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FUNDAMENTALS OF CHEMMOTOLOGY

Manual

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CONTENTS

List of abbreviations and designations

ACEA – (Association des Constracteuis Europeen des Automobiles (European Automobile Manufacturers Association;
A/F – air fuel ratio;
API – American Petroleum Institute;
ASTM – American Society for Testing and Materials;
AtJ – alcohol-to-jet,
BtL – biomass to liquid,
BDC – bottom dead center;
CAAFI – Commercial Aviation Alternative Fuels Initiative;
CAEP – Committee on Aviation Environmental Protection;
CFC – chlorofluorocarbon;
CFR – Cooperative Fuel Research;
CMVO – chemically modified vegetable oil;
CN – cetane number;
CNG – compressed natural gas;
CtL – coal to liquid;
EGR – Exhaust Gas Recirculation;
EROEI – Energy returned on energy invested;
FAME – fatty acids methyl esters;
FSS – fuel supply system
FCC – fluid catalytic cracking;
GHG – greenhouse gas;
GtL – gas to liquid;
HEFA – hydroprocessed esters and fatty acids,
HFC – hydrofluorocarbons
IATA – International Air Transport Organization;
ICAO – International Civil Aviation Organization;
IEA – International Energy Agency;
ILSAC – International Lubricant Standardization and Approval Committee;
ILUC – Indirect Land Use Change;
ISO – International Standard Organization;
JE – jet engine;
LCO – light cycle oil;
LNG – liquefied natural gas;

LPG – liquefied petroleum gas;
LTO – landing and take-off cycle;
MIC – Microbial Induced Corrosion;
MMT – methylcyclopentadienyl manganese tricarbonyl;
MON motor octane number;
MSW – municipal solid waste;
NLGI – National Lubricating Grease Institute
ON – octane number;
PAH – polyaromatic hydrocarbon;
RON – research octane number;
SAE – Society of Automotive Engineers;
SAF – sustainable aviation fuels;
SIP – synthetic Iso-paraffin;
SKA – synthetic kerosene with aromatic;
SPK – synthetic paraffinic kerosene;
TDC – top dead center;
TEL – tetraethyl lead;
TML – tetramethyl lead;
UCO – used cooking oil;
VGO – vacuum gas oil;
VI – viscosity index;
VO – vegetable oil;
VOC – volatile organic compounds;
CH – hydrocarbons;
CO – carbon monoxide;
CO_2 – carbon dioxide;
NO_x – nitrogen oxides;
SO_x – sulfur oxides;

PREFACE

The manual presents a modern interpretation of Chemmotology science, its role in development of technology and society. It shows that development and promotion of alternative fuels and Chemmotology problems solving are impossible without systematic approach. In addition, having both theoretical part and practical application, Chemmotology science ensures energy and environmental security of the country's economy, rational use of traditional and alternative fuels and lubricants in operation of advanced modern equipment. The manual focuses on the fact that in recent years one of the most important issues has been the ecological constituent of Chemmotology science, which is aimed at ultra-minimization of negative impact of fuel lubricants and technical liquids on ecosystems.

It is well-known that transport sector is an important component of the economy that have an impact on the development and prosperity of the population. Efficiency, reliability of operation of transport, rational use of operating materials depends on their correct selection. According to its quality performance materials must conform to both the model and operating conditions of transport means. The use of poor quality fuels and lubricants 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. Thus, knowledge of the range of fuels and lubricants, its functional purpose, operational properties allow using them correctly and efficiently.

The authors tried to integrate and systematize in the presented manual the knowledge of many experts from different countries to characterize main trends in the development of conventional and alternative fuels and lubricants, its modern assortment and tendencies in development.

