	640	NA *		-49
2-Pentane	C—C═C—C—C	36,9	-	80	655	NA *		-49
2-methyl-1-butene		31,2	101,3	82	650	NA *		-48
2-methyl-2-butene		38,6	97,3	85	-	NA *		-45
1-Hexane	C═C—C—C—C—C	63,5	76,4	63	673	NA *		-
2-Hexane	C—C═C—C—C—C	68,8	92,7	81	687	NA *		-
3-Hexane	C—C—C═C—C—C	66,5	94,0	80	680	NA *		-
2-Methyl-2-pentene		67,3	97,8	83	686	NA *		-
2-Methyl-3-pentene		-	99,3	84	-	NA *		-
2-Methyl-1-pentene		54,2	96,0	81	667	NA *		-26
3-Methyl-3-pentene		70,4	-	79	698	NA *		30,2
2-Ethyl-1-butene		64,7	98,3	79	690	NA *		-
3,3-Dimethyl-1-butene		41,2	-	94	655	NA *		-17
3,3-Dimethyl-2-butene		73,2	97,4	80	708	NA *		-
2-Methyl-2-hezene		95,4	90,4	79	709	нд *		-6,6
2,3-Dimethyl-2-pentne		95,1	97,5	80	728	0,05	2	-
2,4-Dimethyl-2-pentene		81,6	100,0	85	694	NA *		-
2,2,3-Trimethyl-3-pentene		-	102,6	90	0	NA *		-
1-Octene	C═C—C—C—C—C—C—C	121,3	28,7	35	722	NA *		13

Table 2 continue

1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
2-Octene	$C-C=C-C-C-C-C-C$	102	56,3	56	715	NA *		-
3-Octene	$C-C-C=C-C-C-C-C$	122,3	72,5	68	719	NA *		-
4-Octene	$C-C-C-C=C-C-C-C$	122,5	73,3	74	721	NA *		-
2-Methyl-1-heptene	 $C=\underset{C}{\underset{\vert}{C}}-C-C-C-C-C$	119,2	70,2	66	720	NA *		-26,1
2-Methyl-2-heptene	 $C-\overset{C}{\overset{\vert}{C}}=C-C-C-C-C$	122,6	75,9	71	724	NA *		-
2,3-Dimethyl-1-hexene	 $C=\overset{C}{\overset{\vert}{C}}-\overset{C}{\overset{\vert}{C}}-C-C-C$	110,5	96,3	84	721	0,08	3	6,7
2-Methyl-6-heptene	 $C-\overset{C}{\overset{\vert}{C}}-C-C-C-C=C$	113,2	63,8	66	712	NA *		-
2,3,4-Trimethyl-2-pentene	 $C-\overset{C}{\overset{\vert}{C}}=\overset{C}{\overset{\vert}{C}}-\overset{C}{\overset{\vert}{C}}-C$	108,4	96,9	80	735	NA *		12,8
Cycloolefinic hydrocarbons								
Cyclopentane		44,2	-	70	772	NA *		lower 23
1-Ethylcyclopentene		103,5	-	72	766	NA *		-
Cyclohexene		83,0	-	63	811	NA *		-6

* - NA – nonavailable

The flash point characterizes the ignition of fuels, defines the safety conditions for the use of fuel in engines. It depends on the fractional fuel composition. The rate of flammability of fuels also characterizes their fire hazards, which is one of the environmental indicators.

Maximum allowable concentration (MAC) – indicator of the safe level of harmful substances content in the environment; maximum amount of harmful substance per unit of volume or mass in aqueous, air or soil environments, which almost does not affect human health [13].

By the degree of influence on the body of harmful substances are divided into four classes of toxicity and danger:

1st class – extremely toxic and extremely harmful;
2nd class – highly toxic and high-risk;
3rd class – moderately toxic and moderately dangerous;
4th class – low-toxic and low-dangerous [14].

On the figures 2–4 there are selected typical representatives of individual hydrocarbons.

The toxicity and carcinogenic of oil and synthetic combustible and lubricating materials in our time is estimated using biological tests on animals. Evaluation methods can be divided into short-term using a large dose of a substance to determine the potential hazard and long-term (from two weeks to three months) using smaller doses. Methods of the second group are useful for identifying the possible consequences of repeated contact with the substance. The most long-term methods – throughout the life of an animal – are used to assess the possibility of cancer and other diseases.

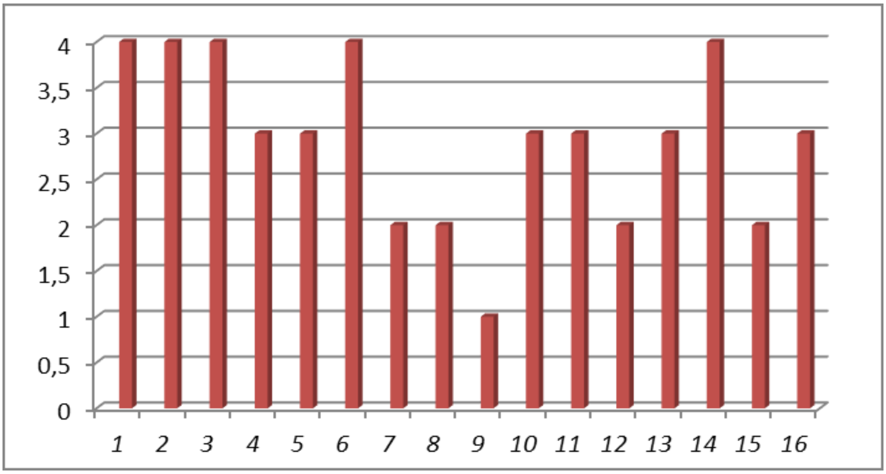


Fig. 2. Danger class of individual hydrocarbons that are in the gasoline component:
1 – *n*-Butene; *2* – *n*-Pentene; *3* – *n*-Hexene; *4* – 2,2-Dimethylbutene (neohexane); *5* – 2,3-Dimethylbutane (diisopropyl); *6* – *n*-Heptene; *7* – 2,2-Dimethylpentane; *8* – 3,3-Dimethylpentane; *9* – 2,3-Dimethylpentaneн; *10* – 3-Ethylpentane; *11* – *n*-Octane; *12* – Benzene; *13* – Toluene; *14* – Isopropylbenzene (Cumene); *15* – 2,3-Dimethyl-2-pentene; *16* – 2,3-Dimethyl-1-hexene

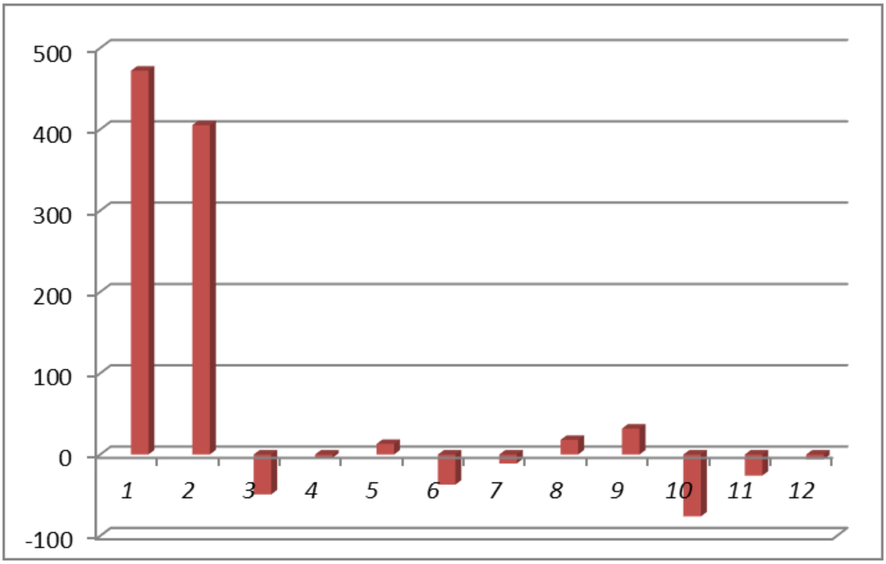


Fig. 3. Flash point of individual hydrocarbons that are in gasoline compound:
1 – Propane; *2* – *n*-Butene; *3* – *n*-Pentene; *4* – *n*-Heptene; *5* – *n*-Octane; *6* – Cyclopentene; *7* – Benzene; *8* – Ethylbenzene; *9* – o-Xylol; *10* – 2-Methylpropene; *11* – 2-Methyl-3-pentene; *12* – Cyclohexene

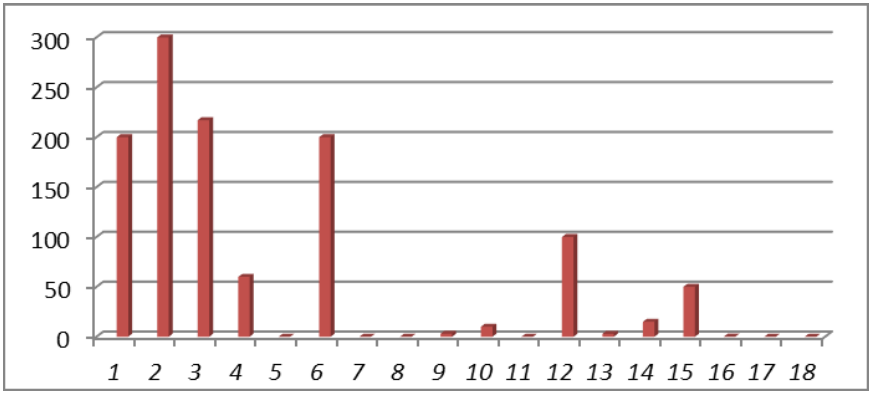


Fig. 4. Maximum allowable concentrations of individual hydrocarbons that are in gasoline compound: *1* – Propane; *2* – *n*-Butane; *3* – *n*-Hexane; *4* – 2,2-Dimethylbutane (neohexane); *5* – *n*-Heptane; *6* – 2,2-Dimethylpentane; *7* – 2,2-Dimethylpentane; *8* – 3,3-Dimethylpentane; *9* – 3-Ethylpentane; *10* – *n*-Octane; *11* – Cyclopentane; *12* – Cyclohexane; *13* – Methylcyclohexane; *14* – Benxene; *15* – Toluene; *16* – Isopropylbenzene (Cumene); *17* – Dimethyl-2-pentene; *18* – 2,3-Dimethyl-1-hexene

The toxicity of oil and its components increases due to the presence of sulfur. The oil, which has little aromatic hydrocarbons, acts like mixtures of paraffins and naphthenes – their pairs have a narcotic effect, often cause convulsive effects. Sulfur compounds of oil can cause acute and chronic poisoning. The most dangerous are hydrogen sulfide, especially dangerous for its connection with hydrocarbons [15].

Paraffin hydrocarbons have the smallest, except olefinic hydrocarbons, toxicity compared with hydrocarbons of other groups. They have a narcotic effect. When paraffin hydrocarbons poisoning appear, there are such symptoms as headache, drowsiness, dizziness, eye irritation and upper respiratory tract. Repeated and prolonged exposure of these products to skin causes dryness and can lead to dermatitis and eczema.

All paraffins belong to the 4-th class of low hazard substances. For hydrocarbons from methane to octane, the MAC of vapors in the working zone air is 300 mg/m^3, for isooctane – 100 mg/m^3. The maximum one-time MAC of butane, pentane and hexane vapors in the atmospheric air is 200, 100 and 60 mg/m^3 respectively.

Methane CH_4, as a source of poisoning, is small compared to its explosion hazard. Since CH_4 is lighter than air, when a person loses consciousness, a person enters the atmosphere with normal O_2 content, but the risk of poisoning still exists. CH_4 is a strong narcotic drug; therefore, certain precautions must be taken when using it.

Ethan C_2H_6 has a narcotic effect on humans.

Known acute human poisoning by steam of propane C_3H_8. Symptoms of poisoning: excitement, deafness, narrowing of the pupils, slow pulse, vomiting, long sleep. On the second day, a slight increase in temperature, a decrease in blood pressure. In case of severe poisoning with prolonged anesthesia, memory loss and pneumonia may be present. C_3H_8 is a strong drug, but because of its meager blood solubility it was dangerous. In chronic poisoning, C_3H_8 does not cause severe organic changes.

Butane C_4H_{10} has narcotic properties. Maximum allowable concentration of C_4H_{10} in air of populated areas is 200 mg/m^3. A person feels the smell of C_4H_{10} in the air when it concentration is 328 mg/m^3. Known cases of people poisoning with gas leakage.

Pentane C_5H_{12}. The smell of pentane is felt at a concentration of vapor 217 mg/m^3. Concentration 14900 mg/m^3 at inhalation for 10 minutes. Does not cause clinical signs of poisoning. Maximum permissible concentration of C_5H_{12} in air of inhabited places is 100 mg/m^3.

Pentane slightly irritates the respiratory tract. There have been cases where C_5H_{12} caused headache, drowsiness, dizziness.

Hexane C_6H_{14} has narcotic properties. Described cases of polyneuritis development in systematic contact with hexane vapor. When in contact with the skin it causes dryness. The highest concentration of C_6H_{14} vapor, which is carried over 8 hours by most people, is 1900 mg/m^3.

Heptane C_7H_{16} in comparison with hexane has a stronger narcotic effect. At a concentration of 0,1 %, insignificant dizziness appears after 6 minutes.

Octane C_8H_{18} with normal conditions – colorless liquid. Slightly soluble in water. Octane is a strong drug that irritates the respiratory tract. With chronic effects, octane does not cause severe poisoning.

C_8H_{18} under normal conditions is a colorless liquid with a specific odor. Drug action of isooctane is poorly expressed. The isooctant pains cause slight irritation of the eyes and upper respiratory tract.

Olefinic hydrocarbons act on the human body as strong drugs, although somewhat weaker than paraffins. Narcotic action increases with increasing number of hydrocarbon atoms in the molecule. The highest members of a number of olefins have, along with narcotics, a pronounced convulsive effect (hexene, heptene), as well as irritating effects on the airways. Hexane pairs act narcotically with the same force as hexane pairs; vapors of hepten are weaker than vapors of heptane.

Naphthenic hydrocarbons. Total toxic effect of naphthenic hydrocarbons is similar to the action of paraffine. The narcotic effect of naphthenic is higher than the corresponding paraffines. The derivative of cyclohexane acts more strongly than derivatives of cyclopentane with the same number of hydrocarbon atoms in a molecule. According to toxicity, naphthenes occupy an intermediate position between paraffinic and aromatic hydrocarbons.

Cyclohexane C_6H_{12} has narcotic properties that irritate the skin. The MAC of cyclohexane vapors in the air of the working zone is 100 mg/m^3.

Methylcyclohexane C_7H_{14} under normal conditions is a colorless liquid with a smell of gasoline. The smell of C_7H_{14} is perceived at a concentration of 3,9–1,8 mg/m^3. Its vapors strongly irritate the mucous membrane, when it hits the skin itching. When chronic poisoning is marked by changes in blood, similar to poisoning with benzene. Poisoning by C_7H_{14} vapor can be, as a rule, only with faulty equipment, poor ventilation of the room; in other cases the risk of poisoning is small.

Light aromatic hydrocarbons in comparison with hydrocarbons of other homologous groups have increased toxicity.

Benzene C_6H_6 under normal conditions is a colorless, easily movable liquid with a characteristic smell. Has an increased narcotic effect. The toxicity of benzene vapor is much higher than that of petrol vapor. Chronic inhalation of benzene vapors, even at low concentrations, can lead to serious illness. In accordance with GOST 12.1.005, benzene belongs to the 2nd class of highly hazardous substances; physiologically very active. In large concentrations of steam, damage to the central nervous system can also cause fatty degeneration of the vascular walls of the internal organs and severe damage to the blood forming organs (bone marrow), decreased blood coagulation, subcutaneous hemorrhage and bleeding.

Toluene C_7H_8 under normal conditions is a colorless, mobile fluid. The MAC of toluene vapors in the working zone air is 50 mg/m^3. The threshold of odor of toluene is 1,8 mg/m^3. MAC in the air of inhabited places – 0,6 mg/m^3, in water – 0,5 mg/dm^3. Toluene vapor at high concentrations has narcotic effect, as well as affect the nervous system, have irritant effects on the skin and the mucous membrane of the nose, eyes and throat. When acute poisoning with toluene appears headache, nausea, loss of consciousness.

Propylbenzene C_9H_{12} under normal conditions is a liquid. MAC has not been established, only the study of the toxic properties of C_9H_{12} on animals (white mice) when introducing propylbenzene into the stomach. There was arousal, quickly transient into oppression, death for 1–4 days. With a long-term supply of C_9H_{12} in the stomach (0,25 g/kg), a tendency towards leukocytosis appears.

Isopropylbenzene (cumene) C_9H_{12} under normal conditions – a liquid with non-diffident odor. Poorly dissolved in water, mixed with organic solvents. The concentration of 0,025–0,1 mg/m^3, which is minimal in smell, is tangible. In acute poisoning acts more strongly than benzene and toluene, anesthesia occurs more slowly, but continues longer, during inhalation causes acute and chronic lesions of blood forming organs (bone marrow, spleen). MAC in air – 0,014 mg/m^3, in water in the reservoir – 0,1 mg/dm^3 [16].

Emissions of harmful substances into the atmosphere continue to grow. Assimilation of harmful substances by the natural process does not have time for their receipt. There is accumulation of these substances in the atmosphere, soil, water. There is a threat to the development of the greenhouse effect, the destruction of the ozone layer of the Earth, the accumulation of carcinogenic and mutagenic products, sometimes falls acid rain. All this has negative effect on the environment, on agricultural production, on public health [17].

In the combustion products liquid fuels derived from petroleum, in addition to the final combustion products, CO_2 and H_2O, usually there are still CO, $SO_x \cdot NO_x$, without burning down and again forming numerous carbonaceous C_nH_m, soot and other products.

Alkanes, saturated hydrocarbons (paraffines) – saturated acyclic hydrocarbons having general formula C_nH_{2n+2}, they are also called paraffines. Most of their chemical reactions with different reagents begin with the breakdown of C–H, whereas their decomposition at high temperatures is primarily due to the C–C bond.

Alkanes form a significant part of hydrocarbons, oil and natural gas. All alkanes of normal structure, from methane to tritriacontane ($C_{33}H_{68}$) inclusive, are isolated from oil and combustible gases. Since alkanes contain the highest possible amount of hydrogen in a molecule, they are characterized by the greatest mass heat of combustion (energy intensity), and with increasing number of atoms, the mass heat of combustion of alkanes decreases (in methane 50207 kJ/kg). Due to low density, the volumetric heat of combustion of alkanes is less than that of hydrocarbons of another structure with the same amount of carbon atoms in the molecule. By aggregate composition, alkanes are divided into gaseous (C_1–C_4), liquid (C_5–C_{17}) and solid (starting with C_{18}), which crystallize at 200 °C.

Alkanes form the main part of hydrocarbons in oil of all deposits and natural combustible gases. The total content of alkanes in the petroleum is mainly 25–30 % (without dissolved gases), taking into account dissolved hydrocarbons, their content increases to 40–50 %, and in some oil – up to 50–70 %, although there is oil with an alkane content of 10–15 %. With increasing average molecular weight of oil fractions, the content of alkanes in them tends to decrease.

Cycloalkanes (naphtenes) are hydrocarbons with one or more carbon cycles. The general formula C_nH_{2n} or $(CH_2)n$.

In general, cycloalkanes are similar in physical properties to the corresponding alkanes, but have a slightly higher melting and boiling point, more density. These properties they have due to stronger London forces, because the cyclic form contributes to the greater surface of intermolecular contacts. Cycloalkanes exhibit virtually the same chemical passivity as alkanes (containing stable C–C and C–H bonds). However, cyclic stress can contribute increasing reactivity.

Alkenes (olefins), unsaturated acyclic hydrocarbons having general formula C_nH_{2n}. Light alkenes, for example, ethylene and propylene, are gases that are obtained from fractions when oil is cracked. Alkenes have one double bond between carbon atoms, so they are called unsaturated. Another name of the series is olefinys (but this term also refers to polyenes).

Olefines are widely used for polymers production, as well as for the synthesis of olefines derivatives: dichloroethane, ethylene glycol, isopropyl alcohol, acetone, acrylic acid nitride and many other compounds of great importance.

The first three members of the series of olefines are gases, followed by liquids that do not mix with water; higher olefines are solids. With increasing molecular mass, the melting and boiling temperatures increase. Alkenes of a normal structure are boiling at a higher temperature than their isomers having an isometric structure. The boiling point of cis-isomers is higher than trans-isomers, and the melting point is the opposite.

Arenes (aromatic hydrocarbons) are organic compounds belonging to the class of carbocyclic compounds. As part of the aromatic hydrocarbon molecule, there is one or more groups of 6 carbon atoms (Carbon) connected in the ring (benzene nucleus) by closed system of conjugate pi-bonds. According to modern notions, Carbon atoms in the benzene nucleus are connected by electrons of two types: some electrons are contained in the plane of the molecule, others are perpendicular to it.

Monocyclic (single-ring: benzene, toluene) arenes – colorless liquids with specific odor, volatile, flammable, lighter than water, do not dissolve in it. Well soluble in organic solvents, are solvents for many organic substances.

Oxygenates – general name of lower alcohols and ethers, high octane components of motor fuels. Usage of oxygenates expands the resources of fuels and can often improve their quality. Oxygenated gasolines are characterized by improved washing properties, combustion characteristics, and during combustion, they form less carbon monoxide and hydrocarbons.

Recommended concentration of oxygenates in gasolines is 3–15 % (volume) [18] is selected so that the oxygen content in the fuel does not exceed 2,7 %. This quantity of oxygenates, despite their lower calorific value in comparison with gasoline, does not have negative effect on the strength characteristics of the engines.

Oxygenates, as components of gasoline, are characterized primarily by octane mixing numbers, saturated vapor pressure, and heat-generating capacity.

Water-absorbing capacity of oxygenates affects the phase stability of fuel mixtures containing oxygenates, which manifests itself as turbidity of fuels at reduced temperatures.

There are used alcohols, ethers, mixtures and alcohol-based wastes from food and petrochemical industries.

Octane numbers of alcohols are reduced by increasing the length of the hydrocarbon chemical group. (Methanol – Ethanol – Isopropanol – Isobutanol).

As additives to gasoline methanol is used infrequently. This is hampered by its toxicity, poor solubility in hydrocarbons and high water-absorbing capacity. It has negative affects on materials of sealants and hot spot according to non-ferrous metals.

As additives to fuels, ethanol has larger interest than methanol, since it is better dissolved in hydrocarbons and has less water-absorbing capacity. It is widely known to use a gasohol (a mixture of gasoline with 10–20 % of ethanol) in the USA and Brazil, which has vast resources of sugar produced from sugar cane. Ethanol is interesting as an additive to fuel in countries rich in plant resources. Adding 5 % of ethanol to gasoline does not lead to deterioration of engine performance and does not require pre-regulation of the carburetor. At the same time there is a significant decrease in emissions of CO and small – hydrocarbons.

Catastrophic pollution of the environment by products of combustion of fuels, the emergence of the greenhouse effect led to the formation of requirements for engine emissions of toxic products.

One of the most important events in the field of environmental policy was the 21st World Climate Summit (COP 21), carried in Paris in November–December 2015. As a result of work COP 21 signed a final agreement, which obliges all countries to take measures to limit the increase in the average temperature of the planet no more than 2 °C in relation to the average temperature before the industrial era (before 1990). This agreement will substitute the existing Kyoto Protocol, which is limited by 2020.

limit increasing of temperature at 2°C, as well as make every effort to limit the temperature increase to 1,5 °C	increase climate resistance and take measures to reduce CO_2 emissions, while not increasing the problem of food shortages (it is a question of gradually stopping the use of crops as raw materials for biofuels)	direct financial flows to stimulate the development of environmentally sustainable development and technology support, which allows to reduce CO_2 emissions

Fig. 5. The main ideas of Paris Agreement

According to Agreement, each country must develop and adopt a series of measures aimed at solving the tasks, as well as enhance multilateral interaction and cooperation.

The toxic properties of hydrocarbons are very different. However, by this time the issue of toxicity of hydrocarbons is not sufficiently studied and the rationing of their content in the exhaust gases are carried out in total. Air control of the working area during operation with gasoline is carried out in the presence of hydrocarbon vapors (MAC=300 mg/m^3, 4th hazard class in accordance with GOST 12.1.005), gasoline (MAC=100 mg/m^3, 4th hazard class in accordance with GOST 12.1. 005), carbon monoxide (MAC = 20 mg/m^3, 4th hazard class according to GOST 12.1.005).

Toxicity is determined by the chemical and fractional composition of fuels.

For prevebtion of harmful substances contamination and defend environment have been established maximum allowable concentrations (MAC). MAC of harmful substances in the atmosphere – maximum concentration of harmful substances, which belongs to a certain period of averaging: 30 minutes, 24 hours, month, year, without causing, under the regulated probability of its occurrence, no direct or indirect effect on the human body, without reducing human activity and not worsening its health state [19].

Toxicity and fire hazards of petroleum fuels are classified in 4 hazard classes in accordance with GOST 12.1007–76 for the degree of exposure to the body. The hazard class of harmful substances is determined according to standards and standards indicators.

The most dangerous is the poisoning of a couple of fuels through the respiratory system with air. The vapor easily passes through the alveolus of lungs and gets directly into the blood circulation circle bypassing the liver, which plays an important role in delaying and neutralizing toxic substances.

Ecological properties of fuel and lubricants are detected in the interaction of products with the environment, that is, when in contact with the means of mechanization in conditions of storage, transportation, transfer and filtration, as well as in contact with the atmosphere, water, man, animals and the plant world. The quality of the fuel and lubricants depends on the reliability of the engines and machines in general, and, consequently, the cost of their maintenance and repair.

The force of toxicity of fuels and oils depends on the properties of the product, its concentration and duration of exposure, as well as on the ways of penetration into the body, external conditions, in which the work is performed, and individual characteristics of man. Fuel and oil can enter the human body through the respiratory tract, skin, digestive organs and mucous membranes of the eyes. The most dangerous is when fuel vapor or oil passes through the respiratory tract, since poisonous substances come from the lungs easily into the bloodstream. In this case, the poison enters the large circle of blood circulation, passing the hepatic barrier, and operates in 20 times faster.

Given tha data above predetermine the need to find ways to reduce emissions of harmful substances into the atmosphere. The most widely used devices on management and neutralization of harmful substances.

The most important decision of environmental problems in the chemotology of fuel and lubricants should be considered improvement of the quality of commodity products, development of new, environmentally nonhazardous fuels and lubricants [20].

Nowadays, there is developed aviation gasoline containe ethanol. Because it is the most massive product among aliphatic alcohols. Ethanol is best suited for use in practice at the expense of high production and low toxicity. Compared to methanol, it is better dissolved in hydrocarbons. Thanks to ethanol, gasoline is enriched with oxygen and contributes to more complete fuels combustion. Today, biobutanol have great actuality as additive among aliphatic alcohols. During literature analysis revealed that it is the least aggressive to the structural details of the engine, it has the greatest stabilization effect in relation to alcohol-gas mixtures, has octane-enhancing properties and reduces the amount of toxic emissions.

Usage of biofuels leads to improvement environmental characteristics of internal combustion engines: with the increasing of ethanol content in the fuel, the concentration of toxic substances (CO, NO_2, SO_2, CH_2O) in the exhaust gases is reduced.

The composition of the fuel includes hydrocarbon and non-hydrocarbon (heteroatomic) compounds of various classes that determine the physical, chemical and operational properties of fuels (Table 3).

Table 3

Characteristics of physical-chemical properties of traditional and alternative gasolines

Characteristics	Aviation gasoline B91/115	Motor gasoline	Methanol	Ethanol	Butanol	Hydrogen
Density at temperature 20 °C, kg/m^3	Not rated	740–760	792	789,3	810	70
Boiling temperature,°C	40–180	35–200	64,5	78,4	117,5	minus 253
Chilling point, °C	minus 60	minus 60	minus 98	minus 114,1	minus 90,2	minus 259
Mass content of oxygen, %	-	-	50	34,7	21,6	-
Combustion heat, kJ/kg	42947	41000–44000	24000	26945	35520	11820
Evaporation heat, kJ/kg	Not rated	200	1115	839,3	591,2	48
Saturated vapour pressure, kPa	29,3–47,9	45–80 (in summer time)	-	17	8,4	-
Water solubilityat temperature 20 °C, %	Insoluble	Insoluble	No limits	No limits	7,9	-
Octane number: - reaserch method - motor method	Not rated 91	80–98 -	111 94	108 92	99,6 94	30–40 Not rated
Viscosity at temperature 20 °C, mm^2/sec	Not rated	0,5–0,7	-	1,52	3,64	-
Percentage limits in gasoline according EN 228:2000	-	-	3 %	5 %	7–10 %	-

Adding aliphatic alcohols to fuel changes their properties: increase octane number, it allows to reduce the content of aromatic hydrocarbons. The results indicate that 25 % of the concentration of ethanol C_2H_5OH is optimal for use in internal combustion engines.

We find that with the increasing of octane number, the concentration of toxic gases in the exhaust decreases, which improves the ecological properties.

Thus, ensuring the ecological purity of traditional and alternative aviation gasoline will increase the climate sustainability, reduce CO_2 emissions, aimed at fulfilling the basic provisions of the Paris Agreement. After analyzing the environmental properties of the components of traditional and alternative aviation gasoline, it can be concluded that with the reducing aromatic hydrocarbons in the gasoline, saturated it with oxygenates, it is possible to improve the composition of aviation gasoline, thereby reducing the formation of carbon monoxide and hydrocarbons during combustion. The most powerful influence is aromatic and olefinic hydrocarbons, oxygen-containing compounds have a lowering effect of fuel deposits and carbon laydown on the details of fuel equipment and combustion chamber.

In turn, the established direction, encourage the continuation of the scientific and applied research direction: the analysis of the environmental properties of components of traditional and alternative aviation gasoline and their component composition.

РЕФЕРАТ

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АНАЛІЗ ЕКОЛОГІЧНИХ ВЛАСТИВОСТЕЙ КОМПОНЕНТІВ ТРАДИЦІЙНОГО ТА АЛЬТЕРНАТИВНОГО АВІАЦІЙНОГО БЕНЗИНУ

У статті проаналізовано екологічні властивості компонентів традиційних і альтернативних авіаційних бензинів. Встановлено, що зі зменшенням ароматичних вуглеводнів у складі бензинів, насичуючи їх оксигенатами, можна покращити склад авіаційних бензинів, у такий спосіб зменшити утворення оксиду вуглецю і вуглеводнів під час згорання. Зі збільшенням октанового числа концентрація токсичних газів у вихлопі зменшується, завдяки чому поліпшуються екологічні властивості. Використання біопалива веде до покращення екологічних характеристик.