Chapter 1

FUNDAMENTALS OF CHEMMOTOLOGY

Today humanity has reached the level, when it possesses huge scientific & technical potential. However, it still doesn't manage to use this potential economically and rationally. Processes of fuel use still faces problem of highly effective fuel burning with production of maximum useful energy. Argument for this is the modern state of energy efficiency, and fuel efficiency in particular, efficiency factor of internal combustion engines. Fuel consumption by car engine is determined by its energy efficiency, in other words, quantity of heat produced during combustion of 1 kg of fuel. It was calculated, that today only 12 % of energy produced during fuel combustion is used for car movement. Today about 10 ton of fossil fuels per capita is extracted during one year. And only 1 % (100 kg) is efficient. All the rest pollute atmosphere, soils and water bodies. Efficiency of fuel use can be shown as energy balance of a car (table 1.1).

Table 1.1

Energy balance of a car

Energy of combusted fuel (100 %)	
12 %	88 %
2,4 % – rolling resistance 3,2 % – air resistance 6,4 % – inertial forces	42 % – cooling system 22 % – exhaust gases 13 % – friction in engine 9 % – friction in transmission 2 % – engine accessory drive

Today efficiency factor of modern gasoline engines is about 35–36 %, diesel engines – 42–44 %, gas engines – 38–45 % (table 1.2).

Table 1.2

Efficiency factor of some engines

Wat heat engine	~ 2,8 %
Internal combustion engine	~ 20–40 %
Steam turbine	~ 35–46 %
Diesel engine	~ 44 %
Jet engine	~ 47 %

Total efficiency factor of engine is divided into main constituents:

- ***fuel efficiency***. It shows what quantity of fuel that was efficiently burned in engine and was turned into the volume of power gas of high temperature and pressure, and what part of fuel was not burned and was emitted as unburned hydrocarbons, carbonized particles (soot, smoke, fly ash, etc). Nowadays only 75 % of fuel is completely burned and transformed into heat in existing engines. Two-stroke engines provide even less amount of completely burned fuel;
- ***thermal efficiency factor***. It shows what amount of heat, produced after fuel burning is transformed into useful work and what amount is uselessly wasted in environment. Let us consider that piston engine has 30% efficiency factor on average. Then 70% of produced heat is emitted uselessly into environment through cooling system and together with exhaust gases;
- ***mechanical efficiency factor***. It shows what quantity of mechanical work is transformed into torque force at the main axle and transmitted to the consumer, and what amount is uselessly wasted for friction or used for other driving supplementary mechanisms of the engine (Fig. 1.1)

The above arguments suggest that mankind has a significant amount of energy from the point of view of the opportunities and the need to improve the technical means, when the source of energy is products of oil refining.

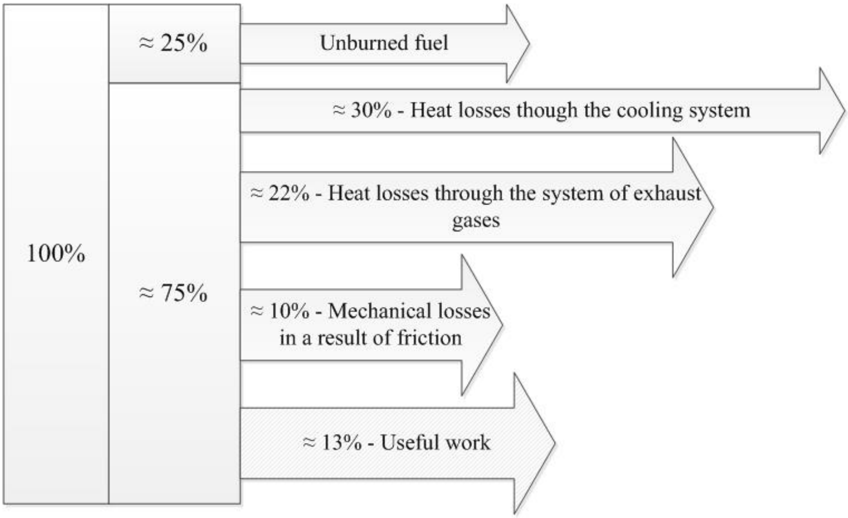


Fig. 1.1. Energy balance of internal combustion engine

The current state of natural resources and the environment causes change of point of view on the future economic development and technological progress and evaluate it considering environmental priorities, environmental risks and state of environmental safety. Rapid industrialization and urbanization together with quick development of transport infrastructure, strengthening of other impacts on environment have disturbed the life cycle of substances, natural metabolic energy processes and regeneration mechanisms in the biosphere. As a result progressive destruction has begun. Air, water and soil are polluted, landscape and biological diversity are depleted; these facts cause negative effect on living organisms and humans.

In order to eliminate this danger, existing environmental management practices should be revised, production and economic activities and environmental systems should be radically restructured, taking into account social and economic needs of society and the biosphere opportunities.

According to the forecasts of the World Energy Council, energy consumption will raise on 55 % till 2020. According to the data of Organization of the Petroleum Exporting Countries, oil takes more than one third in word balance (table 1.3)

Table 1.3

World energy balance

(OPEC forecast, data of World Oil Outlook 2010, p. 48)

Name of energy source	Volume, mln m BOE per day*				Part, %			
	2008	2010	2020	2030	2008	2010	2020	2030
Oil	80,9	80,4	89,9	97,6	35,7	35,0	32,7	30,2
Coal	64,8	66,2	80,1	92,1	28,6	28,8	29,2	28,5
Gas	51,4	52,1	64,5	79,1	22,7	22,7	23,5	24,5
Nuclear energy	14,4	14,7	16,9	20,7	6,3	6,4	6,2	6,4
Hydroenergy	5,5	5,8	7,3	9,0	2,4	2,5	2,7	2,8
Biofuel	8,6	9,2	12,9	17,5	3,8	4,0	4,7	5,4
Other renewable energy sources	1,3	1,5	3,2	6,8	0,6	0,7	1,2	2,1
Total:	226,8	229,9	274,8	322,9	100,0	100,0	100,0	100,0

* Per unit of fuel (coal equivalent) accepted the calorific value of 1 kg of coal = 29,3 MJ or 7000 kcal. The International Energy Agency (IEA) has adopted a unit of oil equivalent, usually abbreviated as TOE (born Ton of oil equivalent). One ton of oil equivalent is equal to 41,868 GJ or 11.63MW•h

It is also used barrel of oil equivalent (BOE). Ratio: 1 toe = 7,11, 7,33 or 7,4 boe

Despite the fact that in the future share of crude oil in total primary energy consumption will be reduced in absolute terms, oil consumption (as well as other energy sources) will only increase. Being an exhaustible and non-renewable natural resource, crude oil requires its rational use. Even Mendeleev paid attention to the rational use of raw materials: «Oil is not a fuel, you can heat by assignats».

Growth in use of natural resources, their depletion and degradation necessitated development and implementation of strategies and tactics for sustainable environmental management and continuous monitoring of changes in the natural and anthropogenic processes for the integrated management of natural resources and environment.

There are no alternatives to environmental management, which is based on considering laws of nature and forming of safe conditions of human life and living organisms. Therefore, humanity has already generated and implemented strategy and tactics of natural resources use, ensuring systematic (integrated) management of natural resources and their rational use, protection from pollution and depletion. It also applies constant monitoring of natural and anthropogenic processes changes in environmental systems.

Chemmotology as an independent science today can systematically solve complex environmental and energy problems, for example, in the transport sector.

Chemmotology firstly comprehensively solved such important practical tasks as design and production of machinery, equipment maintenance, development and use of fuels, oils, lubricants and fluids. Chemmotology unites and embodies the efforts of developers and manufacturers of machinery, oil products, oil refineries and operators of technique.

Modern interpretation of science Chemmotology is as follows: «Chemmotology – a science about technological processes, properties, quality and methodology of rational use of fuels, oils, greases and technical liquids». The Business dictionary defines science as a Body of knowledge comprising of measurable or verifiable facts acquired through application of the scientific method, and generalized into scientific laws or principles. Thus, the primary goals of science are description, explanation and prognosis of the processes and the phenomena of reality, i.e. theoretical reflection of reality. All these signs are attributed to Chemmotology.