Ключові слова: екологічні властивості, альтернативний бензин, токсичність, біоактивні поліциклічні арени (ПА), компонентний склад, вуглеводні, температура спалаху, гранично допустима концентрація (ГДК), викиди, біопаливо.

РЕФЕРАТ

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АНАЛИЗ ЭКОЛОГИЧЕСКИХ СВОЙСТВ КОМПОНЕНТОВ ТРАДИЦИОННОГО И АЛЬТЕРНАТИВНОГО АВИАЦИОННОГО БЕНЗИНА

В статье проанализированы экологические свойства компонентов традиционных и альтернативных авиационных бензинов. Установлено, что с уменьшением ароматических углеводородов в составе бензинов, насыщая их оксигенатами, можно улучшить состав авиационных бензинов, тем самым уменьшить образование оксида углерода и углеводородов при сгорании. С увеличением октанового числа концентрация токсичных газов в выхлопе уменьшается, благодаря чему улучшаются экологические свойства. Использование биотоплива ведет к улучшению экологических характеристик.

Ключевые слова: экологические свойства, альтернативный бензин, токсичность, биоактивные полициклические арены (ПА), компонентный состав, углеводороды, температура вспышки, предельно допустимая концентрация (ПДК), выбросы, биотопливо.

ABSTRACT

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ANALYSIS OF THE ENVIRONMENTAL PROPERTIES OF THE COMPONENTS OF TRADITIONAL AND ALTERNATIVE AVIATION GASOLINE

In this article have been analyzed ecological properties of traditional and alternative aviation gasoline. We determine that with reducing of aromatic hydrocarbons in gasoline, saturated with oxygenates; it is possible to improve the composition of aviation gasoline, thereby reducing the formation of carbon monoxide and hydrocarbons during combustion. With increasing octane number, the concentration of toxic gases in the exhaust decreases, that improves the ecological properties. Using biofuels leads to improve environmental characteristics.

Key words: ecological properties, alternative gasoline, toxicity, bioactive polycyclic arenes (PA), component composition, hydrocarbons, flesh point, maximum allowable concentration (MAC), emissions, biofuels.

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3.4 ECOLOGICAL APPROACH TO EVALUATION OF THE EFFECTS OF TRANSPORT ON ENVIRONMENT IN INTERMODAL TRANSPORTATION

Viktoria Khrutba[1], Vasyl Mateichyk[1], Oksana Spasichenko[1], Svitlana Marunych[2]

In modern conditions of globalization of the economy, most of the international transportation is carried out with the participation of two or more modes of transport in mixed traffic (in different combinations) on the «door to door» principle. The Association Agreement between Ukraine and the EU provides for the development of multimodal transport as one of the areas for the creation of a stable, efficient and safe transport system integrated with the Trans-European Transport Network TEN-T. In Europe, in recent years, two thirds of international traffic has been carried out in mixed traffic. The Po-Po (roll-on roll-off) technology has become the most widespread. Promoting the development and formation of a flexible national policy on mixed freight and developing multimodal and intermodal transportation is a promising direction for the development of the Ukrainian transport system, as it forces us to search for new ways of solving non-standard transportation issues, and constantly develop and implement new technologies for the transportation process. A rational combination of different types of transport can significantly reduce the total cost and time of transportation, increase the volume of cargo and the number of passenger traffic with the participation of national transport companies, increase the country's competitiveness in the world transport services market, develop the network of existing transport corridors, integrate Ukraine's transport infrastructure into the world transport system [1].

In this connection, requirements for the quality of supply of goods are increased, changes are made in the choice of modes of transport, and progressive forms of cargo delivery are introduced. All this leads to changes in the structure of transportation and, in fact, to a new logistical view of transport and the revision of transport policy in the direction of creating an optimal logistics system, reducing the delivery time, improving the quality of goods, reducing the transport costs of the consumer. Underestimation of the role of logistics as a factor of influence on the efficiency and competitiveness of the country's economy worsen the position of our state in international rankings. In 2016, Ukraine ranked 80th in the world by the index of global competitiveness and ranked 85th in the index of logistic efficiency.

Logistic transport processes, which are an integral part of both production processes and consumption, have a significant human-induced environmental impact. This is largely due to the use of vehicles for the provision and movement of material resources and / or finished products in the logistics chain. At the same time, the requirements for preservation of the environment are constantly increasing, so companies in transport should consider the external costs associated with climate change, air pollution, waste, noise, vibration and accidents. Environmental pollution and irrational use of natural resources potential in the implementation of passenger and freight transport lead to a disturbance in the balance of natural ecosystems, exacerbate the ecological crisis, which is accompanied by a crisis of socio-economic system at the global level [2].

World experience shows that the minimization of environmental impacts in the system of transport logistics requires the use of conceptually new approaches and management methods to mobilize reserves to increase environmental and economic efficiency and ensure the transition from quantitative consumption to more qualitative, harmonization of economic, social and environmental interests of the economy. Consequently, systematic research and substantiation of the need for ecologically-oriented management of intermodal transport in order to create an environment in which the needs of the population are provided, the efficiency of delivery of passengers or goods is increased, and the condition for minimizing the negative consequences of anthropogenic interference in the ecosystem is achieved.

The purpose of the work is to develop the basic principles of ecological logistics in intermodal transportation in order to reduce the impact of transport activities on the environment.

To achieve this goal, the following tasks were formed:

– to characterize the implementation of inter / multimodal transportation;

– to determine the peculiarities of the use of aviation and motor transport in intermodal transportation and its impact on the environment;

– to analyze the existing approaches to the formation of logistics systems on the principles of minimizing the environmental impact;

– to form the basic principles of the formation of an ecologically oriented logistics system for intermodal transportation.

The object of research is the processes of forming logistics systems while ensuring minimization of negative environmental impact.

The subject of the study is a set of theoretical, methodological and practical provisions for the optimization of logistics processes in intermodal transport by aviation and motor transport.

In the modern world, there is a concept that the effectiveness of international trade, economic growth and sustainable development is significantly dependent on the implementation of mixed transport, which involves the integrated use of different modes of transport in one transport system. The feature of intermodal transportation is the use of the benefits of each mode of transport. The criteria for efficiency are not only the cost of delivery, but also the speed, accuracy of delivery, as well as environmental safety and many other factors.

The modern concept of the development of European transport is based on the multimodal and intermodal approach, which involves coordinating the capacities of different modes of transport and time of transportation. The advantage of intermodal and multimodal transportation is the efficient combination of several modes of transport, optimization of transit time, reducing warehouse costs and controlling the cost of transport. As a result, due to the reduction of carbon emissions, the state of the environment is also improving [3] .

The legal basis for intra-modal carriages is: the UN Convention on International Multimodal Transport of Goods (1980); European Agreement on Important International Combined Transport Lines and Related Objects (ULKP / AGTC) of 01.02.1991. with the list of standards and parameters ("Yellow Book"); European Agreement on Important Inland Waterways of International Importance (UMVSH / AGN) of January 19, 1996; Protocol on combined transport by inland waterways to the European Agreement (ULKP / AGTC) of 17.01.1997; Association Agreement between Ukraine and the European Union [4].

Ukraine has virtually no legislative framework for multimodal transport. The consequences of this are close to zero level of multimodal and intermodal transport, first of all, container and low quality of transport infrastructure, which results in low efficiency of logistics, high transport component in the price of goods.

In Ukraine, the transport and logistics network of multimodal transportation is only being created. The most actively used are multimodal and intermodal carriage of goods using road, rail and sea transport. There is a gradual increase in the attraction to the abovementioned transportation of air transport.

The peculiarities of air and road transport for intermodal transport and their environmental impact are considered below.

Transport provides communications between industries, enterprises, regions of the country, foreign countries. Cargo turnover and volumes of cargo transportation for the first quarter of 2018 are given in Table 1 [5].

Road transport is one of the most important areas of entrepreneurial activity, as in the process of managing, each firm needs the transportation of materials, raw materials, finished products, while they use their own vehicles or use the services of motor transport enterprises. Automobile transport plays an important role in the socio-economic development of the country.

Table 1

Cargo turnover and volumes of cargo transportation in January–March 2018

	Cargo turnover, mln. tkm	Volume of transported cargoes, mln. t
Transport	**79219,3**	**150,0**
railway	47261,0	79,1
automotive	9611,9	39,6
water	681,8	0,7
pipeline	21602,0	30,6
aviation	62,6	0,02

Today, more than 100 thousand road carriers provide transportation services for 52 % of passengers and 64 % of goods [6]. Its features are flexibility and adaptability to user requirements. The high level of competition in the industry, the small size of most motor transport enterprises, work mainly with small batches of goods, as much as possible orient the motor transport business for the needs of a particular client. Therefore, road transport has become the dominant type of inland transport in most developed countries.

At the same time, motor transport is one of the main pollutants of atmospheric air. The main component of the negative impact on the environment in the functioning of motor transport is associated with environmental pollution by harmful substances, noise and products of wear. The main harmful substances that pollute the atmosphere are: carbon monoxide; hydrocarbons, including those having carcinogenic properties; nitrogen oxides; solid particles and soot; dioxide of sulfur; lead compounds. In addition, concerns are raised about the increase in carbon dioxide concentrations in the atmosphere resulting from the combustion of extractive fuels, resulting in an increased greenhouse effect, which can lead to unpredictable climatic and consequently economic and social consequences. Its emissions of pollutants to the atmosphere in recent years make up about 1796.5 million tons annually or 90 % of the total emissions of pollutants from mobile sources of pollution in Ukraine (Fig. 1).

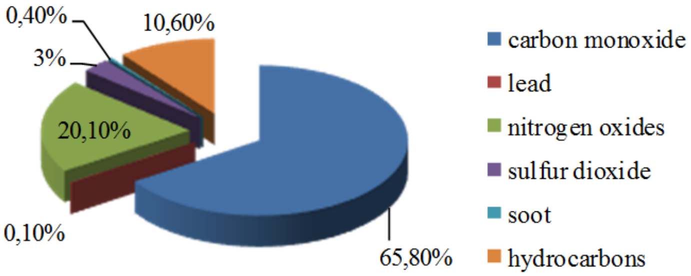

Fig. 1. Composition of exhaust gases of the car

During the operation of motor vehicles, air pollutants are significantly contaminated with solids used for the production of tires. These are isoprene, chloroprene, acrylate and other rubber. As a result of intense movement, the wear of asphalt coatings is increasing, which increases the content of solid particles in the air, including carcinogens. Various mineral salts (sulfates, chlorides and others), which are used on roads during ice-cold, wash off from the roads fall into the soil and reservoirs, cleansing and mineralizing them. The wastewater of the motor transport enterprise, which is polluted by the worked oil products, oils, etc., causes significant losses to the environment. Polluting media used during repair, maintenance and refueling. Toxic are lubricants (motor, transmission, etc.) and mineral-based liquids used for hydrosystems, adhesives and sealants on the basis of formaldehyde and epoxy resins, which are used in the repair and manufacture of cars. Cooling and brake fluids are poisonous. It is known that the share of transport in the total amount of emissions of harmful substances in the atmosphere from stationary and mobile sources is about 70 %, which exceeds the share of any other type of economic activity. In general, according toautomobile engines in Ukraine burn around 2 billion tons of fuel each year. In internal combustion engines, the burning of 1 ton of gas consumes about 15 tons of air, or 2000 liters of oxygen, which is 2.5 times more than its daily consumption by a person. When burning 1000 liters of fuel, the carburetor emits 200 kg of carbon monoxide (CO), 25 kg of hydrocarbons, 20 kg of nitrogen oxides, 1 kg of sulfur oxides and 1 kg of soot. In addition to environmental problems, the economic and social aspects of the functioning of the transport system as an element of the logistics system of the enterprise are equally important.

The features of intermodal transportation for air transport are considered below.

Air transport is one of the youngest and most powerful types of communication. Its advantages are speed, year-round functioning, the ability to deliver goods in hard-to-reach areas. Air transport carries out the overwhelming majority of transcontinental passenger transportation and transportation of goods with a short shelf life for considerable distances.

For the EU, air transport is very important, since it employs 5.1 million workers and accounts for 2.4 % of the gross domestic product (GDP) of the EU (or € 365 billion). Air transport occupies a leading place in the transport of passengers and cargo and promotes economic development, international trade, and opened new markets, especially in the peripheral regions of the EU [7]. In recent decades, their global volume has steadily increased, each year ranging from 5 to 7 %. Ukraine has air connections with many countries, which contributes to the development of intermodal transport. There was a reorientation of passenger flows from domestic to international flights. At present, they account for about 60 % of all passenger traffic. Indicators of Ukrainian airlines are shown in Table 2.

In 2017, passenger and cargo transportation was carried out by 32 companies. 10555,6 thousand passengers and 82,8 thousand tons of cargoes were transported (a decrease from 27,6 % and 11,4 %, respectively, from 2016) [8].

Table 2

Indicators of activity of Ukrainian airlines for the period from 2009 till 2016

	Total								
	Units of measurement	2009	2010	2011	2012	2013	2014	2015	2016
1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*
Passengers transported	thous. people.	5131,1	6106,5	7504,8	8106,3	8110,4	6472,2	6304,3	8277,9
Passenger-kilometers completed	billion pass-km	9,0	11,0	13,8	14,4	12,6	11,6	11,4	15,5
Cargo and mail transported	thous. t	85,1	87,9	92,1	122,6	99,2	78,7	70,6	74,3
Performed ton-kilometers	mln. tkm	350,9	379,1	370,6	363,1	273,1	239,3	218,5	226,4
Commercial flights performed	thous.	84,2	98,9	105,3	106,1	96,0	74,8	66,3	79,5
	International								
Passengers transported	thous. people.	4135,9	5144,3	6328,5	6820,9	6900,3	5828,6	5679,6	7475,4

Table 2 continue

1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*
Passenger-kilometers completed	billion pass-km	8,4	10,4	13,1	13,7	11,9	11,3	11,1	15,2
Cargo and mail transported	thous. t	84,4	87,5	91,9	122,0	98,8	78,2	70,2	74,1
Performed ton-kilometers	mln. tkm	350,5	378,9	370,4	362,8	2792,9	238,9	218,3	226,2
Commercial flights performed	thous.	58,2	71,4	77,8	77,7	71,6	61,3	56,1	67,9

Today, the rapid process of European integration and international environmental standards adopted by forcing enterprises aviation industry to step up its activities to reduce environmental impact. As a result, air transport is contamination of soil, water bodies and the atmosphere, and the specifics of the impact of air transport on the environment found in significant noise performance and significant emissions of various pollutants. It is important to draw attention to the fact that the negative impact of air transport is not limited only to the emission of CO_2 into the atmosphere and the creation of a high level of noise, which is harmful to the health of the population and leads to environmental pollution, and its functioning is primarily due to the use of significant volumes of various resources, in particular natural (Fig. 3).

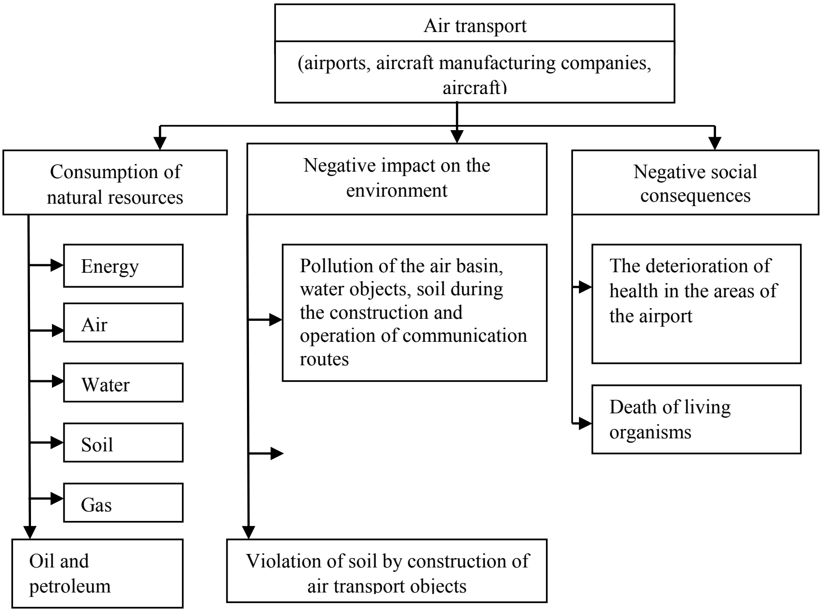

Fig. 3. Influence of air transport on the environment

Aviation transport causes «damage» to nature and population, with a significant proportion of pollution being attributed to airports. For example, flying planes emit thousands of tons of harmful emissions into the atmosphere, with their largest volume coming to take off and the altitude, which indicates their significant concentration in the surrounding areas of the airport, where people live. The share of the total CO_2 emissions from air transport is 2 %. Rapid development of air transport would inevitably cause enormous damage to the environment, but the initiatives that are being implemented by the industry are intended to stabilize, and then reduce noise levels and emissions of greenhouse gases. According to the experts of the world, in order to reduce the noise load and CO_2 emissions, it is necessary to develop the appropriate airport infrastructure, which will eliminate the above-mentioned problems and enable the rapid maintenance of various types of aircraft. The contribution of such measures is estimated by analysts as less significant than the contribution to the renewal of the park and the use of biofuels (about 10 %).

It was determined that aviation transport contributes significantly to the emission of greenhouse gases in the upper atmosphere. Flying at high altitudes and at high speeds results in the dissipation of combustion products, which affects climate change more than other modes of transport. The impact of air transport on the environment is due to the following features of aviation activity: the modern fleet of aircraft and helicopters has gas turbine engines operating on aviation aircraft, the chemical composition of which differs from automotive gasoline and diesel fuel of better quality with a lower content of sulfur and mechanical impurities, the main mass the exhaust gases emitted by aircraft directly in the airspace at relatively high altitudes, at high speed and turbulent flow, and only a small fraction – in the vicinity of airports and settlements. An important problem is the noise of airplanes in the airport area. Factors of the adverse impact of aviation on the environment are noise during the operation of airplanes, emissions of pollutants, electromagnetic radiation, thermal pollution, contaminated drains from the airport [9].

Consequently, an increase in the volume of air transportation in the world leads to the need for effective approaches. It should be noted that Environmental protection is one of the strategic objectives of the International Civil Aviation Organization (ICAO), whose main objective is to reduce the negative impact of global civil aviation on the environment:

– limiting or reducing the number of people suffering from significant noise caused by aviation activities;

– limiting or reducing the impact of aviation emissions on air quality;

– limiting or reducing the impact of aviation emissions of greenhouse gases on the global climate.

Thus, today there are many approaches and methods to minimize the impact of transport activities on the environment, of which the most effective are:

– use of environmental vehicles with electric, gas, hydrogen and hybrid engines, as well as ecological fuel and lubricants;

– driver training, energy efficient driving;

– optimization of routes taking into account the environmental impact;

– an increase in the share of rail and water transportation;

– implementation of schemes of multimodal transportation using mainly rail and water transport, as these transport modes are less harmful to the environment;

– the use of trailers with bunk trailer, and the loading of containers in two tiers, which allows us to rationally use the space of rolling stock and a smaller number of vehicles;

– the use of environmentally friendly loading and unloading equipment.

The most effective approach is to apply a balanced approach to managing environmental impacts during transportation.

Thus, both automobile and aviation transport have a significant anthropogenic impact on the environment and public health. One of the measures to minimize such impact is the introduction of mixed traffic on the principles of environmental logistics. Analyze the existing approaches to the formation of logistics systems on the principles of minimizing environmental impact.

The main task of transport at the present stage is ensuring coordination of the various types of transport on a unified methodological basis; provision of demand for cargo transportation in conditions of system interaction of two or more types of transport; safety and quality of transportation; creation of conditions for financial and economic improvement of transport enterprises and intensification of investment activity; development of scientific and methodological and organizational and technical means of accompaniment of processes of transportation of cargoes under the conditions of interaction of various elements in the structures of logistics.

During the last decade, considerable experience has been gained in improving the general principles and mechanisms of enterprises with the use of logistics. In the writings of domestic and foreign economists, in particular VP Meshalkina, E.V. Mishenina, I.I. Koblianskaya VF Dmitrichenko, PP Levkovtsy, AM Tkachenko, O.S. Ignatenko, LG Zayonchyk, IM The author, K.Klarka, M. Porter, are investigating general theoretical and highly specialized problems of logistics. The literature review shows examples of effective solutions to certain environmental issues faced by modern logistics managers. Müller, for example, has shown the experience of using disposable plastic containers for packaging solid waste management at Proctor & Gamble Company. Shelsey analyzed Canon's program for disposable cartridges for copiers, laser printers and fax machines. Others, such as Polen and Pharys, considered the logistics of channels and issues related to the recycling of plastic waste. Issues relating to the inclusion of an ecological component in the system of logistic management are considered in the works of Yu.V. Chortok, T.M. Skorobogatov, V.P. Mateichyk, V.O. Khrutba, V.I. Zuzjun. It should be noted that their research is most often concentrated within the framework of one functional area of logistics, for example, resource conservation.

Analysis and generalization of domestic and foreign approaches to the interpretation of the concept of "ecological logistics" has made it possible to establish that the scientists who are investigating this problem consider this concept to be largely limited, taking into account the ecological destructive effect of only certain subsystems of the logistic system or only the consequences of such influence. Chortok Yu.V. [10] proposed and theoretically substantiated the interpretation of the concept «ecological logistics» as a subsystem of management of material and associated flows from the primary source to the final consumer, which provides minimization of environmental degradation effects on the environment. This interpretation enables to substantiate the necessity of forming an ecological and economic management mechanism as a macro-logistic system of the city (region) and the micro-logistic system of the transport enterprise. For all levels of drug management it is expedient to consider the following tasks:

- to conduct a permanent audit of carbon emissions in the supply chain;
- transfers of goods mainly to the «green» mode of transport;
- development of «green» vehicles, air and sea vessels;
- reducing environmental impacts during storage;
- increase of ecological efficiency of fuel at cargo and passenger transportations;
- introduction of reverse logistics of waste management;
- creation of a sustainable logistics system of the city;
- state support for the stability of the logistics system.

The experience of well-known companies convincingly proves the high effectiveness of these measures in practice. Thus, Unilever, due to multimodal transportation (reducing road haulage and increasing the share of rail and sea traffic), significantly reduced the level of greenhouse gas emissions and reduced the amount of transport costs. The Japanese shipping company K Line has installed on a separate court a computer system that, on the basis of continuous monitoring of weather and hydrographic conditions, optimizes engine operation, which in turn allows reducing emissions of harmful emissions to the atmosphere by 1 %. The world-renowned express delivery company DHL has developed a service, in the process of implementation customers are being asked to assume responsibility for environmental pollution. The GoGreen service allows you to calculate the amount of CO_2 emissions when transporting cargo from the moment it is accepted by the transport company and until delivery to the recipient. The consumer voluntarily decides to pay additional costs for environmental damage.

The issue of taking into account the full economic and environmental value of transport services is a complex multivariant problem, which involves a comprehensive accounting of economic costs and environmental losses in the logistics system. This approach takes into account the unity of the processes of nature management, consumption of natural resources and the amount of waste that is formed in this case. Below the peculiarities of applying ecological logistics approaches in intermodal traffic are considered.

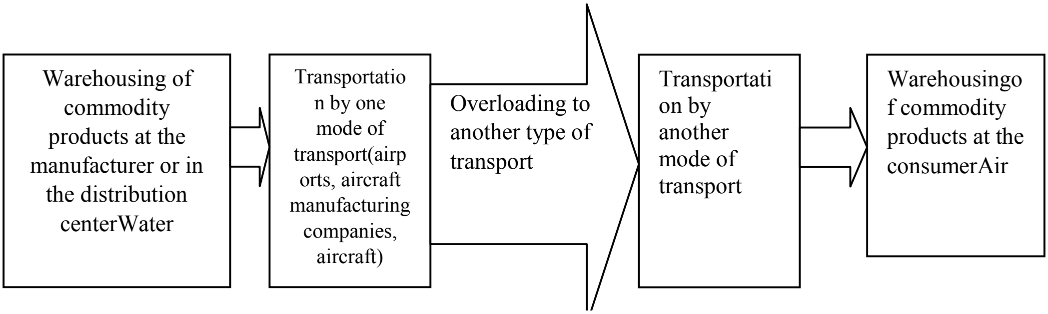

Fig. 4. Logistics chain in intermodal transportation

Transportation is a key integrated component of any process of production or consumption, essence of which is connected with the movement of material resources and finished products by vehicles in the logistics chain. Logistics chain in intermodal transportation includes such processes (Fig. 4).

The conducted researches have determined that modern transportation, in most cases, is a complex object of interaction in the market of transport services. The most frequent cases are the cases of interaction of consumers (senders) of goods with one or two modes of transport (aviation – automobile, railway – automobile, sea (river) – automobile, etc.). The block diagram of the interaction of aviation and automobile type of transport is presented in Fig. 5.

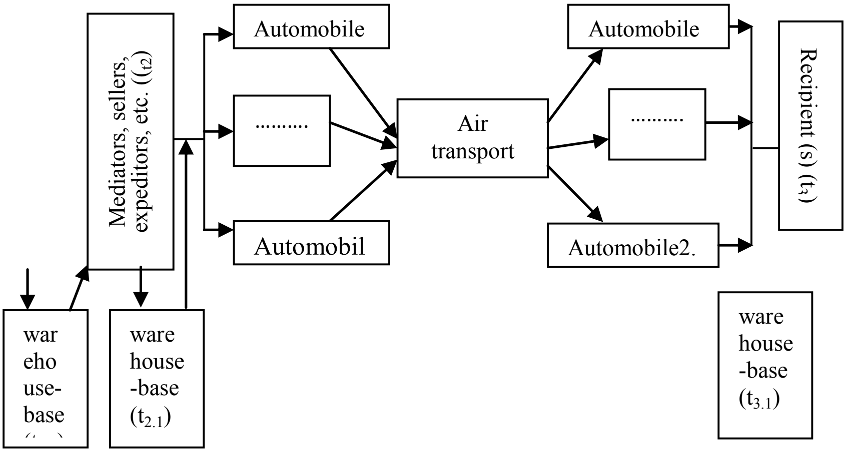

Fig. 5. Structural diagram of interaction of aviation and automobile type of transport

From Fig. 5 it is evident that when using two types of transport, a linear scheme of interaction is implemented, which enables to effectively implement environmental principles in the formation of the logistics system of transportation. Assessment of environmental impacts is carried out for each element of the logistics chain.

We will form a system model for the ecological assessment of the logistic system for intermodal transportation, which is a rolled-up tree of an excessive set of tasks and procedures that can theoretically be carried out in the logistic processes of intermodal transport. The overall assessment of the logistic system for intermodal traffic ($LS_{ІП}$) can be represented by the function:

$$LS_{ІП} = f(W_{ВИР}, W_{СКЛАД}, W^{'}_{ТРАНС.АВТ.}, W_{ТРАНС.ЛІТ}, W^{''}_{ТРАНС.АВТ.}, W_{СКЛ.ЗАМОВН.}), \quad (1)$$

where $W_{ВИР} = f(x_i)$ – the subsystem of production (goods); $W_{СКЛАД} = f(x_j)$ – subsystem of storage of products and goods; $W^{'}_{ТРАНС.АВТ.} = f(x_k)$ – subsystem of transportation by car; $W_{ТРАНС.ЛІТАК} = f(x_n)$ – subsystem of transportation by airplane; $W^{''}_{ТРАНС.АВТ.} = f(x_m)$ – subsystem of transportation by car; $W_{СКЛ.ЗАМОВН.} = f(x_l)$ – subsystem storage of products and goods from the customer; x_i, x_j, x_k, x_n, x_m, x_l – economic and environmental indicators of the system; i, j, k, n, m, l – number of parameters in each subsystem.

The effectiveness of each subsystem is estimated by the local integrated indicator, the effectiveness of the entire drug is determined on the basis of a cumulative approach, taking into account the significance of each subsystem.

$$\begin{aligned} LS_{ІП} &= W_{ВИР} \cdot \alpha_1 + W_{СКЛАД} \cdot \alpha_2 + W^{'}_{ТРАНС.АВТ.} \alpha_3 + W_{ТРАНС.ЛІТ.} \cdot \alpha_4 + W^{''}_{ТРАНС.АВТ.} \cdot \alpha_5 + \\ &+ W_{СКЛ.ЗАМОВН.} \cdot \alpha_6 \end{aligned} \quad (2)$$

The ecological-economic assessment of the logistic system involves solving the multicriterial optimization problem with two targeted functions – minimizing the negative impact on the environment with maximizing the economic efficiency of logistic processes in intermodal transport:

$$W_i = \min \max y_{1_i}(y_{2_i}), \quad (3)$$

where W_i – the minimax optimization criterion of i -*th* subsystem; y_{1i} – the environmental criteria of minimization of i -th subsystem; y_{2i} – the economic criteria of maximization.

The target function for the i -th subsystem of the ecological assessment of the logistic system for intermodal transportation is [29]:

$$W_i = \begin{cases} y_i^1 = \sum_{k=1}^{m} c_{k_i} \cdot x_{k_i} \to \min, \\ y_i^2 = \sum_{k=1}^{m} d_{k_i} \cdot x_{k_i} \to \max \end{cases}, \quad (4)$$

With restrictions:

$$\sum_{i=1}^{m} \sum_{j=1}^{n} a_{ij} \cdot b_{ij} \cdot x'_{ij} < l_{ij}, \qquad x'_{ij} > 0, \tag{5}$$

where y^1_i, y^2_i – ecological and economic efficiency of the i-th subsystem of the logistic system of intermodal transportation; C_{ki}, d_{ki}, – environmental and economic indicators; X_{ki} – input parameters of the i-th subsystems; X'_{Ij} – amount of j-type of waste of the i-th subsystem; m – number of subsystems EOLS; n – quantity of ecological influences in the system; a_j, b_j – correction coefficients of environmental impacts; l_j – maximum permissible and normative ecological indicators.

Determination of optimization parameters of the logistic process will allow to ensure efficient organization of the process of delivery of goods by various modes of transport (intermodal) transportation. The choice of one or another type of transport is due to the relevant criteria, types of goods and other factors that arise in the process of transportation processes.

It is also necessary to take into account that in the case of intermodal transport of goods, two variants of technological processes can be implemented: using the composition (base) between the various transport links and without the use of the latter, which imposes additional tough conditions on the formation of consignments and the work of the respective modes of transport. The conducted studies have shown that the implementation of the above-mentioned options significantly different in terms of cost and performance of transportation and requires the setting and solution of optimization tasks of the logistics system.

Thus, the creation of a logistic system of intermodal transportation taking into account environmental impacts will allow:

– reduce emissions of harmful substances into the atmosphere through the transition to more environmentally friendly modes of transport and vehicles using less fuel, replacing fuel for less harmful;

– reduce costs of material, information and transport flows during transportation;

– take into account environmental factors when placing warehouses;

– minimize material resources when packaging products;

– implement waste recycling systems, reduce the amount of waste generated by the enterprise;

– to finance environmental protection measures in order to create a favorable image for consumers and counteragents, etc.

The obtained scientific results allow to formulate the concept of «Balanced approach» in the organization of intermodal transportation, aimed at increasing volumes of transportation, profit, profitability, reducing the cost of developing a clearly defined business strategy with minimizing human impact on the environment.

Such measures have four main components and require careful assessment of all possible options for reducing environmental impacts, both from road and air transport, including:

– reduction of atmospheric emissions from transport sources,

– planning and use of territories

– technical measures to mitigate environmental impacts,

– operating restrictions, in compliance with the relevant legal obligations and existing agreements, current legislation and implemented strategies.

«Balanced Approach» is an important step towards reducing the level of anthropogenic impact of logistics processes. However, in order to achieve effective and sustainable reduction of environmental damage, it is also necessary to apply more stringent technical standards, such as more stringent environmental requirements, along with measures to decommission obsolete vehicles.

In the framework of a balanced approach, motor transport enterprises and airports are encouraged to first assess the current environmental situation by identifying specific issues using simulation (computer simulation) and monitoring methods. In order to implement effective intermodal transportation for transport enterprises, the following basic elements should be fulfilled:

1. Reducing individual anthropogenic influences through the promotion and support of research, research and technological programs aimed at reducing impacts on the source or other means.
2. Land-use planning and management policies to prevent inconsistent development in sensitive areas. This action combines planning (zoning, easement), mitigation (building codes, isolation, disclosure of real estate information) and financial aspects (tax breaks, fees).
3. Practical application of operating procedures to reduce the harmful effects of transport activities, as far as possible, without affecting safety. These procedures allow to reduce or redistribute environmental damage both in the roadside and in the aerodrome environment.
4. Operating restrictions for a car and aircraft are defined as any limitation related to the environmental consequences. It is used only after considering other elements of the balanced approach. In connection with this, there is a need to address the urgent environmental problems of all spectrum of transport, production, intellectual and social activities at the expense of state and sectoral systems of environmental management.

РЕФЕРАТ

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ЕКОЛОГІЧНИЙ ПІДХІД ДО ОЦІНКИ ВПЛИВУ ТРАНСПОРТУ НА НАВКОЛИШНЄ СЕРЕДОВИЩЕ ПРИ ІНТЕРМОДАЛЬНОМУ ПЕРЕМІЩЕННІ

Сучасна концепція розвитку європейського транспорту заснована на мультимодальному та інтермодальному підходах та передбачає координацію дій різних видів транспорту. Екологічно-орієнтований транспортний менеджмент забезпечує мінімізацію впливу на навколишнє середовище для інтермодальних перевезень.

Метою статті є розроблення принципів екологічної логістики в інтермодальних перевезеннях для зменшення впливу транспортної діяльності на навколишнє середовище.

Для досягнення поставленої мети було поставлено такі завдання: охарактеризувати умови здійснення міжміського транспорту; визначити особливості використання авіаційного та автомобільного транспорту та їх вплив на навколишнє середовище; проаналізувати підходи до формування логістичних систем на принципах мінімізації впливу на навколишнє середовище; сформувати принципи створення екологічно орієнтованої логістичної системи для інтермодального транспорту.

Ключові слова: інтермодальний транспорт, логістична система, автомобільний транспорт, авіаційний транспорт.

РЕФЕРАТ

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ЭКОЛОГИЧЕСКИЙ ПОДХОД К ОЦЕНКЕ ВЛИЯНИЯ ТРАНСПОРТА НА ОКРУЖАЮЩУЮ СРЕДУ ПРИ ИНТЕРМОДАЛЬНОМ ПЕРЕМЕЩЕНИИ

Современная концепция развития европейского транспорта основана на мультимодальном и интермодальном подходе и предполагает координацию действий различных видов транспорта.

Экологически ориентированное управление транспортом обеспечивает минимизацию воздействия на окружающую среду для интермодальных перевозок.

Целью статьи является разработка принципов экологической логистики в интермодальных перевозках с целью снижения воздействия транспортной деятельности на окружающую среду.

Для достижения этой цели были сформированыследующие задачи: охарактеризивать условия осуществления меж / смешанных перевозок; определить особенности использования авиационного и автомобильного транспорта и их воздействия на окружающую среду; проанализировать подходы к формированию логистических систем на принципах минимизации воздействия на окружающую среду; сформировать принципы создания экологически ориентированной логистической системы для интермодальных перевозок.

Ключевые слова: интермодальные перевозки, логистическая система, автомобильный транспорт, авиационный транспорт.

ABSTRACT

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ECOLOGICAL APPROACH TO EVALUATION OF THE EFFECTS OF TRANSPORT ON ENVIRONMENT IN INTERMODAL TRANSPORTATION

The modern concept of the development of European transport is based on the multimodal and intermodal approach and involves coordinating the actions of various modes of transport. The ecologically-oriented transportation management ensures minimization of environmental impacts for intermodal transport.

The purpose of the paperis to develop the principles of ecological logistics in intermodaltransportation in order to reduce the impact of transport activities on the environment.

Following tasks has been formedto acheive the goal: to characterize the conditions of implementation of inter / multimodal transportation; to determine the peculiarities of the use of aviation and road transport and their impact on the environment; to analyze approaches of forming logistics systems on the principles of minimizing the impact on the environment; to form the principles of forming an ecologically oriented logistics system for intermodal transportation.

Key words: intermodal transportation, logistics system, road transport, aviation transport.

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3.5 NOISE MONITORING FOR IMPROVEMENT OF OPERATIONAL PERFORMANCES OF THE AIRCRAFT IN VICINITY OF AIRPORTS

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The aircraft noise is usually the single or somewhere one of the most important local impact factor arising from airport operations which, unless managed effectively, has the potential to constrain the ability of airports to grow in response to demand and hence limit the social and economic benefits that future growth could bring [1]. People living around the airports are driven to complain when some nuisance factor (or stressor) in the environment gives rise to annoyance and/or sleep disturbance when this stressor reaches a threshold of tolerance. Polish Environmental Protection Law (EPL) [2] treats noise as an environmental pollution, hence this Act adopts the same general principles, obligations and forms of proceedings in relation to noise, as to other areas of environmental protection. The EPL also introduces to the legal system of environmental protection a new institution of the so-called noise areas – the areas where the noise level is exceeded to the extent that it requires corrective action via the recovery programs.

According to art. 179 of the EPL, airports are included in list of objects, whose operation may cause a negative acoustic impact on environment in significant areas, and the manager of such airport is obliged to draw up acoustic maps of the area every 5 years, during which the operation of the airport may exceed permissible noise levels for the environment. As required by EPL to control the impact of aircraft noise on population an area of limited usage (noise zone or *obszar ograniczonego użytkowania* in Polish – OOU) is created around any airport in Poland. This area arises when, from an ecological review or from an environmental impact assessment, required by the provisions of the Polish Act of 3 October 2008 on access to information about the environment and its protection, public participation in environmental protection and environmental impact assessments, or post-implementation analysis shows that despite the use of available technical, technological and organizational solutions, environmental quality standards outside the airport area can not be met.

Noise from the aircraft is limited by ICAO standards [3] and due to corresponding Polish Aviation Law, art. 53.1 [4] in the scope not reserved for EASA, the President of the Office shall examine compliance with the requirements to be met by aircraft in the scope of environmental protection against noise and pollution of land, water and air, as defined in international regulations and European Union law and regulations issued on based on paragraph 5. Regulation (EC) No 216/2008 of the European Parliament and of the Council of 20 February 2008 on common rules in the field of civil aviation and establishing a European Aviation Safety Agency EASA states that all aircraft (except aircraft specified in Annex II w / in regulation), they must meet the environmental protection requirements for noise in accordance with Annex XVI of the Convention on International Civil Aviation, December 7, 1944, also known as the Chicago Convention [3]. Meeting these requirements is confirmed by the Civil Aviation Office by issuing a noise certificate.

Directive 80/51/EEC, as amended by Directive 83/206/EEC, set limits on the emission of such noise. Already in the eighties of the twentieth century, the European Communities' environmental action program stressed the need to take appropriate steps in this area. A concrete expression of these was the adoption by the Council of the European Communities on December 4, 1989 of the directive on the limitation of noise emissions from civil subsonic jet airplanes (89/629/EEC). It sought to establish stricter rules for reducing noise emissions, although airplanes with a maximum take-off mass of 34,000 kg or less and with a capacity of 19 or fewer seats were excluded from its scope.

The Member States of the Communities have been required to ensure that from November 1, 1990, civil subsonic jet airplanes registered after that day in their territory may not be operated in that territory or in the territory of another Member State unless they have been granted an noise certificate in accordance with standards at least equal to those specified in Volume 1, Chapter 3, Part II of Annex 16 to the Convention on International Civil Aviation. Exceptionally, exemptions from this prohibition are provided for:

– aircraft of historical significance;

– airplanes used by an entity from a Member State before 1 November 1989 under a still-existing purchase or leasing agreement which in this context was registered in a third country;

– airplanes rented to a third country entity that have been temporarily removed from the register of a Member State of the Community for that reason;

– an aircraft which replaces another one destroyed in an accident and which the entity is unable to replace by a comparable noise-certified aircraft available on the market, provided, however, that the replacement aircraft will be registered within one year of the resulting damage;

– airplanes powered by engines with a transmission ratio of 2 or more.

The ICAO Balanced Approach (EC Directive 2002/30/EC) was transposed into Polish law though the Aviation Law (Noise Restrictions) [4] especially in its art.71a–71e, which were added to the law for this purposeon 29 of April 2004. They allowed the Head of the Civil Aviation Authority (CAA) to introduce by administrative decision the restrictions or prohibitions on performing air operations to reduce the noise emitted at the airport where, in the last three calendar years, no less than 50,000 air operations were carried out on average per year (In accordance with Directive 2002/30/EC). The applicable prohibitions or restrictions may apply to civil subsonic jet airplanes with a maximum take-off weight of not less than 34,000 kg or to accommodate, according to an airplane type certificate, more than nineteen passenger seats, excluding spaces reserved for crew only. As regards the discussed restrictions, marginal compliant planes are therefore located, i.e. with a cumulated noise margin of no more than 5 EPNdB. By the cumulative margin of noise, the legislator understands the sum of the differences between the permissible noise level and the noise level specified in the airworthiness certificate of the aircraft in terms of noise, according to measurements made at three reference points. The permissible sound level and reference points shall be determined taking into account Chapter 3 of Part II of Volume I of Annex 16 to the Convention on International Civil Aviation.

As the noise generated by aircraft can spread (including the spread of the real flight paths/tracks used in operation in airport under consideration, which are much wider than simply tracks shown in AIP for the airport and used for acoustic maps calculation usually), the OOU can also be extended analogically. To this end, environmental noise monitoring is carried out [5]. Measurement results are the basis for the development of acoustic maps that present average values in relation to the year. Noise maps are helpful in spatial planning and environmental protection processes and contribute to improving the acoustic climate of the city close to airport. This information is the basis for noise protection measures adoption – installing sound absorbing screens, additional planting trees and shrubs, or even changing the course of flights, arrival and departure procedures for aircraft operated in the airport under consideration. In any case the acoustical performances of the aircraft in operation are considered currently as one of the basic operational parameters, which may even to limit the operational capacity of the airport (sometimes called environmental in contrary to operational capacity – the limited number of flights per hour in airport under consideration, which allows to noise limits (limited levels of noise) for this airport in points of control, once again – the points of noise monitoring [5]).

Focusing on national regulations, we can say that one of the most important is the Act of April 21, 2001 [2]. Environmental Protection Law (Journal of Laws of 2008, No. 25, item 150, as amended), which specifies environmental protection principles and conditions for using its resources, is taking into account the requirements of sustainable development [6]. The provisions of executive law in the form of the ordinance of the Minister of the Environment of 1 October 2007 on the detailed scope of data included in acoustic maps and their layout and presentation are also important (Journal of Laws from 2007, No. 187, item 1340), ordinance of the Minister of the Environment of 1 October 2012 amending the regulation on permissible noise levels in the environment (Journal of Laws of 2012, item 1109), or the ordinance of the Minister of the Environment of November 10, 2010 on the method of determining the value of the indicator L_{DEN} noise (Journal of Laws of 2010, No. 215, item 1414).

To evaluate the effect of the protection measures implemented, a comprehensive set of surveys to evaluate the short- and long-term effects should be undertaken. A number of the previous studies indicate that when changes in noise exposure are achieved by source-related measures (quieter aircraft and/or low noise flight procedures implemented, air traffic reduced, etc.), the responses could be higher than those predicted from the exposure-response relationships established from a more stable condition. In studies where the changes include noise screens or insulation efforts, the change may be smaller than predicted. For example, inside dwellings of the “experimental” group that received the noise reduction intervention, an average equivalent noise reduction of 7 dBA was calculated inside the dwellings. But some of intervention studies show that people are often satisfied with an intervention regardless of the result of the intervention (Hawthorne effect). For example, one study show the positive effect equal to average equivalent noise reduction of 5 dBA from informing a population about simply a noise monitoring program realised carefully around the airport. A review of different theoretical approaches explaining such differences can be found elsewhere.

The measurements of aircraft noise and the analysis of the results are necessary in order to protect correctly the local community living in the airport surrounding areas. Permanent or/and temporary noise monitoring to be undertaken usually in their local community on the assumption that aircraft noise will exceed what is considered ‘acceptable’ or legally permissible, and in this connection it is necessary to refer to the legislative controls on aircraft noise.The results show that for airports with low intensity of flights the long term equivalent sound level is heavily changing in relation with the long term maximum sound level, but for high intensity flight traffic this interrelation is quite stable. In the vicinity of airports with low flight intensity the maximum sound level as a noise impact metric is more sensitive than the equivalent level.In general case the purposes of monitoring are described elsewhere as:

1) to assess the current status of the resource to be managed or to help determine the priorities for management,

2) to determine if the desired management strategies were followed and produced the desired consequences,

3) to provide a greater understanding of the system being managed,and

4) to show that population involvement in noise management helps to reach the goals of the noise management program, etc.

Although today in most cases the main concern is the negative impact of aircraft noise, the highest goal is to show that measuring and monitoring the aircraft noise can be used for positive purposes. For example to show in routine mode what an aircraft exceeded the permissible level at a point of noise control, to show even why it was exceeded (flight procedure mistake happened or an aircraft type is quite noisy to be operated in particular conditions), any flight safety issues may be raised with monitoring system usage and at the same moment providing confidence to aviation as a whole. A very new challenge should be expected: how to deliver respite from aircraft noise at the airport that is valued by the community, which is consistent with efficient operations?

The number and location of the monitors is important depending upon the specific role they are to play. Quite usual elements of current aircraft noise monitoring systems are the air traffic data connection for flight events detection (correlation with noise events) and the latest point – gathering the complaints from residents living around. A number of technologies is available currently to provide all these necessary functions independently from airports and air traffic providers and in cost-efficient manner, in such way being available for any airport (or community), which is interesting in efficient noise management.

The typical monitoring system (Fig. 1) consists of four main parts: data sources, data collecting and storing mechanism, data correlation and calculation tool and reporting module.

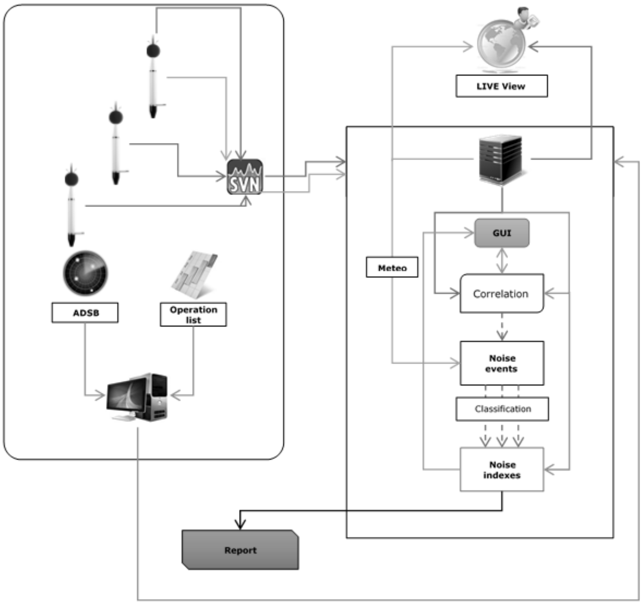


Fig. 1. Architecture of an exemplary noise monitoring system

Data souces:

– Noise monitoring stations, delivering measured acoustic data. For most cases the measured value is $L_{Aeq,}$ logged with a 1 s step but other parameters, such as statistical levels, spectra etc. can also be used. Most measurement instruments can also provide pure audio signal, but despite its versatility and multiple recalculation possibilities it is highly impractical because of large amount of data, which has to be transferred, calculated and then stored.

– Flight path sources, such as radar or ADSB system. Accurate information about the aircraft location, synchronized with noise data is a relevant factor, which improves correct noise events recognition and makes spatial analyses possible.

– Meteorological stations, delivering information about current meteorological conditions. Such information is necessary to assess, whether the acoustic event is correctly measured. Moreover it is relevant for noise modelling.

– Airport flight records, necessary for correct identification of a noise source and also for formal reasons.

The first step to ensure correct functioning of a monitoring system is to properly place the noise monitoring monitors (or terminals). There is a number of criteria which determine correctness of point placement but from technical point of view such placement should ensure low background noise levels, making events extraction possible.

Also there should be no obstacles in the vicinity of the measurement point. Properly located measurement points will strongly influence usefulness of a whole system.

All the data sources described above deliver information in different formats, with varying accuracy and stability. The main task of the collector component is to translate data into common format and common timebase and storing it in a database. This process also includes creating backups of raw data.

This is the key part of the whole monitoring system. Information stored in the system database is correlated, cross-referenced and calculated to obtain desired noise indexes, such as long term noise levels L_{DEN} and L_N. Aircrafts' trajectories and airport operational information are used to extract noise events from the recorded sound level values. Various systems approach this issue differently. Whole task can be performed manually and automatically, with or without possibility of manual supervision. The ideal solution seems to be automatic noise extraction algorithm, which enables the user to manually verify (i.e. with partial audio recording) and correct the output. Each correction should at the same time improve accuracy of the algorithm. Such behavior can be obtained with machine learning approach based on the neural networks. After the events are correctly recognized desired indexes can be calculated.

After the calculations are completed usually the report has to be prepared, considering local requirements and regulations. Report has to cover whole range of activities that had taken place. The monitoring system should also often implement additional functionalities such as live preview of recorded values, automatic verification of data sources condition (most importantly noise monitoring stations).

The noise monitoring systems, which are installed at many airports around the world, range from simple systems measuring the noise levels of individual flights to complex systems, which accumulate and analyze noise data and monitor the flight tracks of aircraft, weather information, complaints of the neighboring population, and so on. It must supply factual analysis of aircraft operations and their consequences for environment and information useful to a surrounding community of the activities taken for environmental noise control. The data and analysis available from the system may improve planning efforts for noise control, such as in aircraft operation, or the best location for residential zones around the airport.

There are many national rules and guidelines that govern the installation of monitoring systems around international airports. During the last two decades around ten airports per year have provided new or improved installations. Initial systems were very simple in design and operation compared with more recent ones.

According to a special ICAO CAEP Work Program, an airport noise monitoring effort should [7]:

(a) compile data on methods used to describe aircraft noise exposure and applications of the data (Fig. 2a);

(b) determine the contribution (general and/or specific by type, route, airlines, etc.) of aircraft to the overall noise exposure (Fig. 2b);

(c) collect data on the characteristics of airports with noise and/or flight path monitoring systems;

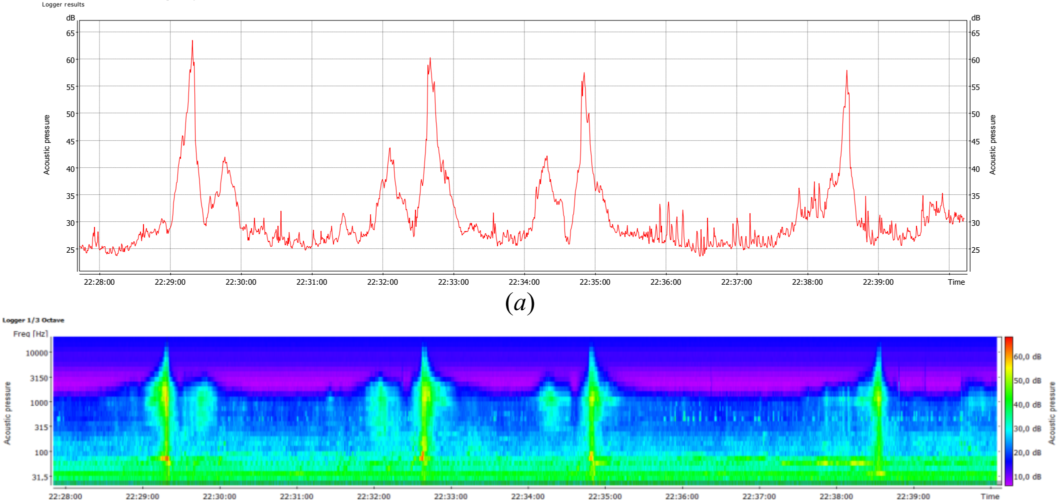
(d) collect details of airport noise monitoring systems such as capabilities, data stored, technical support;

(e) compare calculated and monitored noise levels for a suitable sample of airports;

(f) compare measured noise levels with certificated noise levels for a range of aircraft types and operating conditions;

(g) examine changes in measured noise exposure over a representative time period (Fig. 3);

(h) update advisory documents on methodologies and applications of noise contouring and monitoring, supplemented, for environmental noise management, by the elements of expert and decision-making systems.



(*a*)

(*b*)

Fig. 2. Time history of the registered noise level of aviation noise (*a*) along with the identification of acoustic events (*b*)

This collection of information:

(i) enables determination of the contribution of aircraft to overall noise exposure (Fig. 2);

(ii) enables detection of occurrences of excessive noise levels from aircraft operations;

(iii) enables assessment of the effects of operational and administrative procedures for noise control and compliance with these procedures and/or assess alternative flight procedures for noise control (the tool of objective assessment of efficiency of the proposed operational and administrative procedures for noise control in the vicinity of the airport);

(iv) assists in the planning of airspace usage issues;

(v) increases public confidence that airport related noise is being monitored to protect the public interest (Fig. 3);

(vi) enables validation of noise forecasts and forecasting techniques and their methodologies over an extended period of time (collection of data for noise contouring, system noise exposure forecasting and contouring with compiled data);

(vii) assists relevant authorities in land-use planning for developments and noise impact on areas in the vicinity of an airport;

(viii) enables assessment of a Quota Count system (special mitigation procedure which defines an appropriate number of flights of the aircraft of specific types during a specific period of the day without violation of noise limits), among other possible noise mitigation measures; and

(ix) indicates official concern for airport noise by its jurisdiction and its governing bodies and enables provision of reports to, and responses to questions from, Government and other Members of Parliament, industry organizations, airport owners, community groups and individuals.

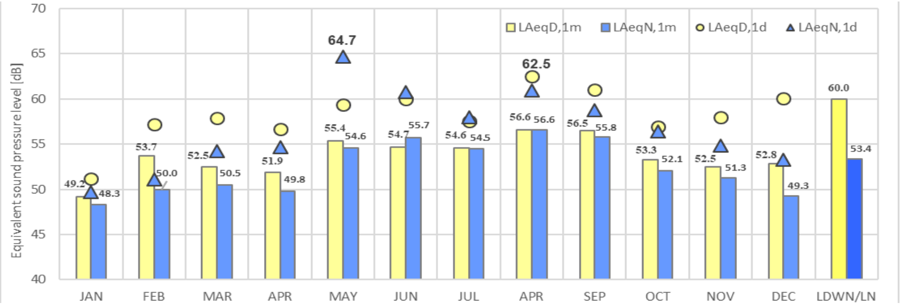


Fig. 3. Equivalent sound level from the period of one day, one month and year for day and night measured at one measurement point

Such a collection of information is basic for assessment of aircraft acoustic performances in real operation in airport under consideration – it is very important for airport capacity assessment from operational and environmental points of view.

Also an airport monitoring system can assist:

(i) in answering noise complaints about aircraft operations from the general public and their enquiries;

(ii) detecting unusual flight events (measurement and verification of noise levels by aircrafts, air companies);

(iii) educating pilots, airlines, airport proprietors, the public (detection of operations which have not complied with flight corridor requirements;

(iv) obtaining statistical data using an objective resources (aircraft types, operating times, usage of flight tracks and routes, of runways, complaints, etc.);

(v) applying research tools to assist the airport in performing certain tasks as required and mandated (planning of airspace usage around the airport, detection of operations which have not complied with flight corridor requirements, determination of the contribution of aircraft to overall noise exposure);

(vi) assessing compliance with mandatory noise levels, established by a governmental entity, etc (measurement and verification of noise levels and flight procedures by aircraft types, air companies, detection of occurrences of excessive noise levels from aircraft operations, etc).

The benefits of operating a noise and flight path monitoring system are substantial. However, these benefits may not be fully realised and the operating agency's credibility may be reduced if insufficient resources are provided to oversee the system's operation and ensure its accuracy. Points to note include the following:

a) The noise and flight path monitoring system generates vast quantities of data, and a methodical process of summarizing and reporting the data is vital. This may take the form of standardized report formats, produced at pre-determined intervals.

b) It is essential to check the accuracy of the data carefully before it is issued publicly. This relates particularly to the noise data, where the system may be performing extensive mathematical calculations on data which has been gathered automatically from unattended instrumentation. With the logarithmic processing which is basic to sound level calculations, it does not require many incorrect inputs to severely distort a summarised average.

c) It is essential to keep records of system outages, particularly in regard to flight track information, to avoid the circumstance where a complainant may be told there was no aircraft operation at the time and place corresponding to that complained about, when in fact there was an operation, but it was not recorded due to a system outage.

d) There is a need to run a preventative maintenance and calibration program, as described in the section on Noise Monitoring Terminals, and this will be an ongoing cost. If the system is used to detect violations of noise limits and/or of flight corridor boundaries, for the purpose of prosecution of offenders, then the records of maintenance and calibration data may become evidentiary material in legal proceedings.

e) The process of installation of a noise and flight path monitoring system may be seen as a service to the community in helping to deal with the adverse affects of aircraft operations. However, while the system will provide for a more informed discussion, it is not in itself a solution to those adverse affects.

РЕФЕРАТ

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МОНІТОРИНГ ШУМУ ДЛЯ ПОКРАЩЕННЯ ЕКСПЛУАТАЦІЙНИХ ХАРАКТЕРИСТИК ПОВІТРЯНОГО СУДНА ПОБЛИЗУ АЕРОПОРТІВ

Повітряні перевезення є дуже вигідними для національної та міжнародної економіки, але вони створюють авіаційний шум – деякі види збитків, особливо для населення та екологічних систем в районі аеропорту. Рівень авіаційного шуму є предметом сертифікації літальних апаратів, виробництво та експлуатація літаків з невідповідним рівнем шуму є незаконною. Постійний та/або тимчасовий шумовий моніторинг повинен проводитись, як правило, у місцевій громаді за умови, що шум повітряного судна перевищує "прийнятний" або законно допустимий рівень шуму, і в зв'язку з цим необхідно послатися на законодавчий контроль шумів повітряних суден. Кількість і місце розташування терміналів у системі моніторингу шумів є важливими залежно від конкретної ролі, яку вони повинні відігравати в цій системі.

Ключові слова: авіаційний шум, шумовий моніторинг, термінали в системі моніторингу шуму.

РЕФЕРАТ

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МОНИТОРИНГ ШУМА ДЛЯ УЛУЧШЕНИЯ ЭКСПЛУАТАЦИОННЫХ ХАРАКТЕРИСТИК ВОЗДУШНОГО СУДНА ВБЛИЗИ АЭРОПОРТОВ

Воздушные перевозки являются очень выгодными для национальной и международной экономики, но они создают авиационный шум – некоторые виды убытков, особенно для населения и экологических систем в районе аэропорта. Уровень авиационного шума является предметом сертификации летательных аппаратов, производство и эксплуатация самолетов с несоответствующим уровнем шума является незаконной. Постоянный и/или временный шумовой мониторинг должен проводиться, как правило, в местной общине при условии, что шум воздушного судна превышает "приемлемый" или законно допустимый уровень шума, и в связи с этим необходимо ссылаться на законодательный контроль шумов воздушных судов. Количество и местоположение терминалов в системе мониторинга шумов важны в зависимости от конкретной роли, которую они должны играть в этой системе.

Ключевые слова: авиационный шум, шумовой мониторинг, терминалы в системе мониторинга шума.

ABSTRACT

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NOISE MONITORING FOR IMPROVEMENT OF OPERATIONAL PERFORMANCES OF THE AIRCRAFT IN VICINITY OF AIRPORTS

Air transportation is very beneficial for national and international economy, but it produces an aircraft noise – some kinds of damages, particularly for population and environmental systems in airport vicinity. Aircraft noise levels are subject of aircraft certification, the aircraft with incorrect levels of noise are illegal to be produced and operated. Permanent or/and temporary noise monitoring to be undertaken usually in local community on assumption that aircraft noise will exceed what is considered ‘acceptable’ or legally permissible level of noise, and in this connection it is necessary to refer to the legislative control on aircraft noise. The number and location of the terminals in noise monitoring system is important depending upon the specific role they are to play inside this system.

Key words: aircraft noise, noise monitoring, terminals in noise monitoring system.

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3.6 ESTIMATION OF RADIOCAPACITY AND RELIABILITY OF WATER ECOSYSTEMS

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After the accident at the Chernobyl Nuclear Power Plant large territories of Belarus, Ukraine and Russia were polluted [1, 2]. Almost all of the contaminated land lies on the water catchment area of the Dnipro, so as a result of the surface runoff, radionuclide falls in waters of the Dnipro reservoirs cascade.

For assessment of radioactive contamination the following main concepts have been used.

Reliability – the fundamental property of biological objects that determines their existence and effective functioning in a randomly varying environmental conditions and time. The measure of reliability – the probability of fail-save existence of the system, which can vary from 0 to 1.

Reliability for sequential and parallel systems is calculated according to the following formulas (Table 1).