1.1. Modern paradigm of the Chemmotology

For the modern science it is the transition from subjective to problematic orientation that becomes more typical. The new areas of knowledge arise because of advancement of some major theoretical or practical problems. This is the reason for the edge sciences to appear, and, Chemmotology, as a problem science being at the edge of Chemistry, Physics, Engineering, Economics and others, in particular. It is even possible to use such word combination as «technical Philosophy», since it describes the essence of this science.

The role of Chemmotology as an applied science is supported by the importance of the problems it solves: securing energy safety of economy of a country, rational use of conventional and alternative fuels, lubricants and technical liquids during the operation of modern and prospective technologies.

There are three main directions of development of the Chemmotology theoretical basis:

- study of the mechanisms of influence of various components and functional additives on the quality of fuels and lubricants;
- search for more general patterns in Chemmotology based on the use of fundamental laws of Physics, Chemistry and other sciences;
- study of Chemmotological processes for the prognosis of fuels and lubricants operation in technological equipment at various conditions.

The main goals of Chemmotology are the following:

1. Optimization of requirements for quality and composition of fuels, lubricants and technical fluids, their service operation, taking into account the primary energy sources reserves, scientific and technological achievements in the development of technology, peculiarities of technological equipment and the conditions of its operation, ecological and economic requirements;
2. Development of recommendations as for unification, interchangeability and determination of conditions of rational and economic use of fuels, lubricants and technical liquids;
3. Improving of oil product supply systems and quality management during production, storage, transportation, and application of fuels, lubricants and technical liquids;
4. Modernization of compliance assessment system (certification, testing, permission to production and application), modernization of methods of qualifying tests for fuels, lubricants and technical liquids;
5. Unification of local standards for testing methods of fuels, lubricants and technical liquids with international ones;
6. Development of new highly efficient kinds of fuels, lubricants and technical liquids that ensure the improvement in technical and environmental operation of technological equipment;
7. Disposal and recycling of the off-grade and worked-off fuels, lubricants and technical liquids;
8. Developing grounds for conducting logistic measures for preserving the quality and decreasing the losses of fuels, lubricants and technical liquids during their storage, pumping and transportation;

9. Developing methods for service operation and quality control assessment of fuels and lubricants, along with disposal of worked-off, unmarketable and off-grade fuels and lubricating materials;

10. Improvement of the existing and development of the new technologies for fuels, lubricants and technical liquids production.

The processes of interdependency and interaction of components of the Chemmotological system (Fig. 1.2) are the main research subject and the essence of Chemmotology.