Table 1

Formulas for reliability for different type of systems

Reliability of the sequential system of n- elements is given by multiplying the probabilities	$P_{sequential} = \prod_{i=1}^{n} P_i$ (1)
Reliability of the parallel system consisting of n-elements is given by multiplying the probabilities	$P_{parallel} = 1 - \prod_{i=1}^{n} (1 - P_i)$ (2)

Radiocapacity factor (by V.I. Korogodin) is defined as the part of radionuclide (tracer – ^{137}Cs) received by separate components of an ecosystem.

In general radiocapacity – a fundamental property of ecosystems, which defines the critical amount of radionuclide that can be stably hold by the biota of the ecosystem without changes of its basic functions (biomass growthand habitat conditioning).

To assess the status and well-being of ecosystems more than 30 different indicators and parameters are used – variety of species, biomass growth, resources abundance etc. An important feature of these indicators is that almost all of them are beginning to change significantly only when the biota is undergoing significant changes. Practically it is very important to have indicators and parameters that allow to assess distribution and redistribution of pollutants in real ecosystems and landscapes. On the basis of theoretical analysis and experimental studies, we proposed to use such a measure – as radiocapacity and radiocapacity factor of ecosystems and their components.

According to general assessments about 40 % of the waastewateris formedin a 30-kilometer ChNPP zone, 40 % isformed in the territory of the polluted regions of Belarus, and the remaining 20 % – from the contaminated territories of Ukraine which are not closed for economic activity. The Dnipro, as is known, as a result of regulation, represents a cascade of six large reservoirs, which flow into the Dnipro-Bug estuary. Analyzing the magnitude and speed of water exchange between the reservoirs, one can see that the exchange between them is not more than 1/30 volume per year. This characterizes the cascade as a system of reservoirs, which are very slowly exchanging water. Methods of radiocapacity estimation can be applied to such system. Main parameters and characteristics of the Dnipro reservoirs are given in Table 2.

Table 2

Characteristics and parameters assessments for Dnipro water reservoirs for ^{137}Cs

Water reservoir	Square, km^2	Volume, km^3	Average depth, m	Silt thickness, sm	$K_н$(water–bottom sediments)	Radiocapacity factor
Kyivske	920	3,7	4	10	100	0,7
Kanivske	680	2,4	4	10	50	0,6
Kremenchutske	2250	13,5	6	10	800	0,8
Zaporizke	570	2,4	4	10	100	0,7
Dniprovske	410	3,3	8	10	230	0,7
Kakhovske	2150	18,2	8	10	280	0,7

It can be seen that each of the reservoirs has low values of the radiocapacity factor with respect to ^{137}Cs. Since the Dnipro reservoirs cascade is a system of reservoirs that slowly exchange water, the following formula can be applied for calculating the general radio volume:

$$F = \frac{Kh}{H + Kh}, \tag{3}$$

where $K$is the coefficient of accumulation in the system “water–bottom sediments”; h is the thickness of the silt sorbing layer; H is the average depth of the reservoir. F indicates the part of radionuclide in bottom sediments and $(1–F)$ corresponds to the part of radionuclide in water.

It follows from this formula that the radiocapacity factor of cascade (F_k) of reservoirs is equal to F_k = 0,9994. This value shows an extremely high degree of radiocapacity factor of a cascade, which is much higher than the radiocapacity factor of Kremenchug reservoir which is the best with respect to radiocapacity.

The formula and estimate of the radiocapacity of the Dnipro reservoirs cascade allowed for the first time in the post-accident period to predict with high accuracy the distribution of ^{137}Cs in the cascade in its sediments and water and predict that the part of ^{137}Cs will be firmly «buried» in the silt of the Kiev reservoir.

The proposed model and the corresponding assessment are made for the case of a single entry of radionuclide into a cascade. For the long-term radionuclide inputs, the model must to be modified by using differential equations. But even 25 years after the accident, the difference in the radioactivity of the water of the Kyiv and Kakhovka reservoirs remains sufficient andits degree is the same as in the first years after the accident.

In the case of other important radionuclide ^{90}Sr, the situation is different. The matter is that for ^{90}Sr the radiocapacity factor of the Dnipro reservoirs cascade does not exceed the values of 0.2–0.3. In this case, the factor of the total radiocapacity of the cascade for ^{90}Sr does not exceed 0,5–0,6, and there is no significant deposit of strontium in the bottom sediments. The content of ^{90}Sr in water is not more than 10 times different from the Kiev and Kakhovka reservoirs. This is well confirmed by the real data of observations in 1987–1993. Thus, the given example demonstrated the heuristic character of analysis of real large and small ecosystems by means of their radiocapacity.

The theoretical analysis of the problem of biosystems radioecological reliability has shown that the dynamics of the radioacapacity factor of the ecosystem biota under the influence of gamma irradiation and the introduction of heavy metals (Cd) almost coincides with the dynamics of such biological index as the growth rate. It is possible to state that the ^{137}Cs tracer behavior in the ecosystem, as an analogue of the potassium mineral nutrition, reflects the degree of well-being of the state of the ecosystem biota. Thus, we get the conclusion: the higher biota’s ability to accumulate and hold the tracer, the better the state, and therefore, the reliability of the ecosystem biota.

As a result of the Chernobyl accident, the ^{137}Cs tracer was "widely scattered" around the world. Therefore, it is possible to use this circumstance to establish the rules for the redistribution of tracer by different types of ecosystems. If in the dynamics of the radiocapacity factor with respect to the tracer shows a sharp change in its content in the ecosystem biota, that may indicate a noticeable reaction of the biota to the received effect [3, 4].

Behavior of the tracer can serve as an "ecological indicator" for assessing the state and reliability of biota. It is known that a decrease in the pH of the water in the lake ecosystem results in the desorption of radionuclides from the bottom sediments and biota into water, which in turn leads to a decrease in the radioactivity of the bottom biota and an increase in tracer content in water. This results in additional dose loads on the biota of the lake water and for people who use water for drinking and irrigation.

Tests of ecosystems biota allowed to establish limits for permissible doses to biota [5, 6]. In particular it has been established that the dose of 4 Gy/year for plants and hydrobionts and the dose of 0.4 Gy/year for animals can serve as a limit for which biota can still be reliably [6, 7].

To assess the content of radionuclides corresponding to these doses, B. Amiro's dose factors [8] were used, which showed that the ^{137}Cs content in biota is capable of producing exactly such a critical dose of 4 Gy / year. That is, an estimate of the radioactive content of the ecosystem biotic component, when the reliability of the ecosystem biota is close to zero, has been obtained. It is shown that in the range of doses for a biota from 0 to 4 Gy, the reliability can vary linearly from 1 to 0. Thus, the radiocapacity parameter can serve as a measure of the reliability of a biota in any ecosystem.

Let's consider some examples. Using theoretical results received by the consistent reliability model, two versions of the reliability measure of the Dnipro cascade were calculated for the process of containing radionuclides in it: without taking into account the participation of the biota of reservoirs and under the conditions of a real adaptive biota response at relatively small radiation dose (about 0.1–0.5 Gy / year, Tables 3–6).

Table 3

Estimation of radioactive factors by ^{137}Cs on the example of the Dnipro reservoirs cascade in conditions of adaptive biota response and without it (assessment of the cascade of reservoirs reliability the with the participation of biota)

Reservoir	F (bottom sediments)	F (biota)	F_i (summarized)
Kyivske	0,7	0,1	0,8
Kanivske	0,6	0,08	0,68
Kremenchutske	0,9	0,04	0,94
Zaporizke	0,7	0,16	0,86
Dniprovske	0,7	0,1	0,8
Kakhovske	0,8	0,14	0,94

General reliability and radiocapacity of Dnipro cascade is calculated by the formula:

$$F_{\text{cascade}} = 1 - \Pi\ (1 - F_i). \qquad (4)$$

Assessments gave the following results:
F_{cascade} (without biota) = 0,9998;
F_{cascade} (with biota and adaptation) = 0,999993.

Table 4

Estimation of radioactive factors by ^{137}Cs on the example of the Dnipro reservoirs cascade in conditions of adaptive biota response and without it, with taking into account the radiation synergy effect and cadmium (assessment of the cascade reliability with the participation of biota)

Reservoir	F (bottom sediments)	F (biota)	F_i (summarized)
Kyivske	0,7	0,09	0,79
Kanivske	0,6	0,07	0,67
Kremenchutske	0,9	0,036	0,936
Zaporizke	0,7	0,14	0,84
Dniprovske	0,7	0,09	0,79
Kakhovske	0,8	0,13	0,93

General reliability and radiocapacity of Dnipro cascade is calculated by the formula:

$$F_{\text{cascade}} = 1 - \Pi\ (1 - F_{\text{i}}).$$

Assessments gave the following results:
F_{cascade} (without biota) = 0,9998;
F_{cascade} (with biota and adaptation) = 0,9999.

Table 5

Estimation of radiocapacity factors for ^{90}Sr on the example of Dnipro cascade in conditions of adaptive biota response and without it (estimation of cascade reliability with participation of biota)

Reservoir	F (bottom sediments)	F (biota)	F_i (summarized)
Kyivske	0,3	0,15	0,45
Kanivske	0,2	0,1	0,3
Kremenchutske	0,5	0,2	0,7
Zaporizke	0,4	0,2	0,6
Dniprovske	0,4	0,18	0,48
Kakhovske	0,5	0,16	0,66

General reliability and radiocapacity is calculated as:

$$F_{\text{cascade}} = 1 - \Pi\,(1 - F_i);$$

F_{cascade} (without biota) = 0,95;
F_{cascade} (with biota and adaptation) = 0,992.

Table 6

Estimation of radiocapacity factors for ^{90}Sr on the example of Dnipro reservoir cascade in conditions of adaptive biota response and without it, taking into account the synergies effect of radiation and cadmium interaction (assessment of the cascade reliability with the participation of biota)

Reservoir	F (bottom sediments)	F (biota)	F_i (summarized)
Kyivske	0,3	0,14	0,44
Kanivske	0,2	0,09	0,29
Kremenchutske	0,5	0,18	0,68
Zaporizke	0,4	0,18	0,58
Dniprovske	0,4	0,16	0,56
Kakhovske	0,5	0,15	0,65

General reliability and radiocapacity of the cascade are:

$$F_{\text{cascade}} = 1 - \Pi\,(1 - F_i);$$

F_{cascade} (with biota) = 0,95;
F_{cascade} (with biota and adaptation) = 0,992.

Radiocapacity assessment also includes radionuclides transfer between various components of affected ecosystems. When process of radionuclide transfer into bottom sediments, which are the main depot of radionuclides accumulation in water bodies is studied, two principal mechanisms are distinguished: biogenic and chemogenic [10]. Biogenic migration means absorption of radionuclides by hydrobionts conducive to transfer of the radionuclides into the bottom sediments as a result of their physiological processes. Chemogenic migration is divided into three directions: first direction means sorption of radionuclides in suspensions of organic origin followed by sedimentation onto the water body bottom where the radionuclides shall be sorbed directly by the bottom sediments. Second direction means simultaneous precipitation with crystalizing calcium carbonate (the most frequent phenomenon with ^{90}Sr). The third direction means sorption capture of radionuclides with coagulating gels of iron, manganese or aluminium hydroxides [10].

Change in the specific activity of the radionuclides in water in the event of its one-time ingress into a water body may be described with the following equation [10]:

$$\frac{\partial C_1(t)}{\partial t} = \frac{D}{L}\frac{\partial C_2(z,t)}{\partial z} - \frac{V_0 K_p C_1(t)}{L} - \lambda C_1(t), \qquad (5)$$

$$z = -V_0 t, t > 0,$$

where: C_1 – stands for the specific activity of the radionuclides in water, Bqcm^{-3}; $C_2(z,t)$ stands for their specific activity in the bottom sediments at depth z and time t; D – stands for efficient diffusion coefficient of radionuclides in the bottom sediments, cm^2 year^{-1}; L – stands for average depth of the water body, dm; V_0 – stands for the in crementrate of the bottom sediment layer (as a result of detrital matter formation), cm year^{-1}; K_p – stands for the coefficient characterising distribution of radionuclides between the solid and liquid phases in a water body; λ – stands for a radioactive decay constant, year^{-1}.

Box models are often used to describe the transfer (transition) and migration of radionuclides in any ecosystems. The entire transfer chain of radionuclides in such models is divided into "boxes". Interaction between boxes in mathematical models is determined by coefficients describing the transfer speed [12].

The box model method adequately describes the transfer of radionuclides in hillside ecosystems exemplified with a system including eight boxes: "Forest", "Outskirts", "Meadow", "Terrace", "Flood Plain", "Water", "Biota", "Bottom Sediments". Impact of the contamination upon the people is considered in the form of a separate ninth box, where collective dose for human population is accumulated [15].

To model the transfer of radionuclides in typical ecosystems of villages in Ukraine, the box model method is applicable as well. Such method allows us to appraise adequately and prognosticate certain radioecological processes between basic links of the trophic chain "soil – hay – cows – milk – forest products – people" in such systems [9, 11, 14].

The box models for migration processes of radionuclides were constructed for Glyboke and Daleke lakes, which are the most radionuclide-contaminated water bodies within the Chernobyl Exclusion Zone. Behaviour of ^{137}Cs and ^{90}Sr was analysed, since they are the main dose-forming isotopes in contaminated water bodies and in their biotic components.The constructed models (Fig. 1) included such boxes as "Land Runoff", "Water", "Biota (common reed)", "Bottom sediments".

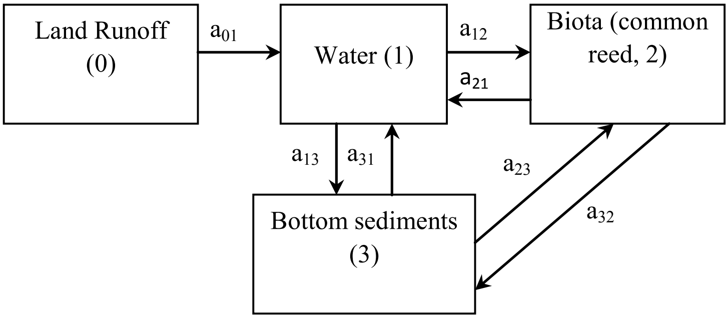


Fig. 1. Schematic diagram of the box model for transfer of ^{137}Cs and ^{90}Sr radionuclides in water bodies of the Chernobyl Exclusion Zone

In the course of modelling, the decay factor of radionuclides was taken into account. Initial data (see Table) for solution of the systems of differential equations were taken from a collective monography [13] (Table 7).

Table 7

Content of the main dose-contributing radionuclides ^{137}Cs and ^{90}Sr in the components of Glyboke and Daleke lakes, MBq [13]

Component of ecosystem	Glyboke Lake		Daleke Lake	
	^{137}Cs	^{90}Sr	^{137}Cs	^{90}Sr
Bottom sediments	962000	444000	51800	37000
Water	6200	50900	236	1650
Seston	2471	800	73	58
Biota	4598	3035	155	96
Communitiesofhigherwaterplants (commonreed, sedge, reedmace, *Sparganium*)	1458.6	260.4	41.90	4.1

Systems of differential equations describing the transfer of radionuclides between biotican dabiotic componentsin Glyboke and Dalekelakeswere solved by virtue of Maple VI software:

$$\begin{cases} \frac{dC_0}{dt} = -a_{01}C_0 - \lambda C_0, \\ \frac{dC_1}{dt} = a_{01}C_0 - a_{12}C_1 + a_{21}C_2 + a_{31}C_3 - \mathrm{a}_{13}C_1 - \lambda C_1, \\ \frac{dC_2}{dt} = a_{12}C_1 - a_{21}C_2 - a_{23}C_2 + a_{32}C_3 - \lambda C_2, \\ \frac{dC_4}{dt} = a_{13}C_1 - a_{31}C_3 + a_{23}C_2 - a_{32}C_3 - \lambda C_3, \end{cases} \tag{6}$$

where a_{01}, a_{12}, a_{21}, a_{23}, a_{32}, a_{13}, a_{31}stand for rates of radionuclides transfer between boxes; C_0–C_3stand for activity of radionuclides as % of their total stock in the ecosystem.

Results of the research with the model are shown on Fig. 2.

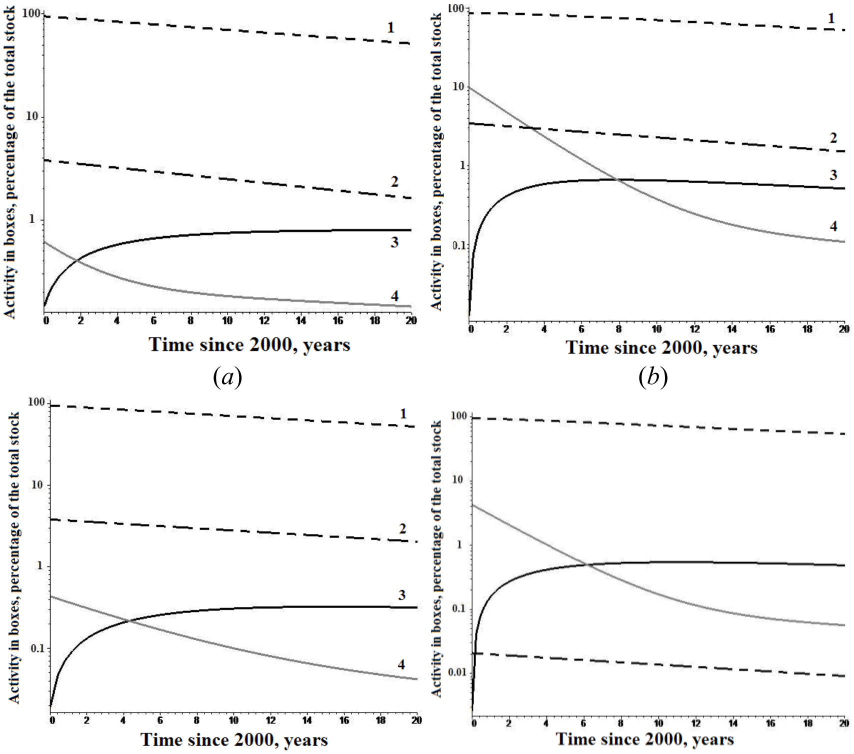
It was found that communities of common reed accumulated less than 1 % at most of ^{137}Cs and ^{90}Sr in Glyboke and Daleke lakes during 20 years following the sampling time in 2000–2004 years. This, most likely, may be explained with that some equilibrium in distribution of radionuclides between components of lake ecosystems has been established after the accident in 1986. Activity in other boxes (land runoff, water, bottom sediments) is reducing gradually.

Reduction of radionuclides activity in water and bottom sediments can be related to the transfer of the radionuclides into other components such as suspensions, detrital products, as well as higher aquatic plants.

Thus, the higher aquatic plants, being an integral component of ecosystems in fresh water, influence on redistribution and migration processes of radionuclides in water bodies.

Although percentage of radionuclides content in common reed communities is slight as compared with the total stock, the transfer of radionuclides to biotic components shall be nevertheless taken into account for elaboration of a set of measures aimed at prevention and minimisation of consequences of ionising radiation impact on the biota in water ecosystems.

Radiocapacity assessment in reservoirs of Dnipro river, plays crucial role in ecosystem stability investigation. By the example of Dnipro reservoirs, radiocapacity factor for ^{137}Cs and ^{90}Sr was determined.



(*a*) (*b*)

(*c*) (*d*)

Fig. 2. Calculations of ^{137}Cs and ^{90}Sr activity change in boxes of Glyboke (*a*, *b*) and Daleke (*c*, *d*) lakes:
1 ▬ ▬ ▬ ▬ ▬ Bottom sediments, 2 ▬ ▬ ▬ ▬ Land runoff, 3 ▬▬▬▬ Biota (Common reed),
4 ▬▬▬▬ Water

Box models of radionuclide-contaminated Glyboke and Daleke lakes in the Chernobyl Exclusion Zone have been designed and analysed.

Slight increase of the radionuclides content (< 1 %) in «Biota (common reed)» box of Glyboke and Dalekelakes in the Chernobyl Exclusion Zone has been obtained.

Generalreductionof^{137}Cs and^{90}Sr radionuclides contentinabiotic components of the water bodies (inparticular, in “LandRunoff”, ”Water” and ”BottomSediments” boxes) as some percentage of their total stockineco systems has been prognosticated.

Research results maybe used to calculate the radio-capacity of radionuclide-contaminated water bodies, to elaborate measures aimed at minimisation of adversecons equences of ionisin gradiation for the biota.

РЕФЕРАТ

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ОЦІНКА РАДІОЄМНОСТІ ТА НАДІЙНОСТІ ВОДНИХ ЕКОСИСТЕМ

Статтю присвячено дослідженню радіонуклідного забруднення водних об'єктів. Дослідження спрямовано на оцінку надійності та радіоємності екосостем Дніпровських водосховищ, а також переходу радіонуклідів між компонентами водних екосистем Чорнобильської зони відчуження.

Визначено фактор радіоємності для ^{137}Cs та ^{90}Sr для різних водосховищ Дніпра. Побудовано камерні моделі переходу радіонуклідів між біотичними та абіотичними компонентами найбільш забруднених озерних екосистем Чорнобильської зони відчуження.

Ключові слова: радіонуклідне забруднення, радіоємність, фактор радіоємності, камерна модель, Чорнобильська зона відчуження, каскад Дніпровських водосховищ.

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ОЦЕНКА РАДИОЕМКОСТИ И НАДЕЖНОСТИ ВОДНЫХ ЭКОСИСТЕМ

Статья посвящена исследованию радионуклидного загрязнения водных объектов. Исследования направлены на оценку надежности и радиоемкости екосостем Днепровских водохранилищ, а также перехода радионуклидов между компонентами водных экосистем Чернобыльской зоны отчуждения. Определены фактор радиоемкости для ^{137}Cs и ^{90}Sr для различных водохранилищ Днепра. Построено камерные модели перехода радионуклидов между биотическими и абиотическими компонентами наиболее загрязненных озерных экосистем Чернобыльской зоны отчуждения.

Ключевые слова: радионуклидное загрязнение, радиоемкость, фактор радиоемкости, камерная модель, Чернобыльская зона отчуждения, каскад Днепровских водохранилищ.

ABSTRACT

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ESTIMATION OF RADIOCAPACITY AND RELIABILITY OF WATER ECOSYSTEMS

Paper deals with the investigation of the water bodies radionuclides contamination. The research is focused on the Dnipro water reservoir ecosystems reliability and radiation capacity assessment, as well as radionuclides transfer between the components of aquatic ecosystems within Chernobyl Exclusion Zone. Radiocapacity factor for ^{137}Cs and ^{90}Sr was determined for various reservoirs of Dnipro river. Box models of radionuclides transfer between biotic and abiotic components of the most contaminated lake ecosystems within Chernobyl Exclusion Zone, were built.

Key words: radionuclide contamination, radiocapacity, radiocapacity factor, box model, Chernobyl Exclusion Zone, cascade of Dnipro reservoirs.

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3.7 MODELS FOR ASSESSMENT OF NO$_x$ EMISSIONS FROM TURBOFAN ENGINE OF AIRCRAFT

Kateryna Synylo

Aircraft emissions are of concern due to the expansion of air traffic over the years (a mean annual rate of 5 to 7 %) and their potential impact on air quality in local, regional and global environments [1,2]. Even if in some the European hubs their capacity is close to the limit (never mind operational or environmental), the transfer of the air traffic to other airports, with less intensive traffic, but usually closer to habitation areas, once again making a rise to concerns about their LAQ tasks.

The analysis of emission inventories at major European (Frankfurt am Main, Heathrow, Zurich and etc.) and Ukrainian airports highlighted that aircraft are the dominant source of air pollution in most cases under consideration, with contribution to inventory higher than 50 % of their total values in most of the airports [3, 4]. The aircraft emission inventory is usually calculated on the basis of certificated engine emission (EE) indices, which are provided by the engine manufacturers and reported in ICAO EE database [5]. It is necessary to mention that ICAO EE database has gained from a very limited number of newly manufactured engines during the certification process [6], even someone may conclude that the best practice is included first of all.

The emission indices rely on well-defined measurement procedure and conditions during aircraft engine certification. Under real circumstances, however, these conditions may vary and deviations from the certificated emission indices may occur due to impact such factors, as:

- the life expectancy (age) of an aircraft – emission of an aircraft engine might vary significantly over the years (the average period – 30 years), usually aging aircraft/engine provides higher emission indices in comparison with same type but new ones;
- the type of an engine (or its specific modification, for example with different combustion chambers) installed on an aircraft, which can be different from an engine operated in an engine test bed (during certification);
- meteorological conditions – temperature, humidity and pressure of ambient air, which can be different for certification conditions.

The impacts of aviation emissions of NO_x, PM, and other gaseous emissions need to be further assessed and understood [1]. In respect to this anassessment of aircraft emission indices under operating conditions, also including from measurements, is an actual task, which must provide more accurate emission inventory and to improve total LAQ modeling systems.

The advanced emission model of turbofan engine (TURBOGAS emission model) was developed for assessment aircraft engine emissions with taking into account of the influence of the operational and meteorological conditions on emission indexes to calculate precisely aircraft emission inventory. Sensitivity analysis of the TURBOGAS advanced emission model to define some key parameters for the estimation of aircraft emission indexes under real operation conditions and to provide precisely aircraft emission inventory.

Aircraft main engines have received a lot of attention in sector of aviation emissions as they are the dominant airport-related source [7, 8].

There are various methodologies, to quantify aircraft emissions – each with a degree of accuracy and an inverse degree of uncertainty. The purpose and need for quantifying aircraft emissions drive the level of accuracy needed in an inventory, which in turn, determines the appropriate approach. A secondary factor is data availability [7].

Aircraft emission is function of following parameters [7, 8]:

$$Q = FF \times EI \times T \times n, \tag{1}$$

where FF – fuel flow rate, kg/s; EI – emission index, g/kg; T – time in mode, s; n – number of aircraft engines.

The basic methodologies [7, 8] rely on the two critical parameters: the fuel flow rate and the emission factor or index.

The Intergovernmental panel on Climate Change (IPCC) [8] presented a tier based approach to report the on level of accuracy and complexity of commonly available methods to compute aircraft emissions, Table1.

Tier 1 represents the simplest method used to compute the emissions of different pollutants. It does not require very complex computational manipulations and the data requirements are very low. One of the main advantages is the speed of the computational procedure but, on the other hand, this category is also considered to be the least accurate among the tiers [8]. An example is the ICAO reference method.

Table 1

IPCC tier categorization

IPCC Tiers	Level of complexity	Level of accuracy	Example of this method
Tier 1	Low	Empirical	**ICAO**
Tier 2	Medium to High	Empirical	**BFFM2**
Tier 3	High	Modeled or measurement based	**P3T3**

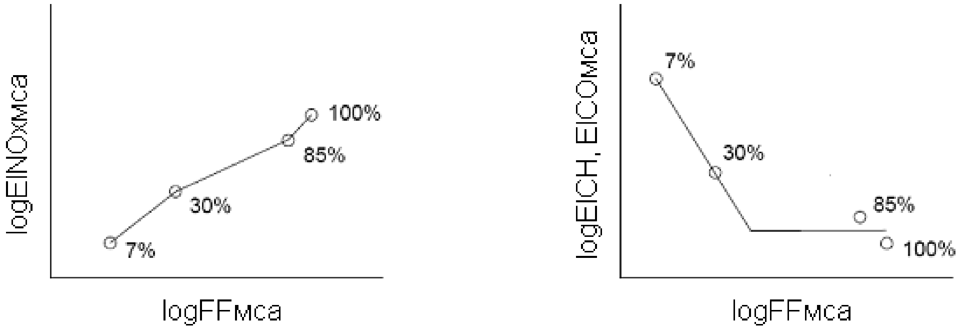
Tier 2 is known as the intermediate method [8]. It requires a higher amount of data to estimate the emissions of different types of pollutants. The related computational process will take longer but the results will provide an increased level of accuracy. An example of this tier is the Boeing Fuel Flow Method 2 (BFFM2).

The final tier (Tier 3 advanced) represents the highest level of complexity. The results generated by this method are considered to be the “most accurate” [8]. The drawback comes from the amount of data required, some of which are not in the public domain or are difficult to obtain, as it will be shown in a later section. The computational procedure is also more intensive, so it will take longer to generate the results as compared to the other two methods. An example of this tier is the P3T3 method.

Both BFFM2 and P3T3 methods have been implemented in the TURBOGAS emission model [9,10]. TURBOGAS which is an emission model of turbofan engine, and which was developed in the scope of TURBOGAS project of Clean Sky JTI company [10].

BFFM2 method is based on the evaluation of the emission index (NOx, CO and HC) of aircraft engines and the fuel flow under real meteorological and operational conditions.

The first stage of the BFFM2 model is to attempt to correct the reference values from ICAO database for “installation effects”; deviations between values from bench tested engines and those found on in service aircraft.



(*a*) (*b*)

Fig.1. Dependencies of EINOx (*a*) and EICO, EIHC (*b*) on fuel flow rate according to the ICAO bank

Secondly, the real meteorological conditions (temperature, pressure and humidity of the air) are translated into the conditions of the ISA by the formulas for correction of humidity and pressure [8, 9].

Real fuel flow value is calculated of the basis of ISA conditions by folowing conversion formula:

$$FF_{MCA} = \frac{FF}{\delta_{amb}} \times \theta_{amb}^{3,8} \times e^{0,2 \times M^2}, \qquad (2)$$

where δ_{amb} – the ratio of atmospheric pressure corrected to ISA conditions; θ_{amb} – the ratio of air temperature corrected to ISA conditions; *FF* – real fuel flow rate, kg/s; *M* – Mach number.

The found values of EINOx, EICO, EIHC for ISA conditions (Fig.1) are converted into real meteorological conditions:

$$EI_{\mathrm{NO_x}} = EI_{\mathrm{NO_x}MCA} \times e^{H} \times \left(\frac{\delta^{1,02}}{\theta^{3,3}} \right)^{x}, \qquad (3)$$

$$EI_{\mathrm{HC}} = EI_{\mathrm{HC}MCA} \times \left(\frac{\theta^{3,3}}{\delta^{1,02}} \right)^{x}, \qquad (4)$$

$$EI_{\mathrm{CO}} = EI_{\mathrm{CO}MCA} \times \left(\frac{\theta^{3,3}}{\delta^{1,02}} \right)^{x}, \qquad (5)$$

where $EI_{\mathrm{NOx}MCA}$, $EI_{\mathrm{CO}MCA}$, $EI_{\mathrm{HC}MCA}$ – emission indexes are calculated under reference conditions (ICAO databank).

The uncertainty of BFFM2 method for assessment of EINOx, EICO, EIHC for aircraft engines is ± 10 % due to the following factors [11]:

1) accuracy of the linear interpolation method for determining the emission index according to the certification curve is significantly reduced for operating modes of the investigated type of aircraft engine with a thrust value less than 7 %;

2) age of aircraft engine;

3) lack of information for some types of engines

Sensitivity analyses were performed for TURBOGAS emission model for aircraft A340-300 with engine CFM 56-5C2/F, using the input data for the cruising modes derived from in-flight measurements data performed by DLH [8, 12]. The averaged values used for sensitivity tasks are shown below:

- FF_{mean} = 0.816761 g/s (Min = 0.555556, Max = 1.040000, Std Dev = 0.083559).
- FF = 2938.0 kg/h = 0.8161 kg/s (FF_{ref} = 2814.48 kg/h = 0.7818 kg/s)
- For temperature Ta = 11.5° C/284.65K
- For humidity H = 65.8 %,
- For pressure Pa = 1009.7 mbar.

The objective of the sensitivity studies was to investigate the changes in output (esp. $EINO_X$) caused by variations of input data. The following parameters are studied, with step-wise variations on 2, 5 and 10 %: fuel flow, temperature, pressure, humidity [13].

The results of the sensitivity analysis of the TURBOGAS model for engine CFM56-5C2 and the appropriate dependence of EI NO_X on fuel flow and ambient atmosphere conditions are represented on the following Table 2 and plot, Fig. 2.

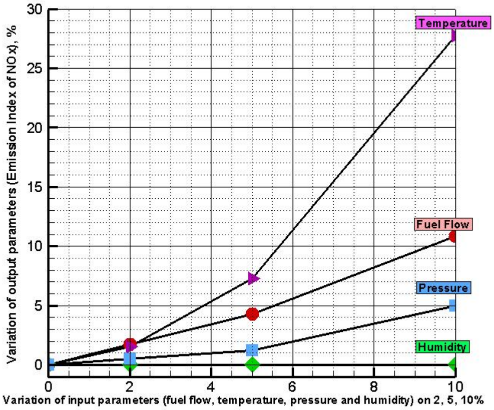


Fig. 2. $EINO_X$ variability vs input parameters for CFM 56-5C2/F

Table 2

Results from sensitivity studies for the CFM56-5C2

Parameter	**Range of parameter**	**Range of NOx (+/- % mean)**
Fuel flow	0.8161/0.8977	10.85
Ambient temperature	285 K to 313 K	27.7 %
Ambient pressure	1010 mbar to 1011 mbar	5.0 %
Ambient relative humidity	66 % to 72 %	1 %

The analysis of obtained results confirmed the sensitivity of TURBOGAS output to the fuel flow rate. The variation of this parameter on 2 % lead to the change of EI NO_x, however, the variation of input value on 10 % implied and increase of EI NO_x on 10.85 %.

Also on the ground of the results obtained and of the comparison of the resulting differences, it can be concluded that the TURBOGAS emission model was not sensitive to air pressure and humidity. That was because the changes of these parameters input by 2 % lead to variations of calculated EI NO_X lower than 2 %. Likewise the changes of input parameters by 5 % implied variations lower than 5 %. The analysis of the modeled data showed that the TURBOGAS emission model was most sensitive to ambient temperature. A change of temperature of 5 % implied an increase of EI NO_X of 7.28 %. At last the change of 10 % lead to an increase in EI NO_X of 27.72 %. Based on this last tendency it can be concluded that the TURBOGAS model was highly sensitive to the ambient temperature. Those results were in agreement with the literature on the topic: it was proved, that "humidity has the least powerful effect upon engine performances of the three ambient parameters" [14].

These results were in line with sensitivity studies conducted by the ICAO CAEP on the AEDECAM model [15, 17] which results are summarized below (Table 3):

Table 3

Results from sensitivity studies for the AEDECAM model

Parameter	**Range of parameter**	**Range of NOx (+/- % mean)**
Ambient temperature	0 °C to 30 °C	34.53 %
Ambient pressure	950 mbar to 1025 mbar	9.04 %
Ambient relative humidity	40 % to 70 %	2.84 %

Sensitivity analysis of TURBOGAS emission model for engine JT9D-7J Sensitivity studies for the engine JT9D-7J used previously in the validation tests were implemented according to the input data named Case 5 and Case 7 (see Table 6 and Table 7) corresponding to cruise flight conditions and obtained in paper [16]:

- Case 5
  - Fuel flow, FF = 0.9028 kg/s;
  - Air temperature, T_A = 226.15K;
  - Air humidity, H = 38 %;
  - Atmospheric Pressure, Pa = 26.2kPa
- Case 7
  - Fuel flow, FF = 0.8889 kg/s;
  - Air temperature, T_A = 226.15K;
  - Air humidity, H = 43 %;
  - Atmospheric Pressure, Pa = 26.2kPa

The Turbogas model sensitivity studies were performed for a Boeing aircraft B747-200 for cruise operation mode (Case 5 / Case7). The full data of the sensitivity are shown in a tabular way in Table 4, 5. In the rest of this sub-section, only results are presented.

Table 4

Results from sensitivity studies for the JT9D-7J (case 5)

Parameter	**Range of parameter**	**Range of NOx(+/- % mean)**
Ambient temperature	226 K to 249 K	34.7 %
Ambient pressure	262 mbar to 288 mbar	7.1 %
Ambient relative humidity	38 % to 42 %	0 %

Table 5

Results from sensitivity studies for the JT9D-7J (case 7)

Parameter	**Range of parameter**	**Range of NOx (+/- % mean)**
Ambient temperature	226 K to 249 K	34.4 %
Ambient pressure	262 mbar to 288 mbar	7.1 %
Ambient relative humidity	43 % to 47 %	0 %

The results shown for case 5 and case 7 compare well with the sensitivity studies prepared for the ICAO with the support from manufacturers which reported an increase of 1.5 % in NO_X emitted per increase of 1 degree [17], Fig. 3, 4.

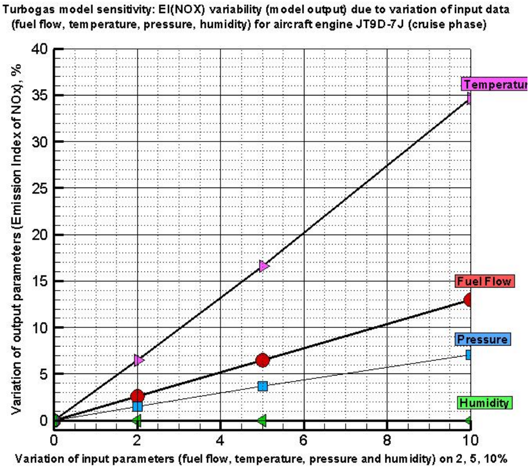


Fig. 3. $EINO_X$ variability with respect to input data Engine JT9D-7J for cruise operation mode (Case 5)

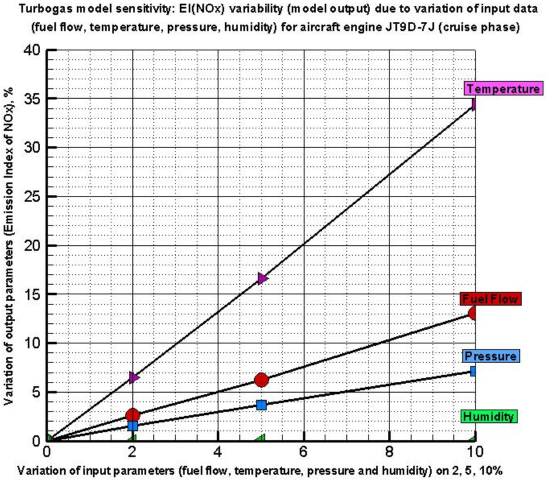


Fig. 4. $EINO_X$ variability with respect to input data Engine JT9D-7J for cruise operation mode (Case 7)

Sensitivity studies for Turbogas have been performed for a Boeing B747-200 fitted with engine P&W JT9D-7J for cruise operation mode (cases 5 & 7).

On the ground of the results obtained for case 5 and case 7, it was concluded as expected that the Turbogas model is sensitive to fuel flow. A 2 % increase in fuel flow lead to variation of EI NO_X above 2 % (resp. 2.58 % and 2.62 %) and the 5 % increase in fuel flow implied a variation of EI NO_X higher than 5 % (resp. 6.47 % and 6.26 %). At last the changes of fuel flow of 10 % lead to variation of results greater than 10 % (resp. 13.01 % and 13.03 %).

According to modelling results, Turbogas was sensitive to ambient temperature. A 2 % increase in temperature lead to variations EI NO_X of 6.49 % and 6.47 % respectively. Variations of fuel flow of 5 % implied increase in results of 16.63 % and 16.57 %. Finally, the changes of temperature of 10 % lead to variation of EI NO_X considerably more than 10 % (34.68 % and 34.39 %). Based on last tendency came to the conclusion that the Turbogas model is highly sensitive to the ambient temperature.

On the basis of modelling results and their comparison of the resulting differences it was concluded that Turbogas is not sensitive to air pressure and humidity. Since the changes of input these parameters on 2 % lead to variation of calculation results llower than 2 % and the changes of input these parameters on 5 % implies variation in results smaller that 5 %.

Those results were in agreement with the literature on the topic : it was noted in «Gas Turbines» on p.696 that «humidity has the least powerful effect upon engine performances of the three ambient parameters».

The model estimates values for P3, T3 and FAR before completing the P3T3 model and providing an estimate for NO_x emissions.

A NO_x emissions rate is calculated based on the standard P3T3 formula presented in SAE AIR 5715 [8].

$$EI_{\mathrm{NO}_{xALT}} = EI_{\mathrm{NO}_{xMCA}} \times \left(\frac{P_{3ALT}}{P_{3MCA}}\right)^{a} \times \left(\frac{FAR_{ALT}}{FAR_{MCA}}\right) \times \exp\left(19 \times \left(h_{MCA} - h_{ALT}\right)\right) \tag{6}$$

where $P_{3\mathrm{ALT}}$ and $P_{3\mathrm{MCA}}$ – pressure at the entrance to the combustion chamber of the aircraftengine at theconsidered altitude (h_{alt}) under operational and reference conditions (h_{MCA}); FAR_{ALT} and FAR_{MCA} – fuelflowratioatthecombustionchamberunderoperationalmode at the altitude (h_{ALT}) and under reference conditions (h_{MCA}); $EI_{\mathrm{NOx}MCA}$ – emission indexes are determined by the certification curve due to ICAO databank [9].

Indicators *a* and *b* are determined on the basis of engine test. Accuracy of P3T3 method depends on the principles to determine the indicators *a* and *b* due to the formula (6). So, in the case where $a = 0.4$, the error of the emission rate of NOx is 11 % for the investigated aircraft engine and in the case of determination *a* according to the data of the experimental investigation, it reaches only 3.5 % [8].

Due to the complexity of obtaining information on the results of engine test, generalized values for these indicators are adopted. So in most works [8], a = 0.4, b = 0. The presented method for assessment the emission indexes o is characterized by highly accuracy. The implementation of this method is complicated due to the complexity of the calculation algorithm and the inaccessibility of the initial data. Currently this problem is crucial object of the research within the international projects [9] by independent calculation of pressure (P3) and temperature (T3) at the entrance to the combustion chamber according to the equations of thermodynamic calculation for the aircraft engine.

Comparison of BFFM2 and P3T3 methods for assessment of EINOx at the different altitudes is represented on Fig.5. The difference between the results for the indicated methods increases with increasing height. The observed observation is due to the effect of humidity of the atmospheric air on the value of EINOx [18].

This emissions index is then converted into an emissions value by multiplying the g/kg value by the fuel flow (kg/s) for each segment.

One of the requirements of the P3T3 is the fuel-air-ratio. Establishing this ratio is in most models calculated by attempting an energy balance across the burner. However, because fuel flow is an explicit input for the Turbogas tool, this can be completed by establishing the mass of air required to achieve stoichiometric combustion. During optimum flight conditions, this is a reasonable assumption. Assuming a mean fuel composition of 13.84 % hydrogen by mass, this results in an emission index of 3.15 for CO_2 and 1.25 for H_2O (which is the value implemented in the EU ETS for aviation). Subsequently, each 1 unit of fuel requires 3.4 units of oxygen for complete combustion [18].

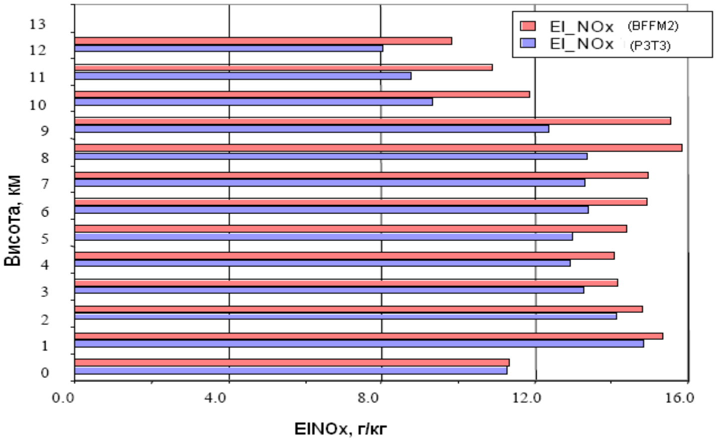


Fig. 5. Comparison of BFFM2 and P3T3 methods for assessment of EINOx at the different altitudes

Sensitivity analyses were performed for Turbogas model for engine FJ44-3A on the ground of ANP flight profile for a Citation 3 for following two points:

- **Point № 1:**
  - Fuel flow, FF = 0.153573523 kg/s;
  - Altitude, m = 457.2
  - Mach number = 0.23044085
  - Thrust, kN = 8.8442306
  - Air temperature, T_A = 284.19K;
  - Air humidity, H = 60 %;
  - Atmospheric Pressure, Pa = 942.1mbar
- **Point № 2**:
  - Fuel flow, FF = 0.1272584 kg/s;
  - Altitude, m =3048.00
  - Mach number = 0.44015261
  - Thrust, kN = 7.63414211
  - Air temperature, T_A = 268.34K;
  - Air humidity, H = 60 %;
  - Atmospheric Pressure, Pa = 696.80mbar

Aim of sensitivity studies is to investigate the changes in output (EINOx) caused by variation of input data. The following parameters are studied, with step-wise variations of 2, 5 and 10 %: fuel flow, temperature, pressure, Mach number and thrust. Obtained results of the sensitivity tests are collected in following tables correspondingly for Point 1 and Point 2 [19].

Table 6

Results from sensitivity studies for the FJ44-3A (point1)

Parameter	**Range of parameter**	**Range of NOx (+/- % mean)**
Ambient temperature	11.2 °C to 39.6 °C	30.70 %
Ambient pressure	942.1 mbar to 1036.3	4.84 %
Ambient relative humidity	60.0 % to 66 %	1 %

Table 7

Results from sensitivity studies for the FJ44-3A (point1)

Parameter	**Range of parameter**	**Range of NOx (+/- % mean)**
Ambient temperature	-4.7 ºC to 22.17 ºC	12.70 %
Ambient pressure	696.80 mbar to 766.48	4.30 %
Ambient relative humidity	60.0 % to 66 %	0.5 %

The results of TURBOGAS model sensitivity and found dependence of EINOx on ambient conditions (temperature, humidity and pressure) is represented on the plot1 for considered cases, Fig.6, 7.

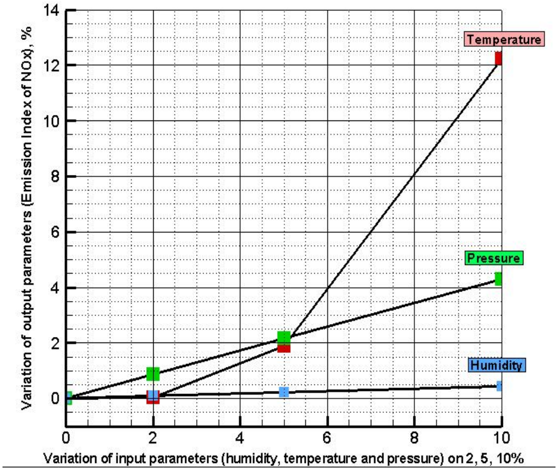


Fig. 6. EINO$_X$ variability vs input parameters for FJ44-3A (point №1)

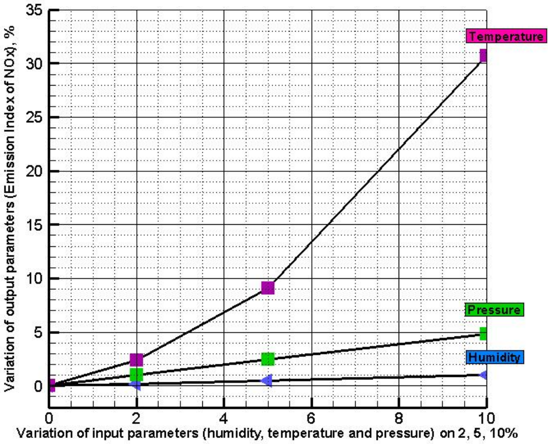


Fig. 7. EINO$_X$ variability vs input parameters for FJ44-3A (point №2)

On the ground of the results obtained for two points and of the comparison of the resulting differences it can be concluded that the Turbogas model (P3T3 method) is not highly sensitive to air pressure and humidity. That is because the changes of these parameters input by 2 % lead to variations of calculated EI NO_X lower than 2 %. Likewise, the changes of input parameters by 5 % implied variations lower than 5 %.

The analysis of the implemented tests showed, that the Turbogas model is sensitive to ambient temperature. Based on obtained results, it was found a dependence of a sensitivity level of model on altitude. As, it was observed, on altitude 457.2 m ambient temperature change on 10 % leads to an increase in EI NO_X of 12 %, while on altitude 3048.0 m – 30.7 %.

In addition, on the ground of investigation was found, that the Turbogas model (P3T3 method) is not sensitive to operational conditions at all: fuel flow, Mach number and thrust.

BFFM2 and P3T3 methods have been implemented in the TURBOGAS emission model.

Results of sensitivity analysis concluded that the emission model of turbofan engine developed to take into account the influence of the real operational (fuel flow rate) and meteorological conditions on emission indexes was robust. According to calculation results by TURBOGAS model, the fuel flow rate and ambient atmosphere conditions (air temperature, pressure and humidity) have a large impact on the EINOX. In particular the sensitivity analysis showed that the model (BFM2) is highly sensitive to the fuel flow rate (increase in $EINO_X$ on 10.85 % in case of change it on 10 %) and ambient temperature (27.72 % increase in $EINO_X$ in case of change it on 10 %).

The TURBOGAS model (P3T3 method) is not sensitive to operational conditions (fuel flow, Mach number and thrust), but it is highly sensitive to ambient temperature (1.5 to 2 % increase in EINOX per 1 degree C).

РЕФЕРАТ

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МОДЕЛІ ОЦІНКИ ВИКИДУ NO_x ВІД ТУРБОВЕНТИЛЯТОРНОГО АВІАДВИГУНА

Протягом останнього десятиліття багато досліджень зосереджено на оцінці впливу викидів авіаційних двигунів на місцеву та регіональну якість повітря поблизу аеропорту. Інвентаризація викидів викидів повітряних суден зазвичай обчислюється на основі сертифікованих емісійних індексів, які надаються виробниками двигунів і відображаються в базі даних Міжнародної організації цивільної авіації (ІКАО). Сертифіковані індекси емісії визначаються під час стендових випробувань. Проте в реальних умовах експлуатаційні (тяга, напрацювання двигуна та витрата палива) і метеорологічні характеристики (температура повітря, вологість і тиск) не відповідають ІКАО умовам, внаслідок чого індекси емісії вирізняються від сертифікованих величин.

Розроблена вдосконалена емісійна модель турбовентиляторного двигуна (модель викиду TURBOGAS) для оцінки викидів авіаційних двигунів з урахуванням впливу експлуатаційних та метеорологічних умов на показники викидів для створення точних кадастрів викидів повітряних суден, а також ймовірності виникнення інверсійних слідів. Обидві методи BFFM2 та P3T3 були впроваджені в моделі TURBOGAS.

Ключові слова: авіаційнийдвигун, навколишнє середовище, турбовентиляторний двигун, забрудненняатмосферного повітря, модельвикидів, емісійніiндекси.

РЕФЕРАТ

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МОДЕЛИ ОЦЕНКИ ВЫБРОСА NO_x ОТ ТУРБОВЕНТИЛЯТОРНОГО АВИАДВИГАТЕЛЯ

В течение последнего десятилетия многие исследования также были сосредоточены на оценке воздействия выбросов авиационных двигателей на качество воздуха в зоне аэропорта и в окрестностях. Инвентаризация выбросов воздушных судов обычно рассчитывается на основе сертифицированных индексов выбросов, которые предоставляются изготовителями двигателей и заносятся в базу данных Международной организации гражданской авиации (ИКАО). Сертифицированные индексы эмиссии определяются при стендовых испытаний. Однако в реальных условиях эксплуатационные (тяга, наработки двигателя и расход топлива) и метеорологические характеристики (температура воздуха, влажность и давление) не отвечают ИКАО условиям, в результате чего индексы эмиссии отличаются от сертифицированных величин.

Усовершенствованная модель выбросов турбовентиляторного двигателя (модель выбросов TURBOGAS) была разработана для оценки выбросов авиационных двигателей с учетом влияния эксплуатационных и метеорологических условий на индексы выбросов для создания точных кадастров выбросов воздушных судов, а также вероятности появления инверсионных следов. Оба метода BFFM2 и P3T3 были реализованы в модели выбросов TURBOGAS.

Ключевые слова: авиационный двигатель, окружающая среда, турбовентиляторный двигатель, загрязнение воздуха, модель выбросов, показатели выбросов.

ABSTRACT

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MODELS FOR ASSESSMENT OF NO$_x$ EMISSIONS FROM TURBOFAN ENGINE OF AIRCRAFT

During the last decade a lot of investigations were focused on the evaluation of the impact of aircraft engine emissions on the local and regional air quality in the vicinity of the airport. The aircraft emissions inventory is usually calculated on the basis of certificated emission indices, which are provided by the engine manufacturers and reported in the database of the International Civil Aviation Organization (ICAO). The certificated emission indices rely on well-defined measurement procedures and conditions during engine test. Under real circumstances, however, operational (power setting, time-in-mode and fuel flow rate) and meteorological (air temperature, humidity and pressure) conditions may vary from ICAO definition, consequently deviations from the certificated emission indices may occur.

The advanced emission model of turbofan engine (TURBOGAS emission model) was developed for the assessment of aircraft engine emissions taking into account the influences of operational and meteorological conditions on emission indices to generate precise aircraft emissions inventories as well as contrails likelihood and lifetime. Both BFFM2 and P3T3 methods have been implemented in the TURBOGAS emission model.

Key words: aircraft engine, environment, turbofan engine, air pollution, emission model, emission indices.

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3.8 EVALUATION OF FUEL CONSUMPTION AND HARMFUL SUBSTANCES EMISSIONS BY VEHICLE WITH SPARK IGNITION ENGINE UNDER OPERATION CONDITIONS WITH USING OF FUEL CONTAINING ETHANOL

Mykola Tsiuman

The most prevalent energy source for motor transport, especially for vehicles of M1 and N1 categories, are spark ignition engines. The main part of them is still the liquid fuel engines. In the last years a problem of finding alternative fuels or raw for the fuels production is very actual. This has a goal to replace gradually conventional oil origin fuels with alternative fuels. For natural, climatic and economic conditions of Ukraine plant or animal biological origin components are the most perspective as raw for the alternative fuels production. On legislative level a stimulation strategy of 20 % conventional fuels replacing with the biological components till 2020 has been determined by the Law of Ukraine «About alternative kinds of fuel». In case of conventional petrol it is using of mixtures the petrol and a dehydrated ethanol (bioethanol). Thus, today as a result of using the stimulation strategy (first of all, economic stimulation) some part of fuels for spark ignition engines is the fuels containing ethanol to 30 %.

As known, main vehicle operation performance is the vehicle environmental safety performance. This performance is determined by vehicular engine fuel consumption and harmful emissions. Opportunity evaluation issues of using fuels containing ethanol for spark ignition engines and improvement vehicle performance when using the fuels containing ethanol were studied in works of many scientists [1–4]. In there searches influenced termination issues of additionless than 20 % bioethanol toconventional fuel on carbure torengines fuel economy and environmental performance and improvement methods of this performance were studied. Also a fuel economy and environmental performance of sparkignition engine equipped fuel injection and exhaust gases cleaning systems, using a fuel containing ethanol to 20 % were studied in the researches. However, with advent on the market fuels containing ethanol to 30 % issue of evaluation environmental safety of spark ignition engine and vehicle equipped with the engine powered by fuel with high ethanol content is got actual.

Previously carried out laboratory experimental researches of fuel economy and environmental performance of sparkignition engine equipped a fuel injection and exhaust gases cleaning system susing a fuel containing ethanol more than 20 % have showed that using the fuel containing 25 % ethanol by mass leads to increasing the absolute fuel consumption on 10.8–10.9 % and to decreasing of efficiency nitrogenoxides cleaning [5]. Here with, the engine power performance and efficiency of use the fuel containing ethanol in a energy equivalent seal most sameas the engine performance when using apetrol. Using the research results polynomial dependencies of engine exhaust gases harmful substances concentrations had been got according to the engine speed and load mode, fuel type and air-fuel mixture content, which is going to engine cylinders. The obtained dependencies are a basic of carrying out further evaluation of fuel consumption and harmful emissions from vehicle equipped with spark ignition engine under operating conditions using the fuel containing ethanol.

At the same time, besides solving of issue of engine and vehicle performance evaluation when using the fuel containing ethanol a choosing of the evaluation method needs a special attention. Issues of studying motor vehicles influence on environment and methods of improvement the vehicles environmental performance, development of research and prognostication methods for vehicle environmental performance, and also development of environmental monitoring systems for transport were studied in works of many scientists, suchas Gutarevych Yu.F., Lukanin V.N., Trofimenko Yu.V., Kanylo P.M. [1, 6, 7] and others.

In previously published works with co-authors [8, 9] peculiarities of formation separate elements of intelligent monitoring system for vehicles environmental safety performance, sucha functioning of vehicle on-board system for obtaining the vehicle motion parameters, and also issues of improvement and using of vehicle motion mathematical model for evaluation the vehicle fuel consumption and harmful emissions in a driving cycle taking into account the engine and catalytic converter heating processes have been presented. Using of the vehicle motion mathematical modelwith taking into account the vehicle motion parameters in a real route conditions will enable to solve of actual practical task of influence evaluation of using a fuel containing ethanol on vehicle fuel consumption and harmful emissions under operation conditions.

The purpose of the study is an evaluation of vehicle fuel consumption and harmful emissions with a spark ignition engine equipped a fuel injection and exhaust gases cleaning systems, using a fuel containing ethanol more than 20 %. It is based on the vehicle motion parameters under real route conditions.

The object of evaluation of fuel consumption and harmful emissions when using a fuel containing ethanol under operating conditions isBOGDAN 21101 1.6L equipped with engine VAZ-21114. The Table 1 contains main technical parameters of the vehicle.

Table 1

Technical parameters of BOGDAN 21101 1.6L with engine VAZ-21114

Title	Specification
1	*2*
Weight of the vehicle with a driver and a passenger, kg	1200
Maximum speed, km/h	180
Fuel type	petrol
Number / arrangement of engine cylinders	4 / inline
Engine displacement, l	1.596
Diameter of cylinder / piston stroke, mm	82 / 75.6
Compression ratio	9.8
Engine power, kW/ crankshaft rotation speed, min^{-1}	59 / 5200

Table 1 continue

1	*2*
Torque, N·m/ crankshaft rotation speed, min^{-1}	120 / 2700
Number of inlet / exhaust valves per cylinder	1 / 1
Exhaust gases cleaning system	three-component catalytic converter
Gearbox ratios	3.636 1.950 1.357 0.941 0.784
Final drive ratio	3.706
Transmission efficiency coefficient	0.941
Wheel rolling radius, m	0.282
Aerodynamic resistance coefficient	0.34
Area of the vehicle frontal section, m^2	1.931

Source: based on manufacturing plant data.

As researched fuels the conventional petroland fuel containing 25 % ethanol (FCEE25) by mass had been used.Physical and chemical characteristics of used fuels are presentedin Table 2.

Table 2

Characteristics of used fuels

Characteristic title	Specifications	
Fuel type	petrol	FCE
Ethanol content by mass in fuel, %	0	25
The heat of fuel combustion, MJ/kg	43.7	39.7
Fuel density for 20 °C, kg/l	0.7325	0.754
Need of air for full fuel combustion, kg/kg	14.82	13.36
Carbon content in fuel, kg C/kg	0.855	0.772
Hydrogen content in fuel, kg H/kg	0.145	0.141
Oxygen content in fuel, kg O/kg	0	0.087
Molar mass, g/mole	115	98

Source: based on fuels laboratory research and reference data

For carrying out of experimental part of the study the on-board system for obtaining vehicle motion parameters is used. The on-board system basedona information device, which connected to On-Board Diagnostic (OBD) connector using a wireless adapter (Fig. 1).For determination of current vehicle location and further obtaining current values of longitudinal road inclination angle, the Global Positioning System (GPS) was used.

At measuring of the vehicle motion parameters using the on-board system for data obtaining the following parameters are determined: coolant temperature t_{COOL}, throttle position φ_{thr}, engine crankshaft rotation speed n_e, ignition timing angle θ, vehicle speed V_{a}, oxygen sensor voltage and status, fuel injection time, mass air consumption, diagnostic trouble codes, vehicle geographic location coordinates.

Based on the obtained parameters with using the vehicle motion mathematical model the following parameters are determined: vehicle passed way S, fuel consumption persecond g_{FUEL}, total fuel consumption $_{\mathrm{FUEL\_\Sigma}}$, catalytic converter efficiency according to excess air coefficient λ

and catalytic converter temperature t_{CAT}, carbon monoxide emission persecond g_{CO}, total carbon monoxide emission g_{CO_Σ}, hydrocarbons emission persecond g_{CmHn}, total hydrocarbons emission g_{CmHn_Σ}, nitrogen oxides emission persecond g_{NOx}, total nitrogen oxides emission g_{NOx_Σ}.

Done

Tcool, C: 24
Fidr, %: 0
nd, rpm: 1360
dPXX, %: 1,010
Kinj: 1,042
IGN, deg: 5,5
Va, km/h: 0
U, V: 13,75

(*a*) (*b*)

Fig. 1. On-board system elements for data obtaining in vehicle motion: (*a*) informationdevice; (*b*) adapter with connector for OBD connection

Source: developed by author

A calculating unit of the mathematical model determines engine operating cycle parameters, air and fuel consumption, harmful substances concentrations in exhaust gases and exhaust gases cleaning efficiency according to necessary value of engine torque during the vehicle motion, which depend on excess air coefficient, ignition timing angle, inlet and exhaust systems characteristics, fuel type, number, bore size and capacity of engine cylinders, engine compression ratio and other parameters. The calculating unit is based on the volume balance method suggested by Professor M. Glagolyev and modified in scientific works of V. Dyachenko [10], M. Shokotov and others, principles of the theory of mechanisms and machines.