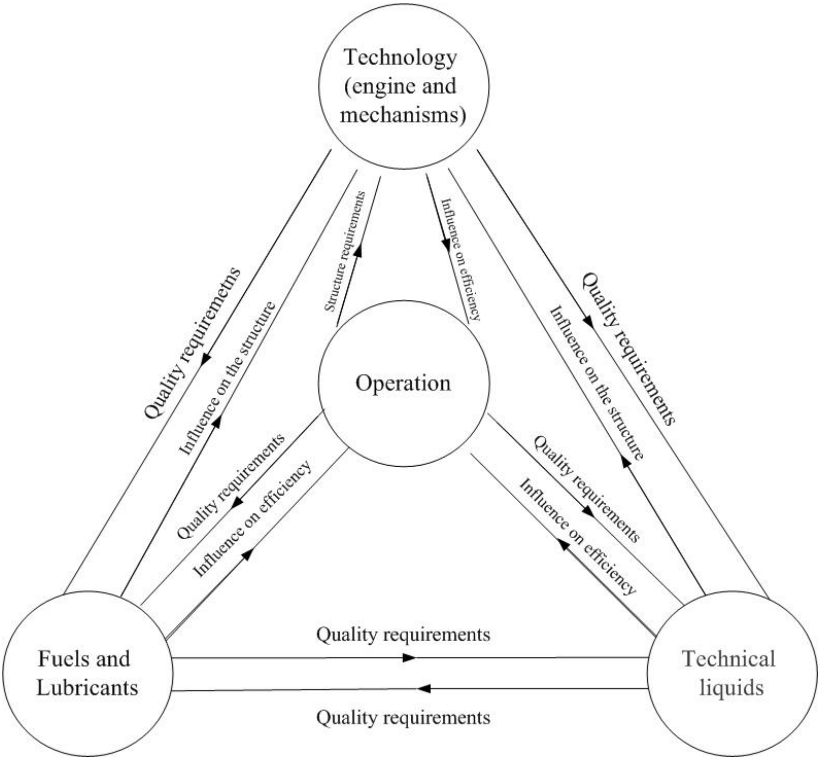


Fig. 1.2. Fundamental Universal Four Tiers Chemmotological System

The subject of Chemmotology is service operation of fuels, lubricants and technical liquids. The main scientific and practical goal is rational use of fuels, lubricants and technical liquids during equipment operation.

From economic standpoint Chemmotology is aimed at achieving maximal economy of raw materials, fuels, lubricants and technical liquids through optimization of balance and quality of products, their rational and efficient use.

Theoretical bases of Chemmotology includes the development of general theory and establishing laws to bound the quality of fuels, lubricants and technical liquids with their reliability, durability, ecological compatibility, economy and efficiency of technical equipment; substantiation of optimal requirements for the quality; selection (development) of the new grades; unification of types and grades; ensuring the quality preservation; study of physical, chemical, and ecological properties during the storage, transportation and distribution; decreasing specific consumption and acceptable losses; decreasing the overall volume of quality control; development of quality regeneration methods; solving the problems of interchangeability of fuels, lubricants and technical liquids grades produced in different countries; developing methods, equipment and service operation testing systems and quality parameters tests; protection of the environment from the influence of the Chemmotological system.

Chemmotology creates the necessary “basis” for ensuring optimal conditions of oil products rational use and modern requirements to their quality. The structure and content of the science of Chemmotology can be described with Fig. 1.3.

The generalized function of oil products as materials useful for society can not be described with the single set of corresponding design papers and engineering drawings as opposed to the generalized function of vehicles utility. It is this principal distinction of oil products from the products of engineering industry that has created an objective ground for the origins of Chemmotology. The use of fuels and lubricants with overstated quality parameters (quality level) leads to exceeding in costs of their production, and, in the case of their underestimation – to increasing costs in engineering and equipment operation.

The general diagram of connections between the steps of development, production, quality assessment, multi-level testing and use of fuels, lubricants and technical liquids is shown in Fig. 1.4, whereas Fig. 1.5 shows the generalized universal model of the chemmotological system with interconnections and inter-impacts between engines, machines, their exploitation and fuels, lubricants and technical liquids.