Determinations of harmful substances emissions persecond and total emissions are based on current engine fuel and air consumption during vehicle motion, exhaust gases harmful substances concentrations and exhaust gases cleaning efficiency.

The carbon monoxide concentration (C_{CO}, %) is described by the equation:

$$C_{CO} = \begin{pmatrix} 6.999 \cdot 10^{-4} \cdot n_e \cdot \eta_v + 1.281 \cdot \eta_v^2 - 2.504 \cdot \eta_v + \\ + 2.542 - 1.378 \cdot 10^{-3} \cdot n_e + 2.474 \cdot 10^{-7} \cdot n_e^2 \end{pmatrix} \cdot (21 - 20 \cdot \lambda) \cdot k_{fuel}^{CO} \qquad (1)$$

,

where η_v is cylinder volume efficiency coefficient; k_{fuel}^{CO} is fuel type influence coefficient on *CO* concentration.

The hydrocarbons concentration (C_{CmHn}, ppm) is described by the equation:

$$C_{CmHn} = \begin{pmatrix} 0.036 \cdot n_e \cdot \eta_v + 423.4 \cdot \eta_v^2 - 442.4 \cdot \eta_v + \\ + 270.66 - 0.047 \cdot n_e + 7.371 \cdot 10^{-6} \cdot n_e^2 \end{pmatrix} \cdot (5 - 4 \cdot \lambda) \cdot k_{fuel}^{CmHn} \qquad (2)$$

,

where k_{fuel}^{CmHn} is fuel type influence coefficient on C_mH_n concentration.

The nitrogen oxides concentration (C_{NOx}, ppm) is described by the equation:

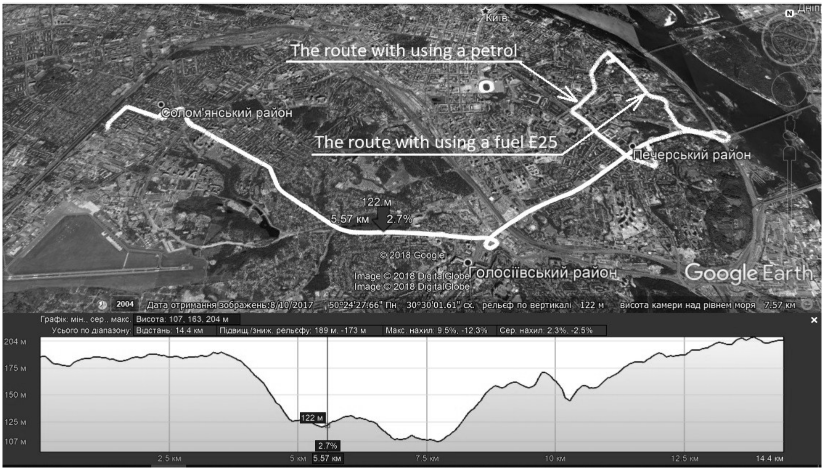
$$C_{NOx} = \begin{pmatrix} 0.373 \cdot n_e \cdot \eta_v - 9271 \cdot \eta_v^{\,2} + 9208 \cdot \eta_v - \\ -1685 + 0.238 \cdot n_e + 5.543 \cdot 10^{-5} \cdot n_e^{\,2} \end{pmatrix} \cdot (3.85 \cdot \lambda - 2.85) \cdot k_{fuel}^{NOx}, \tag{3}$$

where k_{fuel}^{NOx} is fuel type influence coefficient on NO_x concentration.

The exhaust gases harmful substances concentrations have been determined using results of carried out laboratory experimental researches of the engine.

Exhaust gases cleaning efficiency depends on a catalytic converter temperature state, an air-fuel mixture content, which is going to engine cylinders during an inletprocess, the degree of catalytic converter active coataging. The peculiarities of the exhaust gases cleaning efficiency determination were described in detailin [6, 9].

Experimental part of the study contained the obtaining and further processing the following data: the vehicle motion parameters, the engine modes and control parameters, the temperature state of the engine and the catalytic converter, the fuel and air consumption, the harmful emissions during the vehicle motion in Kyiv centre using the conventional petrol and fuel containing ethanol. The routes scheme, obtained with GPS technology, is show in Fig. 2. Both routes coincideal most for 80 %, but have some different parts.



Дата отримання зображень:8/10/2017 50°24'27.66" Пн 30°30'01.61" сх. рельєф по вертикалі 122 м висота камери над рівнем моря 7.57 км

Графік: мін., сер., макс. Висота: 107, 163, 204 м

Усього по діапазону: Відстань: 14.4 км Підвищ./зниж. рельєфу: 189 м, -173 м Макс. нахил: 9.5%, -12.3% Сер. нахил: 2.3%, -2.5%

Fig. 2. The vehicle routes during using the studied fuels
Source: developed by author

The experimental studies were carried out inreal traffic conditions the sameas daily operation. Anambient temperature during the vehicle motion is 19 °C when using the petrol and 15 °C using the fuel E25.

Using the obtained current vehicle location coordinates and Google Earthe levation tool the vehicle routes characteristics by the value of longitudinal road in clination angle α for studied fuels had been obtained (Fig. 3). The obtained routes characteristics are used for vehicle fuel consumption and harmful emissions prognostication in different road conditions.

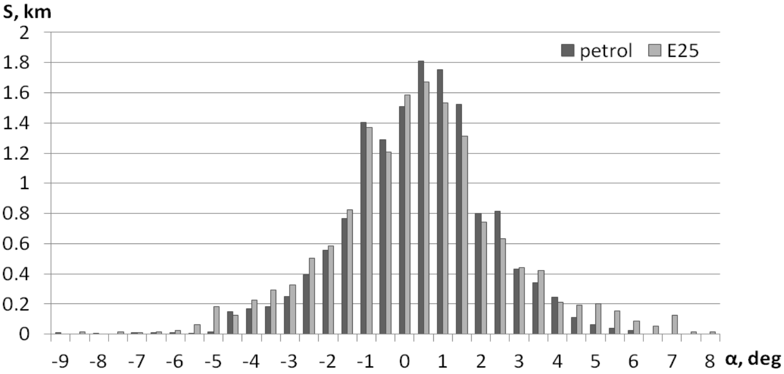


Fig. 3. The routes characteristics by the value of longitudinal road in clination angle
Source: developed by author

Based on the vehicle OBD data, the current vehicle speed, passed way and motion time have been determined for both fuels. As it shown on presented dependencies (Fig. 4), the vehicle speed mode is the almost same for both fuels. But, when FCE E25 is used, areas with speed lowered to 10 km/h have a place. This is traffic conditions influence, which is characterized by a traffic flow density and intensity. This is external random factors, which leads to increasing the total motion time from 1635 s when using the conventional petrol to 1863 s when using the E25 fuel. The total vehicle passedway is 14.705 km with using the petrol and 15.197 km with using the E25 fuel.

Asitshown at the vehicle motion time $\tau$and passedway Spartition by engine modes (Fig. 5), the engine has a more big time for partial load and idling modes when using the E25 fuel than when using the petrol. But, engine operation in for ceidling mode with out fuel supply when using the petrol has a more big time than when using the E25 fuel. Here with, the vehicle passed way with using both fuels is almost same for partial load mode. But, the vehicle passed way with using the E25 fuel is bigger for idling mode. Correlations of passed way and motion time for different engine modes enable to determine an average motion speed for the modes when using the petrol and E25 fuel. They are 41.4 km/hand 37.8 km/h for partial load, 55.8 km/h and 62.5 km/h for forceidling mode, 17.8 km/h and 17.5 km/h for idling mode. Thus, the average vehicle speed modes for different engine modes when using different fuels are also similar.

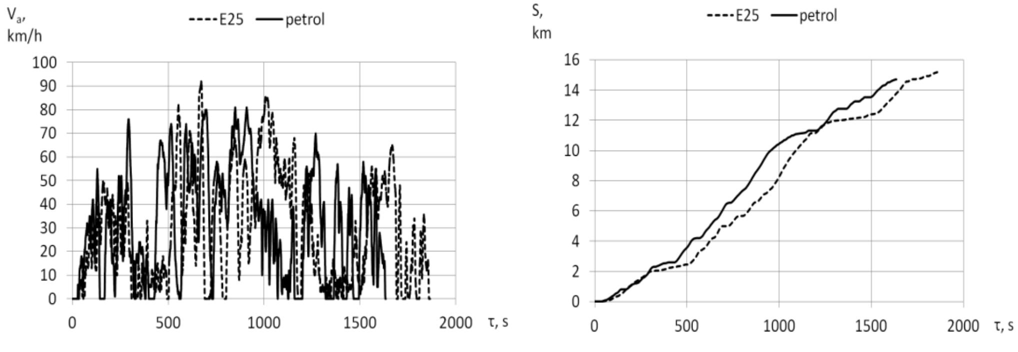


Fig. 4. Dependencies of the current vehicle speed V_a and passed way S from motion time when using the studied fuels
Source: developed by author

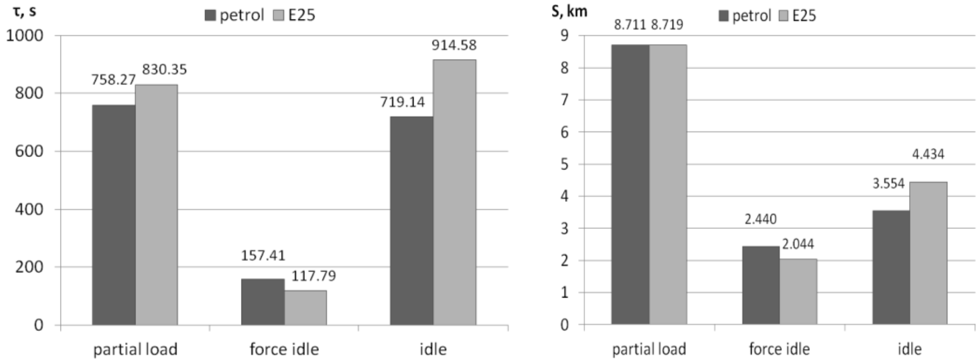


Fig. 5. The vehicle motion time $\tau$and passed way Spartition by engine modes when using the studied fuels
Source: developed by author

Dependencies of coolant t_{COOL} and catalytic converter t_{CAT} temperatures from the vehicle motion time when using the studied fuels are shown on Fig. 6. The dependencies show, that heating time of coolant to the operating temperature of 90 °C is 350 s when using the petrol and 435 s when using the E25 fuel. The heating time of catalytic converter to the temperature of exhaust gases effective cleaning is 132 s when using the petrol and 301 s when using the E25 fuel.

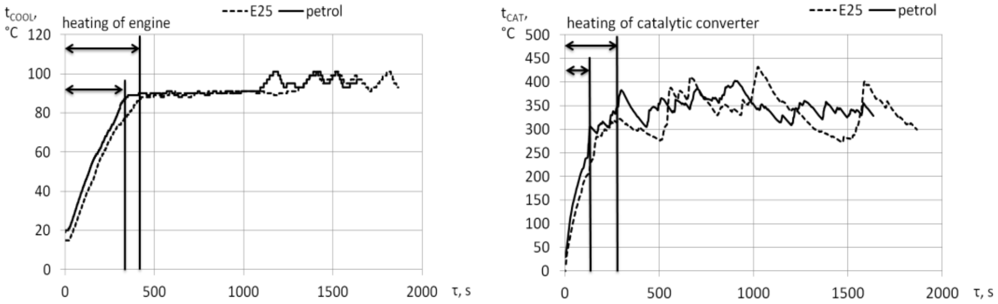


Fig. 6. Dependencies of coolant t_{COOL} and catalytic converter t_{CAT} temperatures from the vehicle motion time when using the studied fuels
Source: developed by author

The different time of operating temperatures achieving for coolant and catalytic converter when using the different fuels has been caused by common influence of anambient temperature and speed and load engine modes (Fig. 7). Fig. 7 shows, that engines modes have been shifted to higher values of crankshaft rotation speed n_e and throttle position φ_{thr} when using conventional petrol comparatively with using the E25 fuel.

Dependencies of total fuel consumption $g_{\text{FUEL\_}\Sigma}$ on the vehicle motion time and their partition by the engine modes when using studied fuels are shown on Fig. 8. As it shown on Fig. 8, the total fuel consumption per route is 891 g when using the petrol and 1098 g when using the E25 fuel. Thus, the total fuel consumption of E25 is on 23.2 % more than total petrol consumption. Herewith, the E25 fuel consumption is more than petrol consumption on 20 % for engine partial load mode and on 33.5 % for engine idling mode. This difference is caused by much bigger vehicle motion time for these engine modes when using the E25 fuel.

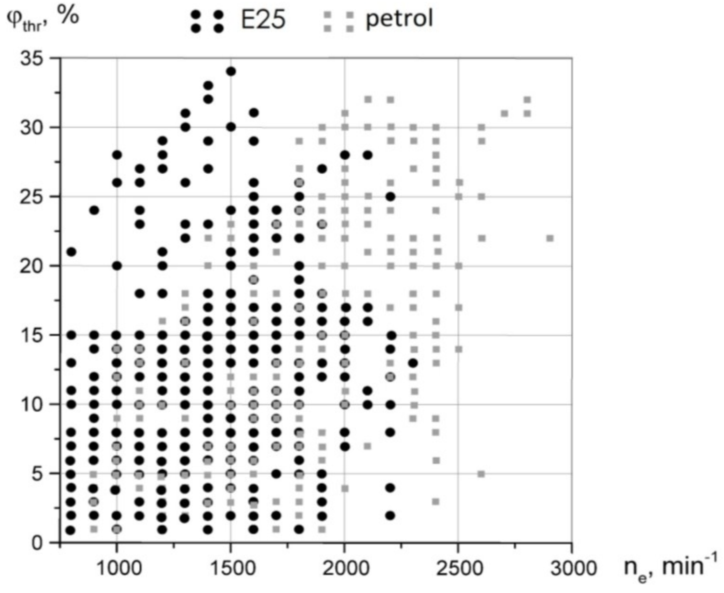


Fig. 7. Partition of the engine speed and load modes during the coolant and catalytic converter heating
Source: developed by author

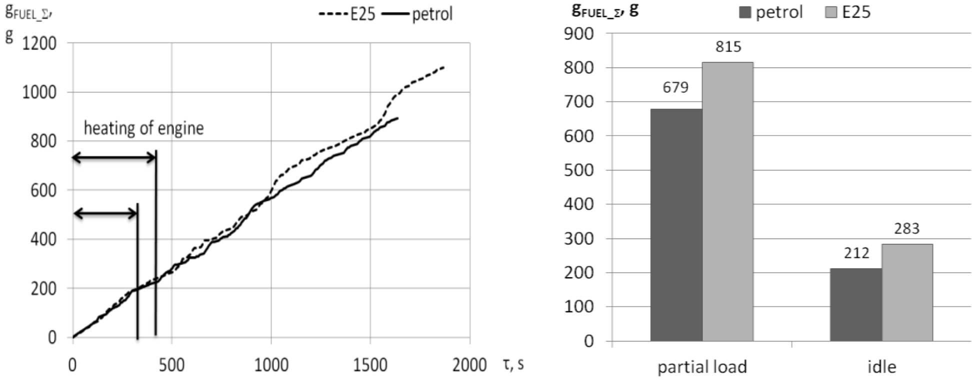


Fig. 8. Dependencies of total fuel consumption on the vehicle motion time and their partition by the engine modes when using studied fuels
Source: developed by author

Dependencies of total carbon monoxide emission g_{CO_Σ} on the vehicle motion time and their partition by the engine modes when using studied fuels are show non Fig. 9. As it shown on Fig. 9, the total carbon monoxide emission per route is 38.864 g when using the petrol and 63.935 g when using the E25 fuel. Thus, the total carbon monoxide emission when using the E25 fuel is on 64.5 % more than when using the petrol. Herewith, the carbon monoxide emission when using the E25 fuel is more than when using the petrol on 85.1 % for engine partial load mode and on 6.2 % for engine idling mode. This difference is caused by much bigger catalytic converter heating time to the temperature of exhaust gases effective cleaning when using the E25 fuel. This factor influences significantly on the total value of carbon monoxide emission and other harmful substances. It has a place because emission of carbon monoxide, which is emitted for catalytic converter heating period, is near 14 g or 36 % from his total emission when using the petrol and 32 g or 50.1 % from his total emission when using the E25 fuel. Relative increasing of the carbon monoxide emission for catalytic converter heating period is 128 % when using the E25 fuel comparatively with when using the petrol. Thus, the much higher value of carbon monoxide emission when using the E25 fuel is caused by the catalytic converter heating duration, which is influence result of engine modes during heating.

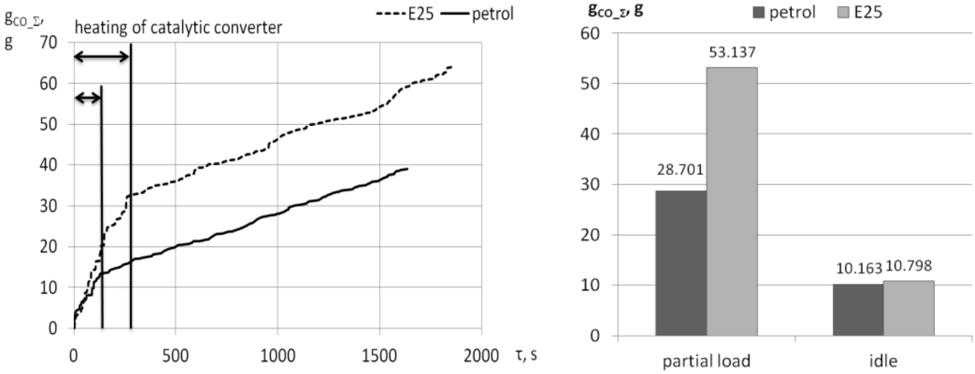


Fig. 9. Dependencies of total carbon monoxide emission on the vehicle motion time and their partition by the engine modes when using studied fuels
Source: developed by author

Dependencies of total hydrocarbons emission g_{CmHn_Σ} on the vehicle motion time and their partition by the engine modes when using studied fuels are show nonFig. 10. As it shown on Fig. 10, the totalhydrocarbons emission per route is 1.161 g when using the petrol and 1.530 g when using the E25 fuel. Thus, the total hydrocarbons emission when using the E25 fuel is on 31.8 % more than when using the petrol. Herewith, the hydrocarbons emission when using the E25 fuel is more than when using the petrol on 36.9 % for engine partial load mode and on 17.7 % for engine idling mode. Main reason of higher hydrocarbons emission when using the E25 fuel is also caused by catalytic converter heating time. The hydrocarbons emission, which is emitted for catalytic converter heating period, is near 0.25 g or 21.5 % from their total emission when using the petrol and 0.5 g or 32.7 % from their total emission when using the E25 fuel. Relative increasing of the hydrocarbons emission for catalytic converter heating period is 100 % when using the E25 fuel comparatively with when using the petrol. Thus, influence of the catalytic converter heating time on the hydrocarbons emission when using the E25 fuel is significant, but it is less than for the carbon monoxide emission.

Dependencies of total nitrogen oxides emission $_{NOx\_\Sigma}$ on the vehicle motion time and their partition by the engine modes when using studied fuels are show non Fig. 11. As it shown on Fig. 11, the totalnitrogen oxides emission per route is 1.774 g when using the petrol and 1.838 g when using the E25 fuel. Thus, the total nitrogen oxides emission when using the E25 fuel is on 3.6 % more than when using the petrol. Herewith, the nitrogen oxides emission when using the E25 fuel is more than when using the petrol on 4.9 % for engine partial load mode and less than when using the petrol on 13.1 % for engine idling mode. This data is due to the fact that nitrogen oxides emission significantly depends on the engine modes. The nitrogen oxides emission is significantly increased with increasing of the engine load and crankshaft rotation speed. The catalytic converter heating period influence on the nitrogen oxides emission is not same significant as for other harmful substances emissions. It is due to the factthat engine load and crankshaft rotation speed are not high at this period. The nitrogen oxides emission increasing when using the E25 fuel is mostly caused by the bigger vehicle motion time. This is external factors influence.

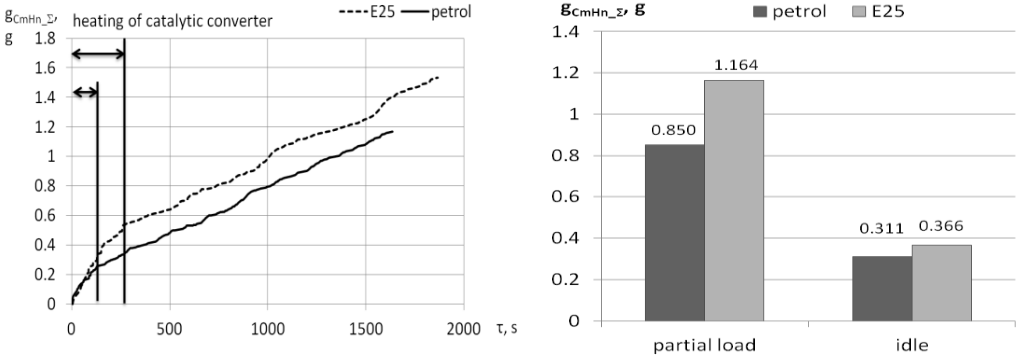


Fig. 10. Dependencies of total hydrocarbons emission on the vehicle motion time and their partition by the engine modes when using studied fuels
Source: developed by author

The obtained data evidences about ambiguous influence of different operating factors on the vehicle fuel consumption and harmful emissions when using the fuel containing ethanol. For objective evaluation of the influence of the fuel containing ethanol using on vehicle performance the more detailed partition of the obtained fuels consumption and emissions by engine speed and load modes must be done.

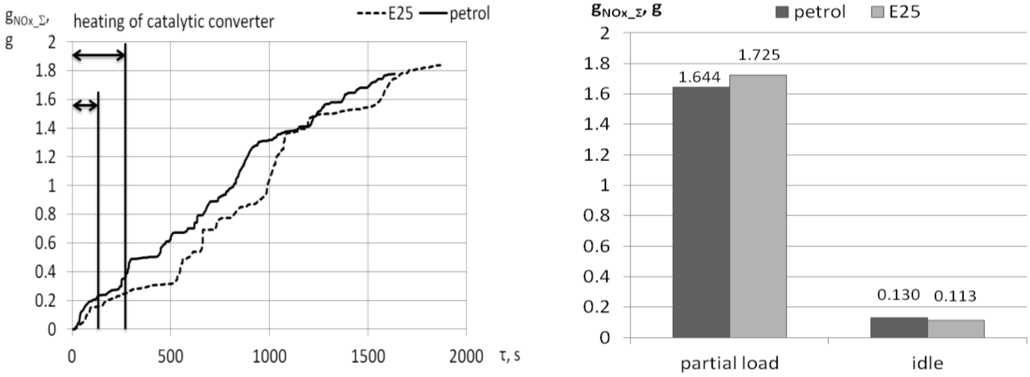


Fig. 11. Dependencies of total nitrogen oxides emission on the vehicle motion time and their partition by the engine modes when using studied fuels
Source: developed by author

Herewith, peculiarities of engine control system operating for steady state and transient modes should be taken into account. The modes with constant values of crankshaft rotation speed and throttle position or their slowly changing for heated engine are the steady state modes. Other engine modes and heating modes are transientones.Thus, correct comparison of engine performance when using different fuel sispossibleonlyforthe same modes of engine operation. For example, dependencies of the engine fuel consumption per second for the engine steady state modes when using the conventional petrol and fuel containing ethanol are presented on Fig. 12.

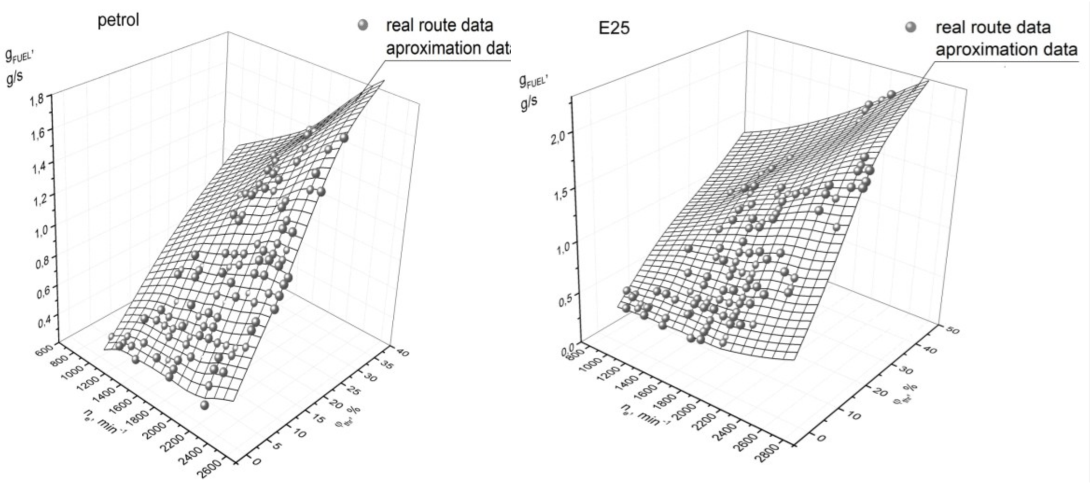


Fig. 12. Dependencies of the engine fuel consumption persecond for the engine steady state modes when using the petrol and E25 fuel containing ethanol

Source: developed by author

The dependencies have been obtained using the fuel consumption and operation time for appropriative engine mode during the vehicle motion on real route. The experimental data approximation has been carried out using the specialized soft ware. The obtained dependencies describe the engine fuel consumption under the operating conditions. These dependencies are the engine operating characteristics, which can beused for vehicle technical condition monitoring.

An approximation error (δ_{appr}, %) is evaluated by weighted average relative error value:

$$\delta_{appr} = \sum_{i=1}^{n} \frac{\tau_i}{\tau_\Sigma} \cdot \delta_i \qquad (4)$$

where n is total quantity of the engine modes, which are characterized by combination of the crankshaft rotation speed n_e value and the throttle position φ_{thr} value; τ_i is the engine operation time for i-th mode, s; τ_Σ is the total time of the vehicle motion on the route, s; δ_i is relative approximationerror of the engine performance for i-th mode, %.

The approximation errors of the fuel consumption persecond, carbonmon oxide emission persecond, hydrocarbons emission persecond and nitrogen oxides emission persecond are 2 %, 3.68 %, 2.38 %, 4.81 % accordingly when using the petrol and 1.9 %, 4.43 %, 2.15 %, 5.09 % accordingly when using the E25 fuel.

The comparative operating characteristics of the fuel consumption per second (g_{FUEL}, g/s), carbon monoxide emission per second (g_{CO}, g/s), hydrocarbons emission per second (g_{CmHn}, g/s) and nitrogen oxides emission per second (g_{NOx}, g/s) when using the studied fuels are shown on Fig. 13.

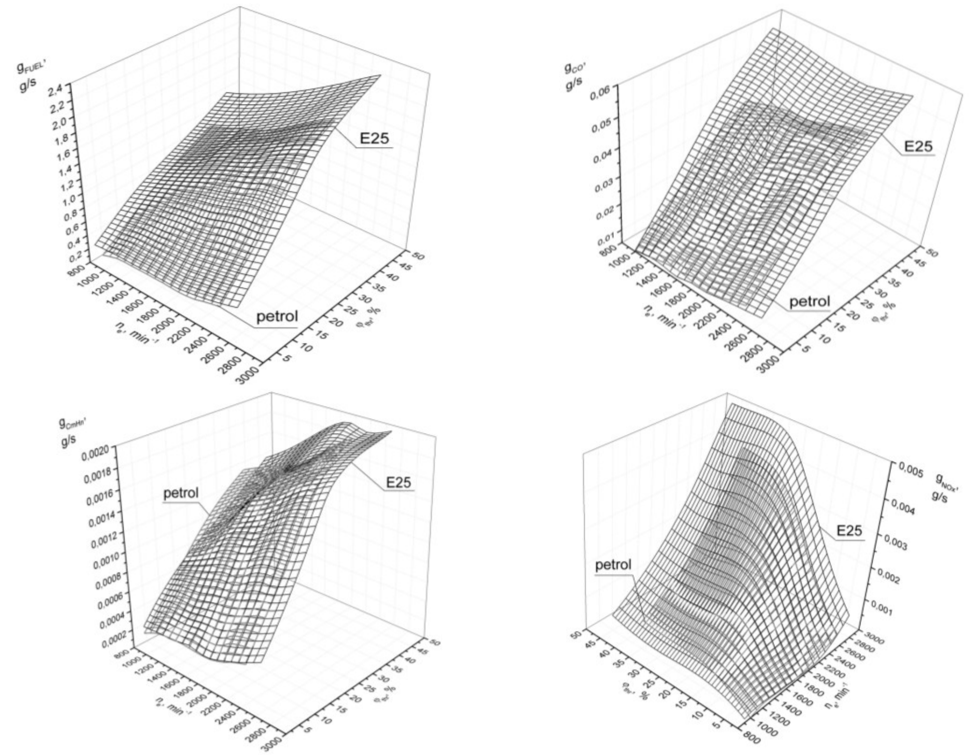


Fig. 13. The comparative operating characteristics of the fuel consumption per second (g_{FUEL}, g/s), carbon monoxide emission per second (g_{CO}, g/s), hydrocarbons emission per second (g_{CmHn}, g/s) and nitrogen oxides emission per second (g_{NOx}, g/s) when using the studied fuels
Source: developed by author

Using the operating characteristics the most common engine mode range for the vehicle motion in city traffic conditions has been determined. An idling mode and partial load modes with values of crankshaft rotation speed from 1500 to 2500 min^{-1} and throttle position from 5 to 20 % compose the range. For these modes with using the engine operating characteristics for the petrol and fuel containing ethanol the vehicle fuel consumption per second and harmful emissions per second have been determined. The obtained data and relative difference (*diff.*, %) of the data for studied fuels are given in Table 3.

Table 3

The vehicle fuel consumption per second and harmful emissions per second whenusingthepetrolandthe fuel containing ethanol

	Performance	g_{fuel}, g/s			g_{CO}, g/s		
	Fuel type	petrol	FCE	*diff.*, %	petrol	FCE	*diff.*, %
1	*2*	*3*	*4*	*5*	*6*	*7*	*8*
Engine mode	Idling mode	0.262	0.288	9.92	0.00707	0.00646	-8.63
	n_e= 1500 min^{-1}; φ_{thr} = 5 %	0.461	0.534	15.84	0.0119	0.0110	-7.56
	n_e= 1500 min^{-1}; φ_{thr} = 10 %	0.681	0.778	14.24	0.0173	0.0172	-0.58
	n_e= 1500 min^{-1}; φ_{thr} = 20 %	1.068	1.191	11.52	0.0299	0.0352	17.73

Table 3 continue

1	*2*	*3*	*4*	*5*	*6*	*7*	*8*
	$n_e = 2000$ min^{-1}; $\varphi_{\text{thr}} = 5$ %	0.513	0.583	13.65	0.0135	0.0131	-2.96
	$n_e = 2000$ min^{-1}; $\varphi_{\text{thr}} = 10$ %	0.792	0.856	8.08	0.0203	0.0193	-4.93
	$n_e = 2000$ min^{-1}; $\varphi_{\text{thr}} = 20$ %	1.274	1.413	10.91	0.0340	0.0344	1.18
	$n_e = 2500$ min^{-1}; $\varphi_{\text{thr}} = 5$ %	0.653	0.705	7.96	0.0184	0.0163	-11.41
	$n_e = 2500$ min^{-1}; $\varphi_{\text{thr}} = 10$ %	0.895	0.987	10.28	0.0244	0.0230	-5.74
	$n_e = 2500$ min^{-1}; $\varphi_{\text{thr}} = 20$ %	1.463	1.638	11.96	0.0374	0.0381	1.87
Engine mode	Idling mode	0.000279	0.000273	-2.15	0.000069	0.000065	-5.80
	$n_e = 1500$ min^{-1}; $\varphi_{\text{thr}} = 5$ %	0.000491	0.000496	1.02	0.000459	0.000545	18.74
	$n_e = 1500$ min^{-1}; $\varphi_{\text{thr}} = 10$ %	0.000722	0.000739	2.35	0.00109	0.00111	1.83
	$n_e = 1500$ min^{-1}; $\varphi_{\text{thr}} = 20$ %	0.00122	0.00120	-1.64	0.00158	0.00163	3.16
	$n_e = 2000$ min^{-1}; $\varphi_{\text{thr}} = 5$ %	0.000545	0.000552	1.28	0.000578	0.000623	7.79
	$n_e = 2000$ min^{-1}; $\varphi_{\text{thr}} = 10$ %	0.000843	0.000830	-1.54	0.00139	0.00142	2.16
	$n_e = 2000$ min^{-1}; $\varphi_{\text{thr}} = 20$ %	0.00137	0.00139	1.46	0.00264	0.00273	3.41
	$n_e = 2500$ min^{-1}; $\varphi_{\text{thr}} = 5$ %	0.000704	0.000698	-0.85	0.000978	0.00103	5.32
	$n_e = 2500$ min^{-1}; $\varphi_{\text{thr}} = 10$ %	0.000963	0.000973	1.04	0.00178	0.00189	6.18
	$n_e = 2500$ min^{-1}; $\varphi_{\text{thr}} = 20$ %	0.00155	0.00160	3.23	0.00369	0.00389	5.42

Source: developed by author

As it seen from Table 3, relative value of the fuel consumption in creasing when using the E25 fuel is from 7.96 % to 15.84 % comparatively with when using the petrol. Here with, influence of used fuel type on the carbon monoxide emission is ambiguous. For more part of engine modes the carbon monoxide emission is decreased from 0.58 to 11.41 % when using the E25 fuel comparatively with when using the petrol. Butfor $n_e = 1500$ min^{-1}; $\varphi_{\text{thr}} = 20$ % mode the carbon monoxide emission is increased on 17.73 % when using the E25 fuel. The value of fuel type influence on hydrocarbons emission is insignificant. This value does not exceed 2.5 % for more part of engine modes. This is as approximation error level. The nitrogen oxides emission is also increased from 1.83 to 6.18 % when usingtheE25 fuel for all engine modes besides idling mode and $n_e = 1500$ min^{-1}; $\varphi_{\text{thr}} = 5$ % mode. In idling mode the nitrogen oxides emission is decreased on 5.8 % when using the E25 fuel. In $n_e = 1500$ min^{-1}; $\varphi_{\text{thr}} = 5$ % mode the nitrogen oxides emission is increased on 18.74 % when using the E25 fuel.

Taking in to account the ambiguous influence of used fuel type on the vehicle fuel consumption and harmful emissions, it is expedient to evaluate the fuel consumption and harmful emissions when using of different fuel types for vehicle motionin 900 sconditional driving cycle with out transient motion modes. The engine modes for the driving cycle appropriate to the engine modes specified in Table 3. The idling mode duration is accepted equalto 450 s. Duration of each of other modes is 50 s.

The total fuel consumption (g_{FUEL_Σ}, g) in the driving cycleis

$$g_{FUEL\_\Sigma} = \sum_{i=1}^{n} g_{FUEL\ i} \cdot \tau_i , \tag{5}$$

where n is quantity of the engine modes, $n = 9$; τ_i is the engine operation time for i-th mode, s; $g_{\text{FUEL}\ i}$ is the engine fuel consumption per second for i-th mode, g/s.

The total carbon monoxide emission (g_{CO_Σ}, g) in the driving cycle is

$$g_{CO\_\Sigma} = \sum_{i=1}^{n} g_{CO\,i} \cdot \tau_i , \tag{6}$$

where $g_{\text{CO}\ i}$ is the engine carbon monoxide emission per second for i-th mode, g/s.

The total hydrocarbons emission (g_{CmHn_Σ}, g) in the driving cycle is

$$g_{CmHn\_\Sigma} = \sum_{i=1}^{n} g_{CmHn\,i} \cdot \tau_i , \tag{7}$$

where $g_{CmHn\,i}$ is the engine hydrocarbons emission per second for i-th mode, g/s.

The total nitrogen oxides emission (g_{NOx_Σ}, g) in the driving cycleis

$$g_{NOx\_\Sigma} = \sum_{i=1}^{n} g_{NOx\,i} \cdot \tau_i , \tag{8}$$

where $g_{NOx\,i}$ is the engine nitrogen oxides emission per second for i-th mode, g/s.

Using the values of fuel consumption per second and harmful substances emissions per second from Table 3 and the equations (5–8) it is done the calculation of the vehicle total fuel consumption and harmful emissions per driving cycle when using the conventional petrol and the E25 fuel containing ethanol. Based on the calculation results it is found that the total vehicle fuel consumption per driving cycle, carbon monoxide emission per driving cycle, hydrocarbons emission per driving cycle, nitrogen oxides emission per driving cycle are 508 g, 13.537 g, 0.546 g, 0.740 g accordingly when using the petrol and 564 g, 13.287 g, 0.547 g, 0.773 g accordingly when using the E25 fuel. The relative increasing of fuel consumption is 11 % when using the E25 fuel. The relative decreasing of carbon monoxide emission is 1.8 % when using the E25 fuel. The relative increasing of hydrocarbons emission is 0.2 % when using the E25 fuel. The relative increasing of nitrogen oxides emission is 4.5 % when using the E25 fuel. Thus, the using of the E25 fuel containing ethanol leads to some decreasing of the carbon monoxide emission and insignificant increasing of the nitrogen oxides emission.

Taking into account that the petrol and the fuel containing ethanol have a different density (Table 2), the volume petrol consumption per the driving cycle is 0.694l and the volumeE25 fuel consumption per the driving cycle is 0.748l. Thus, the relative increasing of the E25 fuel consumption comparatively with the petrol consumption is 7.8 % by volume equivalent.

Here with, the engine operation efficiency is also characterized by energy consumption. Taking into account the fuels combustion heat (Table 2), the equivalent petrol consumption per the driving cycle is 22.2 MJ and the equivalent E25 fuel consumption per the driving cycle is 22.39 MJ. The relative increasing of the E25 fuel consumption comparatively with the petrol consumption is 0.9 % by energy equivalent. This evidences about in significant impairment of the engine operation efficiency when using the E25 fuel containing ethanol.

Thus, the using of fuels containing ethanol more than 20 % has significant influence on fuel economy and environmental performance of sparking nition engine because the physical and chemical characteristics of the fuels containing ethanol have significant differences comparatively with conventional petrol.

The operating conditions, which are characterized by complex of road, traffic and atmosphere conditions, have significant influence on vehicle motion modes and vehicular engine operation modes. The operating vehicle fuel consumption and harmful emissions significantly depend on these vehicle and engine modes.The temperature state of engine and catalytic converter, the engine crankshaft rotation speed and load have the highest influence on the vehicle fuel consumption and harmful emissions.Thus, for the correct evaluation of vehicle performance when using the conventional petrol and the fuel containing ethanol, the fuel consumption and harmful emissions determination for separate engine speed and load modes during the vehicle motion is necessary.

Based on the experimental study resultsof fuel consumption and harmful emissions during motion of BOGDAN 21101 1.6 l, which equipped with VAZ-21114 spark ignition engine, in city

traffic using the conventional petrol and the E25 fuel containing ethanol, the operating characteristics of the fuel consumption per second, carbon monoxide emission per second, hydrocarbons emission per second and nitrogen oxides emission per second for the range of engine speedandloadmodes are obtained. The weighted average approximation errors of experimental data are 1.9–5.09 %.

Using the obtained operating characteristics, the fuel type influence on the fuel consumption and harmful emissions for separate steady state operating engine modes and conditional driving cycle, which consists the complex of these operating modes, have been found. The results of this study show that the fuel consumption is increased on 11 % bymass, on 7.8 % by volume and on 0.9 % by energy equivalent when using the E25 fuel containing ethanol comparatively with using the conventional petrol. The last value evidences about insignificantimpairmentof the engine operation efficiency when using the E25 fuel containing ethanol. Also the using of the E25 fuel containing ethanol leads to some decreasing of the carbon monoxide emission, insignificant increasing of the nitrogen oxides emission and with practically unchanged hydrocarbons emission.

Fur ther research will beaimed on cause's analysis of engine operation efficiency impairment and nitrogen oxides emission increasing when using fuels containing ethanol more than 20 %, improvement methods determination of these performances.

РЕФЕРАТ

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ОЦІНКА СПОЖИВАННЯ ПАЛИВА ТА ВИКИДІВ ШКІДЛИВИХ РЕЧОВИН МОТОРНИМИ ТРАНСПОРТНИМИ ЗАСОБАМИ З ДВИГУНОМ ВНУТРІШНЬОГО ЗГОРАННЯ ЗА УМОВ ЕКСПЛУАТАЦІЇ З ВИКОРИСТАННЯМ ЕТАНОЛОВМІСНОГО ПАЛИВА

Підвищення паливної економічності та зниження шкідливих викидів транспортних засобів є актуальним для досягнення високого рівня екологічної безпеки транспорту та його сталого розвитку. Метою дослідження є оцінювання витрати палива та викидів шкідливих речовин транспортним засобом з двигуном з іскровим запалюванням, системою впорскування і каталітичною нейтралізацією відпрацьованих газів під час використання спиртовмісного палива з вмістом біоетанолу більше 20 % на основі даних про параметри руху транспортного засобу в умовах реального маршруту. Подальші дослідження буде направлено на аналіз причин погіршення показників транспортного засобу та визначення способів їх поліпшення при використанні спиртовмісних палив.

Ключові слова: витрата палива, шкідливі викиди, транспортний засіб, двигун з іскровим запалюванням, умови експлуатації, спиртовмісне паливо.

РЕФЕРАТ

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ОЦЕНКА ПОТРЕБЛЕНИЯ ТОПЛИВА И ВЫБРОСОВ ВРЕДНЫХ ВЕЩЕСТВ МОТОРНЫМИ ТРАНСПОРТНЫМИ СРЕДСТВАМИ С ДВИГАТЕЛЕМ ВНУТРЕННЕГО СГОРАНИЯ ПРИ ЭКСПЛУАТАЦИИ С ИСПОЛЬЗОВАНИЕМ ЭТАНОЛСОДЕРЖАЩИХ ТОПЛИВ

Повышение топливной экономичности и снижение вредных выбросов транспортных средств актуальны для достижения высокого уровня экологической безопасности транспорта и его устойчивого развития. Целью исследования является оценка расхода топлива и выбросов вредных веществ транспортным средством с двигателем с искровым зажиганием, системой впрыска и каталитической нейтрализацией отработавших газов при использовании спиртосодержащего топлива с содержанием биоэтанола более 20 % на основе данных о параметрах движения транспортного средства в условиях реального маршрута. Дальнейшие исследования будут направлены на анализ причин ухудшения показателей транспортного средства и определения способов их улучшения при использовании спиртосодержащих топлив.

Ключевые слова: расход топлива, вредные выбросы, транспортное средство, двигатель с искровым зажиганием, условия эксплуатации, спиртосодержащее топливо.

ABSTRACT

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EVALUATION OF FUEL CONSUMPTION AND HARMFUL SUBSTANCES EMISSIONS BY VEHICLE WITH SPARK IGNITION ENGINE UNDER OPERATION CONDITIONS WITH USING OF FUEL CONTAINING ETHANOL

Increasing of fuel economy and reducing of harmful emissions of vehicles are actual for achieving a high level of transport environmental safety and sustainable development. The purpose of the study is an evaluation of vehicle fuel consumption and harmful emissions with a spark ignition engine equipped a fuel injection and exhaust gases cleaning systems, using a fuel containing ethanol more than 20 %. It is based on the vehicle motion parameters under real route conditions. Further research will be aimed to analysis of vehicle performance impairment causes and determination of their improvement methods when using fuels containing ethanol.

Key words: fuel consumption, harmful emissions, vehicle, spark ignition engine, operating conditions, fuel containing ethanol.

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3.9 FEATURES OF INTERACTION OF ORGANIC BINDER AND SLAG FILLER

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In conditions of constant development of the road transport followed by fast increase in the scope of truck fleet, increase in carrying capacity and dynamic features of cars, overall performance of vehicles to a great extent depends on riding qualities of motor roads which is assessed with regard to strength, evenness and roughness. The dominant role here belongs to asphalt pavements protecting road structure from direct effect of climatic factors impact and ensuring design speeds.

Asphalt pavements well proved themselves in the most complicated activity of road operational services during winter period when due to slipperiness formed on the surface of the road pavement, significant reduction in vehicles speed, traffic intervals and increase in the number of road accidents took place that negatively affected economic parametres of the state.

One of priority tasks of road branch is increasing operational reliability of motor roads during different seasons of the year. The main ways of of this task solution is application of asphalt pavements having sufficient durability that allows to ensure standard riding qualities and improvement of of road pavement design for the purpose of reduction of winter slipperiness formation.

Recently, in connection with increasing cost of road-building materials, the most actual problem in highway engineering was a wide application of local materials. In the regions with well developed iron and steel industry the most widespread local materials are coproducts of black and nonferrous metallurgy, that are the slags. Numerous researches define possibility of their use for preparation of asphalt mixes.

Use of asphalt concrete with slag materials is restricted for the pavements of the III-rd technical category highways and for lower road categories by existing regulations. This results from the fact that the properties of asphalt concrete with slag materials as road-building materials are considered in comparison with the properties of asphalt concrete on traditional (granite mineral) materials and insufficientl attention is given to studying operational and deformatsion-strength properties of asphalt pavements with slag materials, especially on the highways of the highest categories.

The urgency of the problem which is considered can be explained by the fact that in the regions with highly developed iron and steel industry the use of asphalt concrete with slag materials in the pavements of highways allows to gain certain economy of funds at their construction and maintenance, and also helps to solve the problem of metallurgical industry waste use.

Asphalt concrete with slag materials is an artificial construction conglomerate, which is a mixture of different types of metallurgical slags and bitumen, produced under certain technological conditions, laid and compacted in the upper layers of road pavement.

The study of the possibility of using metallurgical slag in asphalt concrete is the work of many scientists and the author: Belyatynsky, Krayushkina, Eremina, Korolev, Rastegayeva, Samodurov, Yudina, Hushek, Kandhal, Li et al. (2012), Sivilevicius et al. (2011), Shen et al. (2009), Sofilid et al. (2011), Takahashi et al. (2011), Wang et al. (2011), Wu et al. (2007). As a result of literary analysis, a fairly wide range of metallurgical slags was considered.

Based on the study of physical and mechanical properties, the possibility of using different types of metallurgical slags for the preparation of hot and cold asphalt concrete has been proved.

Of all types of slags of ferrous and nonferrous metallurgy, blast furnace slags, which are less prone to different types of decay, are most suitable for road construction. Slag materials with desired properties are obtained by controlling the speed of the cooling process of the slag melt.

The cooling rate determines the chemical, hydraulic activity of the material, its physicomechanical properties, structure and mineralogical composition, as well as features of interaction with bitumen in asphalt concrete. With rapid cooling, the slag melt turns into sand with a grain size of 0–2.0 mm, which has high hydraulic properties. During the slow cooling of the slag melt, heat energy is mainly spent on crystallization processes. The material is gaining high strength, but largely loses its hydraulic knitting properties.

Asphalt concrete with slag materials, as well as asphalt concrete from traditional materials, is divided into crushed-stone (fine-grained, coarse-grained) and sandy. Slag crushed stone, sand (natural or slag) and mineral powder are present in the crushed stone asphalt concrete as a mineral part. In the sandy asphalt concrete, at the base of the mineral part, there are slag, slag-and-sand sands and granulated slags. Depending on the laying temperature of asphalt concrete with slag materials, mixtures can be hot and cold.

Studying asphalt concrete with slag materials, all the above authors note the following: while maintaining the regularities inherent in asphalt concrete from traditional materials, the properties of asphalt concrete with slag materials are determined by the type of slag, its structure and porosity, which determine the nature of its interaction with bitumen.

The high chemical activity of slags and the high content of adsorption centers, in the form of divalent and trivalent cations Ca^{+2}, Mg^{+2}, Fe^{+2}, Fe^{+3}, leads to the formation of a solid bitumen – mineral material. In the interaction of bitumen with slag materials, the physical and chemical sorption bonds that have been formed firmly hold the bitumen film on the surface of the mineral material. The high porosity of slag materials, when combined with bitumen, leads to filtration of the binder and its components in the middle of the grains of the mineral material.

In the process of filtration, the oils penetrate through the capillaries into the grains to the greatest depth, the resins, due to their lower mobility and greater activity, penetrate to a lesser depth. Having a developed porous structure, slag crushed stone in asphalt concrete contributes to a more complete conversion of bitumen to a structured state. At the same time, due to selective diffusion of bitumen, enrichment of the structured layer with asphaltenes occurs. Selective filtration of bitumen components leads to the formation of more rigid and less elastic bitumen films on the surface of the slag aggregate.

The interaction of bitumen with slag aggregate leads to the realization of physical, mechanical, chemical, electrostatic and diffusion processes; as a result, adhesive bonds at the bitumen – mineral interface become durable and resistant to climatic factors, both at the time of combining and in time. The nature of the slag crushed stone surface, the viscosity of bitumen and its interaction with mineral material provide asphalt concrete with high indicators of internal friction angle φ (from 40° to 50°), which exceeds the value for asphalt concrete prepared using granite crushed stone (from 33° to 41°) .

The dependence of bitumen capacity indicators on the structural and textural signs of slag rubble was established: slag of a pumice-shaped structure with a porosity of 69 % has the greatest bitumen capacity, then slags of a capillary-porous structure with a porosity of 37 %, slags with a porosity of up to 14 % have the least bitumen capacity.

Asphalt concrete with slag materials has a greater value of residual porosity and, accordingly, a greater rate of water saturation than similar compositions on traditional (granite) mineral materials. Moreover, it should not be considered as a disadvantage, but as a feature of this type of asphalt concrete. Indicator of water saturation, as well as bitumen intensity, depends on the open porosity of the material. Gezentsvey (1956), Kovalev (1991), Rudensky (1992), comparing asphalt with slag materials with highly porous asphalt concrete from natural mineral materials, concluded that they were not sufficiently resistant to water, as well as freeze-thaw cycles.

But observations of the arranged asphalt concrete coatings with slag materials and studies carried out by Kovalev (1991) showed that the coating has a high frost resistance. This is due to the peculiarity of asphalt concrete porosity from traditional mineral materials and asphalt concrete with slag materials. In the latter, the residual porosity is mainly represented by closed pores.

Closed porosity creates a rigid structure of the material, the linear expansion coefficient of which is 1.5 times lower than in asphalt concrete from traditional materials. This leads to a decrease in temperature stress with sudden changes in temperature, and increased frost resistance and, consequently, durability of coatings.

The peculiarity of asphalt coatings with slag materials, in comparison with traditional ones, is a longer process of their formation. Rudensky (1992) found that the formation of coatings from asphalt concrete mixtures with slag materials does not occur immediately, but continues for some time. When the traffic intensity is more than 1 000 auto/day, the formation of asphalt concrete on slag sand ends in 1–1.5 years, on granulated slags – in 2–5 years from the moment of construction. At the same time, coatings already at the initial stage of operation have high shear resistance and do not exhibit ruts and sagging on them.

During the operation of the coating, with the stabilization of the structure of asphalt concrete, there is a decrease in pore volume, an increase in the density of asphalt concrete, an increase in the value of the angle of internal friction. The greatest increase is observed in the first year, in subsequent years, the angle of internal friction remains almost unchanged. The value of the internal adhesion in asphalt concrete with slag materials is steadily increasing as a result of the strengthening of coagulation structural bonds and irreversible processes that occur in the bitumen film.

When studying asphalt concrete with granulated slags and slag-and-sand sands, the features of preparation, laying and compaction of asphalt concrete with slag materials were established. Thus, on the basis of large-scale studies, it was established that the temperature regime for the preparation of such mixtures is within 110–130 °C, laying in the coating of mixtures on viscous bitumens is possible at a temperature of 70–80 °C, and the sealing temperature is in the range of 50–70° WITH. Thus, asphalt with slag materials occupies an intermediate position between the hot and cold type of asphalt.

Studies in the US by scientists Hunt, Boyle (2000) describe that in 1994, experimental sites were built in Oregon to assess the use of steelmaking slag in hot asphalt concrete mixes (HMAS). The research covers construction and observation, for five years, of the condition and TEC of a coating made of asphalt concrete, which included 30 % of the slag of steelmaking.

The production of asphalt concrete and the construction of pavement is not difficult, even when crushed steelmaking slag is used as aggregate. If the unit cost of production of asphalt concrete mixtures modified by steelmaking slags is the same as asphalt concrete mixtures of granite materials, the total project costs may increase due to a decrease in the specific surface area due to the use of a more “heavy” mixture made using steelmaking slag production.

For the pilot site for (NMAS), built on 30 % of the steelmaking slag, the specific surface area was 15 % less than when using the traditional “B” type asphalt mix.

Studies conducted in Turkey by scientists Ahmedzade, Sengoz (2009) demonstrate the effect of using steelmaking slag as a mineral material on the properties of hot mix asphalt. Four different types of asphalt mixes were used to prepare Marshall samples, and determine the optimal bitumen content.

The physicomechanical characteristics of all the mixtures were evaluated for stability according to Marshall, the modulus of tensile elasticity, and the determination of the tensile strength. Samples were examined for electrical sensitivity. It was noted that the slags of steelmaking production, used as a mineral material, improved the physical and mechanical properties of asphalt concrete mixtures.

Studies began with an assessment of the toxicity, chemical and physical properties of slags in steelmaking. Then, 0 %, 25 %, 50 %, 75 % and 100 % of the amount of limestone mineral material in the asphalt mixes was replaced with slag material from steelmaking.

The effectiveness of the slag aggregate of steelmaking was evaluated by improving the indicators of tensile strength, elastic modulus, resistance to groove formation, fatigue life of asphalt concrete samples. It was found that the replacement of up to 75 % of the amount of large limestone aggregate with aggregate from the steelmaking slag (SISP) improved the physical and mechanical properties of asphalt concrete mixtures. The results also showed that a 25 % replacement was the optimal replacement level.

Studies conducted by scientists from Oman, Asi et al. (2007), Hassan, Al-Jabri (2011), report on laboratory testing of granulated copper slag as fine aggregate in hot mix asphalt. The selection of the composition of the mixture according to Marshall was carried out on various mixtures containing up to 40 % of aggregate – copper slag. Testing of the dynamic module as the main indicator of material properties in the Guidelines for the design of road pavement using the mechanical – empirical method (IU – PDG) was carried out at different frequencies (from 0.1 Hz to 16 Hz) and at different temperatures (from 25 °C to 60 °C).

Baseline curves and shear coefficients for the dynamic modulus for control mixtures and slag-containing mixtures were developed. The curves developed were compared with the predictive model according to Witczak for 2 and 3 IU – PDG. The results showed a decrease in strength with increasing slag content in the mixtures compared with the control mixture.

As a result, the aggregate, which includes the steelmaking production slag, due to its physical and chemical properties, is a 100 % recycled product with great potential as a replacement for natural aggregates in road construction. In most works, using aggregates from steelmaking production slag, it is reported that asphalt concrete mixtures with its use have higher porosity, adhesion to the binder, due to the surface structure and chemical composition, favorable particle shape.

High porosity of aggregates from steelmaking slag can increase water resistance in asphalt mixes and improve slip and aquaplaning resistance, and adhesion to bitumen can solve the problem of moisture penetration into underlying layers of pavement due to damage to the surface. These properties contribute to improving the quality of asphalt mixes and coatings with their use, and the level of road safety.

Studies also suggest that asphalt mixtures, including aggregates from steelmaking slags, can also increase resistance to rutting and cracking. From an economic point of view, the use of steelmaking slag, as a filler in road construction, can reduce the cost of mining and processing of natural mineral materials.

The steel industry can also reduce the cost of slags intended for the processing and disposal of a huge amount of slag reserves. While the lifespan of the roadway can be increased, maintenance costs for the coating can also be reduced, thus providing additional funds for other development projects. With regard to the impact on the preservation of the environment, the use of materials from the slag of steel production can in different ways directly reduce both dependence on natural aggregates and the number of projects for the extraction of raw materials.

On the other hand, the inclusion of steelmaking slag in road construction projects can reduce the area used for waste disposal.

Despite the positive qualities of asphalt concrete with slag materials, a number of authors have noted the negative effect of the porosity of slag rubble on the properties of asphalt concrete. Selective diffusion of volatile bitumen fractions into mineral material leads to its aging in the coating. This increases the stiffness of the asphalt concrete, reducing its deformation properties. The increase in coating strength over time is regarded by researchers as a lack of asphalt concrete with slag materials, which leads to the appearance of cracks on the coating in winter.

In order to increase the crack resistance of asphalt concrete coatings with slag materials in winter, it is recommended to use less viscous bitumens, which, without reducing the strength of asphalt concrete, will increase its deformation capacity and slow down aging processes.

In the case of using new types of mineral materials in asphalt concrete, which differ significantly in their properties from traditional ones, it is necessary to conduct a comprehensive, comprehensive study of not only their physical properties, but also TEP during the service of the road. Assessment of the status of asphalt concrete pavements made of asphalt concrete with slag materials during the operation of the road will make it possible to justify the need for their use in road pavements.

To study the features of the operation of roads with asphalt concrete pavements with slag materials, as the main TEC, you should choose: the strength of the pavement, the flatness of the coating and the coefficient of adhesion. As an indicator that reflects the transport and operational condition of roads, adopted the speed of traffic flow.

Dynamics of changes in the strength of the pavement during operation

One of the main indicators of the transport and operational condition of the road and its efficiency, is the strength of the pavement. The strength of the pavement is estimated by the factor of safety (Cpc), which is defined as the ratio of the average actual modulus of elasticity of the road structure during the billing period of the year (Ef) to the required modulus of elasticity (En) during the existing traffic.

The strength of the pavement is considered sufficient if its actual modulus of elasticity (Ef), determined as a result of field studies, exceeds the required by type of coating and driving conditions (Yn), that is, for the value of the safety factor, there is a ratio:

$$K_{зп} > K_{зп}^{дор} = 0{,}95 > 0{,}85 \text{ for roads of different categories,} \quad (1)$$

where $K_{зп}^{дор}$ – the minimum acceptable value of the pavement safety factor.

The actual strength of the pavement varies over the entire period of operation of the road. The nature of the development of deformations is significantly influenced by loads from the movement of vehicles, weather and climate conditions, the stability of the water-thermal regime of the roadbed, the strength properties of the used road-building materials, the quality of construction and the level of operation.

At high positive temperatures and heavy intensive traffic, there is a risk of plastic deformation, which is accompanied by a decrease in the thickness of the coating layer in some places and its increase in adjacent areas. The appearance of such deformations is affected by the color of the coating. Darker coatings due to radiation heating can have a temperature of 15–20 °C higher than air temperature.

From this point of view, lighter coatings, for example, of asphalt concrete with slag materials, heat up less, i.e., are less susceptible to shear forces.

A decrease in the strength of the road structure also occurs as a result of the occurrence of cracks on asphalt concrete pavement, the appearance of which is characteristic mainly for the cold season — in winter or at a negative temperature in the spring period. The process of changing the elastic modulus of the pavement can be divided into three stages.

The first stage is the formation of the pavement after construction, reconstruction or major repair, during which the roadbed and the structural layers of the pavement are consolidated, rigidity and distribution capacity of the monolithic layers increases, the modulus of elasticity slightly increases, followed by stabilization.

At the second stage, there is a gradual decrease in the strength of the pavement under the influence of the movement of vehicles and weather and climatic factors, which is associated with fatigue processes, grinding of mineral material and a decrease in the distribution capacity of the structural layers. Significantly affect the reduction of strength factors such as: the appearance of cracks and wear of the coating.

This process continues until the condition (1) is fulfilled for the strength of the road construction, after which the third stage of a sudden loss of strength occurs, which is characterized by significant deformations on the floor and in the structural layers of the pavement.

During this period, due to the active interaction of the wheels of a car with an uneven coating, the deformations that already exist and the appearance of new ones develop rapidly. In the spring, the compaction of the subgrade soil and the sharp decrease in the strength of the road structure occur.

A mathematical model to describe the process of reducing the values of the modulus of elasticity of the pavement within its standard service life T_H. Theoretical dependencies were obtained for calculating the values of the decrease in the elastic modulus Et during road operation. One of these dependencies is as follows:

$$E_t = a + b\left[\lg\left(\frac{q^{T_H+1} - q^t}{q^{T_H+1} - 1}\right)N_{np} - 1\right], \qquad (2)$$

where a – the parameter depends on the type of coating and the group of calculated load, MPa; b –parameter that characterizes the effect of load repetition, MPa; q – movement rate indicator; t – year for which the pavement strength is predicted; N_{np} – traffic intensity of settlement cars for the current year of operation of the road structure, auto/day.

The evenness of the pavement is an important TEC, which determines the service time between covers of non-rigid pavement coatings and characterizes the safety and comfort of driving on the road. Evenness is determined by a complex of the same parameters as the strength of the pavement and depends on its condition.

The deterioration of the road surface evenness has a significant effect on the speed of travel, comfort of travel, fatigue of drivers and passengers due to harmful vibrations, leading to a decrease in traffic safety and an increase in the cost of transportation.

To determine the dynamics of changes in the flatness of asphalt concrete pavements for the purpose of planning repair work, Krasikov (2000) developed a mathematical model based on the study of the influence on the dynamics of the process of changing the value of the primary flatness. This mathematical model is represented by the following expression:

$$S_t = S_0\left[1 + cE_{\min}^{d} N_c(t)^{aE_{\min}^{b}}\right], \qquad (3)$$

where S_0, S_t, – the value of evenness on the tolkommer after putting the road into operation and for the predicted year t respectively, cm/km; $N_c(t)$ – total traffic intensity, reduced to the design load, auto; $E_{\min}$ – minimum modulus of elasticity, MPa; a, b, c, d – empirical coefficients.

The mathematical model was used by him to predict the dynamics of flatness changes on traditional asphalt concrete pavements and can be used to conduct comparative assessments with asphalt concrete pavements with slag materials.

The value of the coefficient of adhesion affects the roughness of the coating, which, respectively, the magnitudes and heights of irregularities are divided into macro- and micro-roughness. The macro-roughness includes irregularities with a length of more than 2–3 mm and a height of 0.2–0.3 mm, formed by the stone material used in the construction of asphalt concrete pavements or during special surface treatment.

The microroughness is characterized by irregularities with a length of less than 2–3 mm and a height of less than 0.2–0.3 mm and is determined by the intrinsic roughness of the material.

The assessment of the surface roughness is carried out using the «sandy spot» method according to DSTU 3587. This method determines the average depth of the roughness of the road surface.

During the operation of the road, the values of micro and macro-roughness of the coating gradually decrease, which leads to a decrease in the value of the coefficient of adhesion.

Analysis of previously conducted research has shown that the nature and intensity of changes in micro and macro roughness depends on the following indicators:

– mechanical (rolling friction, sliding friction and shock load from the car wheel);

– climatic (temperature change, humidity);

– properties of the mineral material, which is part of the asphalt concrete (grain, porosity, the degree of weathering of the rock);

– the amount of abrasive on the coating (dust, coating wear products).

The main reason for reducing the roughness (wear) of the coating are mechanical indicators, depending on the intensity and composition of the traffic flow.

As a result of their impact, there is a constant exposure and grinding of large mineral grains of asphalt concrete. A significant increase in the intensity of the movement of heavy trucks leads to an acceleration of the process of grinding gravel grains.

The degree of reduction in the coefficient of adhesion, especially in the first year of operation of the coating, is significantly influenced by the initial height of macroscopic irregularities and the size of rubble. If gravels provide a sufficiently high macroroughness, then the decrease in the coefficient of adhesion is small. When the protrusions of the macroroughness of the pavement are worn, the shape of the protrusions of the mineral material changes, the gravel is reoriented in space, and its upper part becomes rounded.

Grinding grains of gravel helps to reduce the value of the coefficient of adhesion, which stabilizes, reaches its minimum value and then does not change, but is determined only by the microroughness of the stone material.

Simultaneously with polishing, the reverse process occurs – weathering, which is especially enhanced in the winter period. As a result of the complex of weather and climatic factors, microcracks arise in the stone material, which gradually increase and lead to the destruction of its surface layer. In this regard, on roads with low traffic, the surface of the coating for a long time retains the necessary microroughness. With a significant traffic flow, the grinding process in intensity is much higher than the weathering process.

Studies have shown that the greatest residual microroughness and, consequently, the highest minimum value of the coefficient of adhesion, is characterized by asphalt concrete based on different strength and heterogeneous materials.

As a result of long-term observations of traditional asphalt concrete pavements, a graphic dependence of the dynamics of change in the friction coefficient on the micro and macro roughness of the coating, which, in turn, depends on the intensity and composition of the traffic flow, has been established. The general pattern of changes in the roughness of the coating is presented in the form:

$$R(t) = a \cdot e^{-b} N_p + c, \tag{4}$$

where $R(t)$ – averaged height of macro roughness, mm; N_p – number of cars passing; a, b, c – coefficients depending on crushed stone size, coating hardness and traffic flow composition.

This graphical dependence can be used to compare the dynamics of changes in the value of the coefficient of adhesion of asphalt concrete pavements made of asphalt concrete with slag and traditional mineral materials.

In this chapter the system approach to the construction of mathematical models for the definition of basic riding qualities highways changes with traditional and asphalt pavements produced of slag materials is considered.

Change of strength of a pavement due to various factors can be presented in the form of the following mathematical model:

$$E_{\phi}(t) = f_1(N, S_{tp}, m, \nu, p), \tag{5}$$

where N – is a traffic volume, vehicle/day; S_{tp} – composition of traffic flow; m – a set of the parametres describing pavement design and strength properties of used materials; ν – a set of the parametres describing the influence of weather–climaticfactors; p – a set of the parametres describing the influence of measures on construction and operational maintenance of road.

Accoding to the results of conducted researches, the change of an actual modulus of the pavement’s strength at the stage of highway maintenance can be described as a three stages process, and its dynamics can be presented as a graph in Fig. 1.

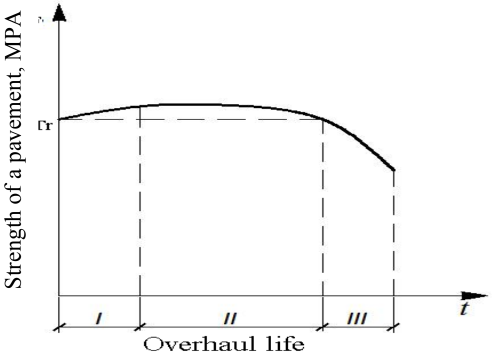

Fig. 1. Change of strength of a pavement during inter-repair period

The dynamics of evenness of an asphalt pavement, $S(t)$ can be presented in the form of the following mathematical model:

$$S(t) = f_2(N, S_{tp}, E, m, \nu, p), \tag{6}$$

where E – pavement modulus, MPa.

Regularity of change of evenness of asphalt pavements during inter-repair periods ($t_{д.п.}$) is presented in the form of a graph in the Fig. 2.

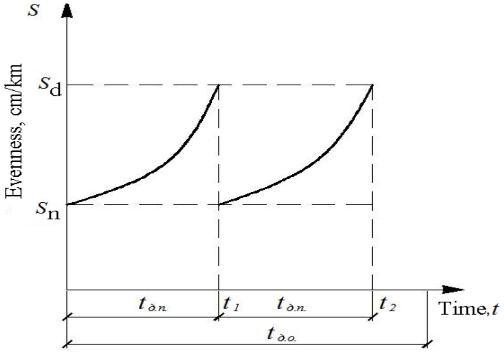

Fig. 2. Change of evenness of asphalt pavement during highway operation

According to the research results, change of cohesion factor value of an asphalt pavement in the course of a long-term maintenance after the construction or repair of a highway can be presented in the form of the graph (see Fig. 3) and the following mathematical model:

$$k_{сц} = f_3\left(N_p,\ S_{тр},\ m,\ v,\ p\right), \tag{7}$$

where N_p – total number of passed design vehicles during operation.

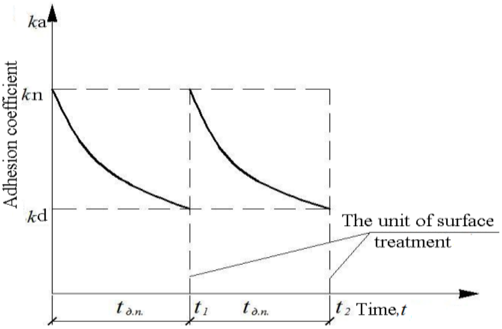

Fig. 3. Change of cohesion factor value of asphalt pavement during highway operation

Change of cohesion factor value from standard values (k) to admissible ($k_{доп.}$) ones, results from the impact of mechanical and natural-climatic factors on a highway.

The process of cohesion factor value change during the period of winter slipperiness formation and in terms of works on its liquidation can be presented in the form of the graph on Fig. 4.

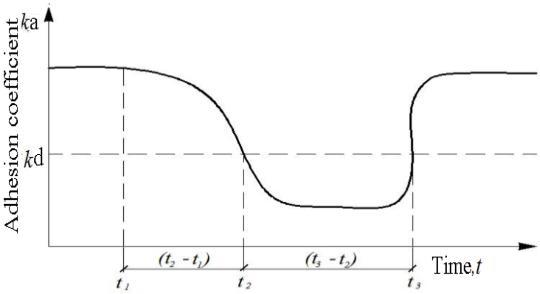

Fig. 4. Change of cohesion factor value on asphalt pavement during the period of winter slipperiness formation and its liquidation

As a result of slipperiness formation during the change of weather conditions (time span $t_2 - t_1$) cohesion factor value decreases below admissible value ($k_{доп}$.), with regard to traffic safety requirements. When taking the anti-slipperiness measures (time span t_3–t_2), cohesion factor remains below admissible value, and after «the effects» produced by de-icing materials – its value increases, thereby improving riding qualities of a highway.

According to the statement of a problem, an interaction scheme of external and internal parametres of the subsystem «Road–Car–Environment» was developed.

Internal parametres of the subsystem influencing the dynamivs of riding qualities change are divided into two groups:

- Inherent parametres of the subsystem to which refer road $\overline{d(t)}$ and $\overline{h(t)}$ transport parametres;
- Parametres affecting the environment to which refer weather-climatic $\overline{v(t)}$ factors.

As an external (initial) parameter of the subsystem ‘Road–Car–Environment’ the following basic riding qualities of a highway can be mentioned: strength of road pavement, evenness of a pavement, cohesion factor and a generalising parameter – traffic flow speed. For the problem solution it is necessary to consider the dynamics of their change in time.

Thus, mathematical model for the description of changes of basic riding qualities in a long-term gap in the subsystem ‘Road–Car–Environment’ looks like that:

$$\overline{y'(t)} = F_{Д-А-С}\left[\overline{v'(t)}, \overline{d'(t)}, \overline{t'}\right], \tag{8}$$

where $\overline{y(t)} = \{E_{ф}(t), S(t), k_{сц}(t), V(t)\}$ – Vector of external parameters of the subsystem; $F_{Д\text{-}А\text{-}С}$ – the law of operation of the subsystem; $\overline{v(t)} = \{v_1(t), v_2(t), v_3(t)\}$ – vector of external environment impact (weather and climatic parameters); $\overline{d(t)} = \{m_1, m_2, E_0, S_0, R_0\}$ – vector of parameters of their own subsystems (traffic specification); $\overline{h(t)} = \{N(t), N_p(t), S_{tp}(t)\}$ – vector of inherent parameters of the subsystems (road parameters); t – time.

As an external parameter of the subsystem «Environment – Road» the state the road surface in winter is accepted. To solve the problem slippery condition of the pavement is considered, i. e. presence of slipperiness as a glassy ice on its surface.

Thus, mathematical model for describing the state of the pavement for shor intervals of time during winter in the subsystem «Environment – Road» is as follows:

$$\overline{y'(t)} = F_{\text{с-д}}\left[\overline{v'(t)}, \overline{d'(t)}, \overline{t'}\right], \tag{9}$$

where $\overline{y'(t)} = \{S_p\}$ – vector which components are the state of the road pavement in winter; $F_{\text{с-д}}$ – the law the subsystem operation; $\overline{v'(t)} = \{T(t), v_1'(t), v_2'\}$ – vector of environmental impact (weather parameters); $\overline{d'(t)} = \{m_1', m_2', \ldots, m_5'(t), T_n'(t)\}$ – vector of inherent parameters of the subsystem (road parameters); t' – time during which winter slipperiness formation as a glassy ice is possible.

To assess the dynamics of elastic modulus change of road pavement with the surfacing of asphalt concrete produced using traditional materials, mathematical models developed by Krasikov (2000) were used.

For a relatively small deformations of road pavement, that is,during the first and the second stages of road design work, its strength $E_{ф}(t)$ is described using the following mathematical model:

$$E_{ф}(t) = E_0\{1 - [a_m + b_m(\lg N_c(t) + \lg t)]\}, \tag{10}$$

where E_0 – mathematical expectation of elasticity modulus during the first year of road pavement life after the completion of its formation, MPa; a_m and b_m – the parameters of the equation defined on the basis of experimental studies; $N_c(t)$ – total traffic volume calculated to the design load of the group A, vehicles / day; t – predicted period of service of the pavement, in years.

The study of dynamics of evenness of traditional asphalt pavemenst had been based on the following mathematical model, also proposed by Krasikov (2000):

$$S_t = S_0\left[1 + c\,E_{\min}^{d}\,N_c(t)\,a\,E_{\min}^{b}\right], \tag{11}$$

where S_0 – the value of evenness according to impact measuring device after putting the road into operation, cm/km; E_{min} – the minimum modulus of elasticity, MPa; a, b, c, d – parameters of the equation defined on the basis of experimental studies.

It is possible to assess the change of riding qualities of the roads with the surfaces made from slag and traditional asphalt materials during short time intervals (in winter) through the study of the processes of various types of winter slipperiness formation on their surfaces.

Mathematical formulation of the problem contains the differential equation and single-valuedness condition including thermal parameters and dimensions of the road structure, as well as the boundary conditions and the initial temperature distribution. Temperature conditions of the road structure on the surface under the influence of temperature, which changes periodically, for the issue under consideration can be described as a monospaced heat conductivity equation:

$$c\rho \frac{\partial T(x,t)}{\partial t} = \frac{\partial}{\partial x}\left[\lambda \frac{\partial T(x,t)}{\partial x}\right] + q, \tag{12}$$

where $T\,(x,\,t)$ – temperature inside the road structure and subgrade soil at the depth of x at time t, °C; q – heat flow density in the structure, W/m^3; c – specific heat capacity, J/kg K; ρ – density of the material, kg/m^3; λ – thermal conductivity, W/m K.

As road pavement is a multilayered system, equation (8) for the issue under consideration is transformed into a system of differential equations:

$$\begin{cases} c_i\rho_i \dfrac{\partial T}{\partial t} = \dfrac{\partial}{\partial x}\left(\lambda_i \dfrac{\partial T}{\partial x}\right) & H_{i-1} \le x \le H \\ c_{\text{м}}\rho_{\text{м}} \dfrac{\partial T}{\partial t} = \dfrac{\partial}{\partial x}\left(\lambda_{\text{м}} \dfrac{\partial T}{\partial x}\right) & H_4 \le x \le H_{\text{ф}} \\ c_T\rho_T \dfrac{\partial T}{\partial t} = \dfrac{\partial}{\partial x}\left(\lambda_T \dfrac{\partial T}{\partial x}\right) & H_{\text{ф}} \le x \le H \end{cases} . \tag{13}$$

On condition on the boundary of the phase transition in the soil of subgrade:

$$\lambda_m \left.\frac{\partial T}{\partial x}\right|_{x=H_{\text{ф}}} \lambda_T \left.\frac{\partial T}{\partial x}\right|_{x=H_{\text{ф}}} = Q_\rho \frac{\partial H_{\text{ф}}}{\partial t}, \tag{14}$$

where $H_{\text{ф}}=H_{\text{ф}}(x,t)$ of the phase transition, m; Q – latent heat of ice melting, kJ/kg.

The rate of destruction of ice formation on the surfaces of pavements under the impact of passing vehicles and the quality of cleaning depends on the force of adhesion (adhesion) of these formations to the surface of the pavement.

Bond strength of ice and material of the surface ($R_{\text{сц}}$) is defined as the difference of bending strength of frozen and tested at a given temperature saturated ($R_{\text{в}}$) and dried ($R_{\text{сух}}$) samples:

$$R_{\text{сц}} = R_{\text{в}} - R_{\text{сух}}, \tag{15}$$

or

$$R_{\text{сц}} = \frac{3}{2}\cdot\frac{1}{bh^2}\left(R_{\text{в}} - R_{\text{сух}}\right), \tag{16}$$

where $P_в$, $P_{сух}$ – breaking load; l – distance between the supports; b – width of the sample; h – height of the sample.

Determination of bonding strength of ice with asphalt pavement surface produced using traditional materials and slag according to this method allows to determine the differences in winter slipperiness formation on these types of pavements.

Evaluation of the strength of the pavement was carried out by determining the modulus of elasticity in characteristic areas annually for five years of operation of the road. The modulus of elasticity was defined as the elastic deflection of the pavement, obtained by the method of static load wheel of the car. For testing, a loaded two-axle dump truck MAZ-503A was used. To measure the deflection, a PC-204 deflector was used with a deflection accuracy of ± 0.01 mm. Evaluation of the strength of the pavement and processing of research results was carried out in accordance with VBN B.2.3-218-186.

Processing the results of determining the elastic deflection was carried out on the basis of mathematical statistics methods. The actual deflection of the pavement was determined for the normative level of reliability Kn = 0.90. The modulus of elasticity at the site was determined by the formula:

$$E_{фл} = \frac{0,36 Q_K}{l_ф}, \tag{17}$$

where $E_{фл}$ – the modulus of elasticity of the road structure at the control point at a given time, MPa; Q_K – wheel load, кН; $l_ф$ – actual deflection at reliability $K_н$=0,90, см.

If the field studies were conducted in the off-design period of the year, then in order to obtain an objective characteristic of the state of the road pavement, a corresponding adjustment was made. The actual modulus of elasticity, reduced to the estimated period of the year and estimated temperature, was determined according to VBN B.2.3-218-186, respectively. The calculation was carried out according to the formula:

$$E_ф = E_{фл}\left[\frac{1}{K_\Theta} - \frac{1,5DK_Г}{H_K}\left(1 - \frac{W_{фл}}{W_p}\right)\right]K_Д K_T, \tag{18}$$

where K_Θ – temperature coefficient equal to the ratio of the deflection at the calculated temperature of the coating to the deflection at a temperature corresponding to the test period; D – calculated wheel print diameter, 33 см; $K_Г$ – the empirical coefficient, depending on the type of subgrade soil at the test point, is assumed $K_Г$=2,15 – for loam, silty dust loam; $H_к$ – pavement thickness, cm; $W_ф$, W_p – measured and calculated relative humidity of the roadbed during the test period; $K_д$ и $K_т$ – empirical coefficients.

Analysis of the obtained results shows that the values of the elastic moduli in 2013–2018 exceed the required one, which is assumed to be equal to 243 MPa. The minimum value of the modulus of elasticity, equal to 226 MPa, on which the tests were carried out almost immediately after the completion of work on laying the top layer of the coating of asphalt concrete with slag materials.

It should be noted that the entire cycle of construction work on this section was carried out from August to October, at the time when in other sections the embankment of the roadbed was poured in 2015, that is, it had a year of exposure before the pavement device. One year after operation, the values of the elastic moduli in the sections were leveled and had approximately the same values in both areas.

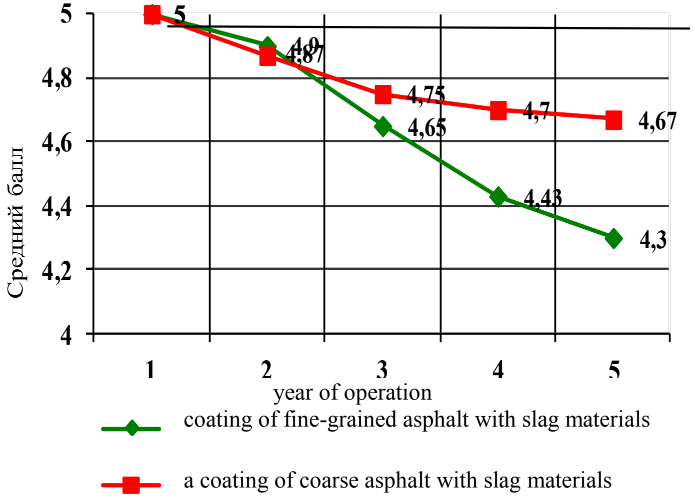

Fig. 5. Change in scoring used for evaluation of road pavement condition with fine and coarse bituminous concrete surfacing produced of slag materials

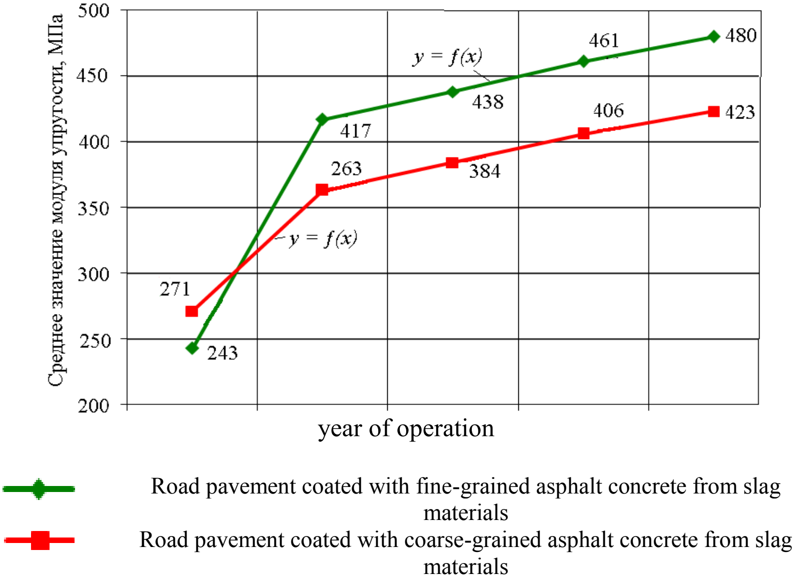

Fig. 6. Change in the elastic modulus values of pavement with the surfacing of fine and coarse bituminous concrete produced of slag materials

When monitoring the strength of the pavement during the operation period, an increase in the strength of the road structure was noted. This feature can be explained by the processes of hydration that occur in the layers of the slag base, which lead to their monolithic, and thereby hardening of these layers. On the basis of the conducted studies, it is possible to predict a further increase in structural strength, which will ensure reliable operation of the pavement under the influence of increasing transport loads.

Recommendations:

1. Overhaul life for the highways with asphalt pavements produced of slag materials should be of the same duration as for the roads with asphalt pavements produced of traditional materials but taking into consideration intensity of traffic flow, type of pavement, safety factor and road-climatic zone.
2. Service life of asphalt pavement produced of slag materials should be evaluated by the degree of surface pavement wear and reduction of the modulus of elasticity of the pavement by more than 25 % of the values obtained on the basis of diagnostic tests.
3. For the repair of asphalt pavements produced of slag materials it is recommended to use the most efficient and cost-effective technologies based on the principles of regeneration.
4. The main defect of asphalt pavement with slag materials are cracks. At its operational maintenance it is necessary to fill the cracks with mastic or viscous bitumen during the transition from summer to winter operational period.

Conclusions:

1. The fulfilled study aimed at determining the most important factors that affect the change of riding qualities of asphalt pavements with slag materials proved that for the assessment of changes in the strength, evenness and cohesion factor of the pavement overhaul life can be adopted, and to assess the road conditions in winter – the time interval, corresponding to the formation of winter slipperiness can be used.
2. Experimental research has confirmed that the possibility of winter slipperiness formation as a glassy ice on the asphalt pavement with slag materials due to higher thermal inertia – is by 15 % lower than on the asphalt pavements produced of traditional materials, and the value of bonding strength with ice is almost 2 times lower than it is for the surface pavements produced of traditional materials.
3. For the first time it was theoretically substantiated and experimentally confirmed that the riding qualities, namely, strength, modulus of elasticity estimated for 5 years of operation for coarse and fine–grained asphalt from slag materials increased by 55 % compared with the initial ones; evenness increased by 10 %, cohesion factor remained virtually unchanged for the coarse-grained asphalt (initial value was 0.57, and after 5 years of operation -0.53) and it increased for fine-grained asphalt concrete (respectively 0.37 and 0.46).

РЕФЕРАТ

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ОСОБЛИВОСТІ ВЗАЄМОДІЇ ОРГАНІЧНОГО В'ЯЖУЧОГО ТА ШЛАКОВОГО НАПОВНЮВАЧА

У статті приведені результати досліджень взаємодії органічних в'яжучих з шлаковими матеріалами в асфальтобетонних сумішах. Визначено, що шлаковий щебінь, оброблений в'яжучим, являє собою високоякісний матеріал, який широко застосовують для будівництва покриттів і основ. Обробка щебеню в'яжучим забезпечує його повне обволакування плівкою завданої товщини. Товщина плівки пов'язана як з в'язкістю в'яжучого, так і з властивостями шлакового щебеню. Чим більше в'язкість в'яжучего, тим тоньше плівка на зернах. Із зменшенням розміру зерен зменшується і товщина плівки, із збільшенням шорсткості зерен товщина плівки в'яжучого збільшується. При ущільненні за рахунок наближення зерен, вкритих в'яжучим, утворюються коагуляційні зв'язки, які мають достатню міцність і високу водостійкість. Порівняно з способом просочування і змішування на дорозі цей спосіб дає економію в'яжучого.

Ключові слова: органічне в’яжуче, шлаковий матеріал, асфальтобетон, фізико-механічні характеристики.

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ОСОБЕННОСТИ ВЗАИМОДЕЙСТВИЯ ОРГАНИЧЕСКОГО ВЯЖУЩЕГО И ШЛАКОВОГО НАПОЛНИТЕЛЯ

В статье приведены результаты исследований взаимодействия органических вяжущих со шлаковыми материалами в асфальтобетонных смесях. Определено, что шлаковый щебень, обработанный вяжущим, представляет собой высококачественный материал, который широко применяют для строительства покрытий и оснований. Обработка щебня вяжущим обеспечивает его полное обволакивание пленкой заданной толщины. Толщина пленки взаимосвязана как с вязкостью вяжущего, так и со свойствами шлакового щебня. Чем больше вязкость вяжущего, тем тоньше пленка на зернах. С уменьшением размера зерен уменьшается и толщина пленки, с увеличением шероховатости зерен толщина пленки вяжущего возрастает. При уплотнении за счет сближения зерен, покрытых вяжущим, образуются коагуляционные связи, обладающие достаточной прочностью и высокой водостойкостью. По сравнению со способом пропитки и смещения на дороге этот способ дает экономию вяжущего.

Ключевые слова: органическое вяжущее, шлаковый материал, асфальтобетон, физико-механические характеристики.

ABSTRACT

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FEATURES OF INTERACTION OF ORGANIC BINDER AND SLAG FILLER

The article presents the results of studies of the interaction of organic binders with slag materials in asphalt concrete mixtures. It is determined that slag crushed stone treated with a binder is a high-quality material that is widely used for the construction of coatings and bases. The processing of crushed stone with a binder ensures that it is completely covered with a film of a given thickness. The thickness of the film is interrelated with both the viscosity of the binder and the properties of slag rubble. The greater the viscosity of the binder, the thinner the film on the grains. With a decrease in the grain size, the film thickness also decreases, with an increase in the grain roughness, the thickness of the binder film increases. During compaction, coagulation bonds are formed due to the convergence of the grains coated with the binder, which have sufficient strength and high water resistance. Compared with the method of impregnation and displacement on the road, this method saves the binder.

Key words: organic binder, slag material, asphalt concrete, physical and mechanical characteristics.

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«Any invention and discovery leaves an indelible mark in the minds of people,
and this allows us to hope that in the generations that will replace us,
there will be more of those who are able to change
culture, make it better and more perfect»

Alfred Nobel

CONCLUSIONS

Rational use of Fuels and Lubricants, Advance in Petroleum and Gas Industry and Petrochemistry, Energy efficiency and Environmental safety are among the most important problems of our time. Their solution largely determines the sustainable development of the World economy and the preservation of human comfortable conditions. Transport is the largest consumer of the world's oil. About 60 % of all oil production is used for transportation. It is also the second largest emitter of greenhouse gases. About 20 % of CO_2 emissions is derived from the transport sector.

Field of science that became responsible for ensuring the integrity in dealing with a variety of tasks connected to these problems, is Chemmotology. Encyclopedic concept of Science defines it as a sphere of human activity, the function of which is the development and theoretical systematization of objective knowledge of reality. The direct goals of the Science are Description, Explanation and Prediction of the processes and phenomena of reality, which are the subject of its study on the basis of public law, e.g. the theoretical reflection of reality.

Chemmotology as a unique science studies the technological processes, properties, quality and methodology for the rational use of fuels, oils, greases and technical liquids on the operational stage of machine life cycle. Generalizing a utility function of fuels and lubricants as socially useful products (as opposed to a generalized function of vehicles, for example) it could not be described by the appropriate design documentation and drawings. This fundamental difference among the fuels and lubricants and mechanical engineering products will objectively lead to the emergence of Chemmotology studying and application.

The prominent role of the Chemmotology is in the consolidating function of the system, improving of integration function in scholars and practitioners communication, chemical, oil-refining and petrochemical sectors of the economy together with operator's technique for solving evolution problems of scientific and technological progress.

Initially Chemmotology science is characterized by systematicity. Chemmotology, as well as system technology and system engineering, has such methodological tools in science and technology, which covers the design, development, testing and operation of complex systems. From a philosophical point of view, we can easily state that Chemmotology science makes the consolidating function of system, integration of communication scholars and practitioners of engineering, chemical, oil-refining and petrochemical sectors of the economy, together with operator's technique for solving evolution problems of scientific and technological progress.

Quality of Fuels and Lubricants determines of the chemmotological reliability of the vehicles.

Recognizing the modern global challenge generated «energy trillem», providing balance between energy safety, economic development and environmental protection and efforts of of states around the world for reaching sustainable development, Chemmotology as a science has a unique specific mission that emphasizes it among other applies sciences and scientific directions. The World Energy Council locates the concept of modern energy outlook in such a manner that there are no unuseful resources or unsuccessful technologies. But there is insufficient or unreasoned choice, unwell or uncapability to apply new technologies in practice.

Providing balance between three key aspects of energy trillem – energy safety, acceccability and environmental stability is the most important task during development of energy strategies. One of effective methods of sovling trillem's tasks in the world's scale is international collaboration and integration. They are the key to revealing unsed potential of energy resources, natural routes of energy transfer and possibilities for its storage, in particular in transport sector.

Today the world is in the conditions of the sixth Technological Mode and Green Economy (or the Fourth Industrial Revolution). Experts predict that in 2020–2025 a New Scientific, Technical and Technological Revolution will take place, the basis of which will be developments synthesizing Technological Environmentally Friendly Advances in the field of Biochemical Engineering, Nanotechnology, Energy, Membrane and Quantum technology etc. In transport – there are New Types of Engines, Energy Sources, a new Vehicle control concept, a new production and service infrastructure. And all these technological elements are directly related to the quality of fuels and lubricants.

Thus, the importance of chemotological reliability is obvious, and the prospects and role of chemmotology in these conditions are greatly expanded.

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