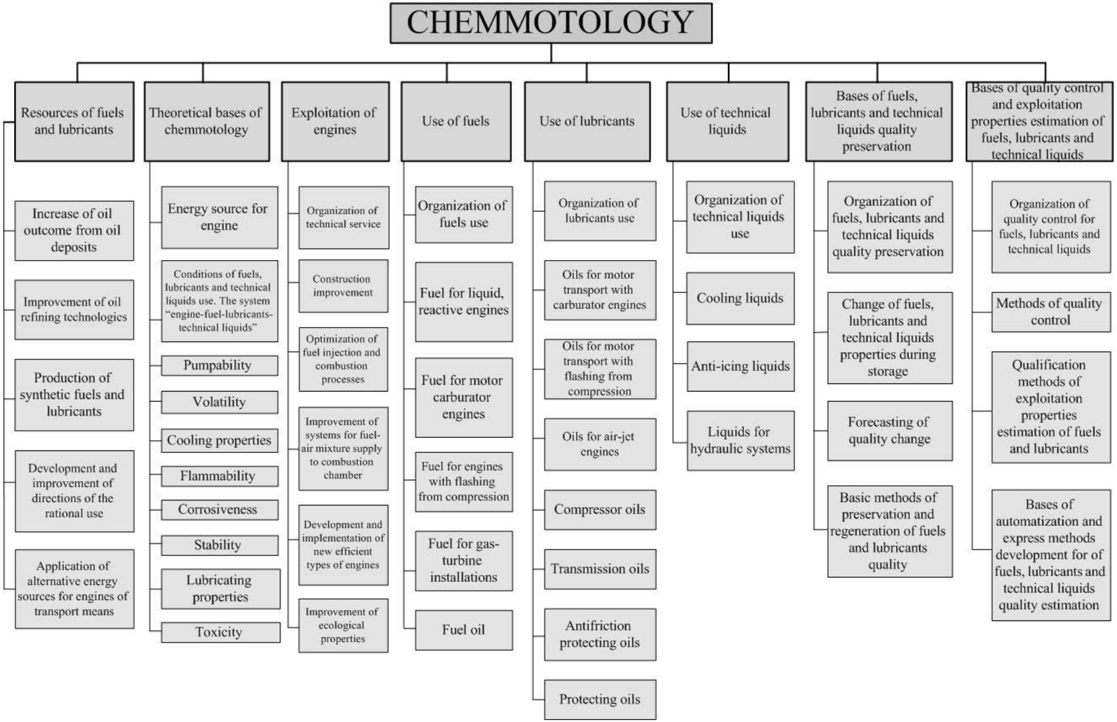


Fig. 1.3. The Structure and Content of Chemmotology

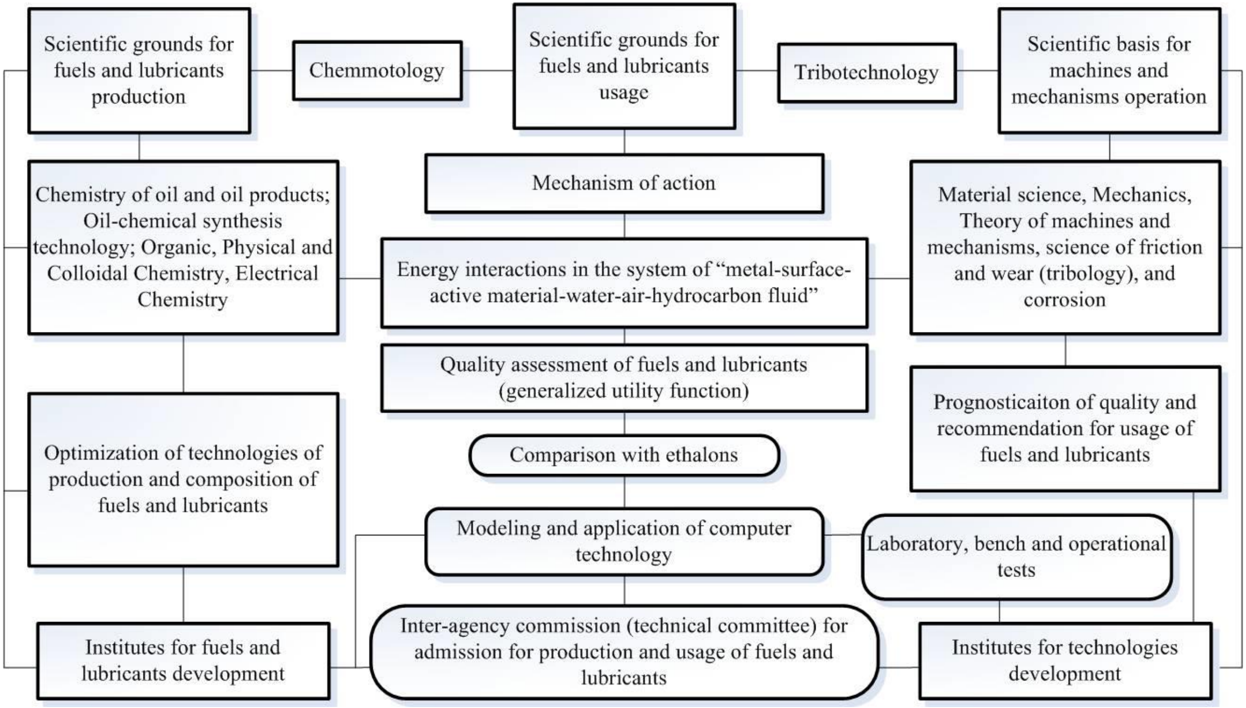


Fig. 1.4. The diagram of development, quality assessment and usage of fuels and lubricants

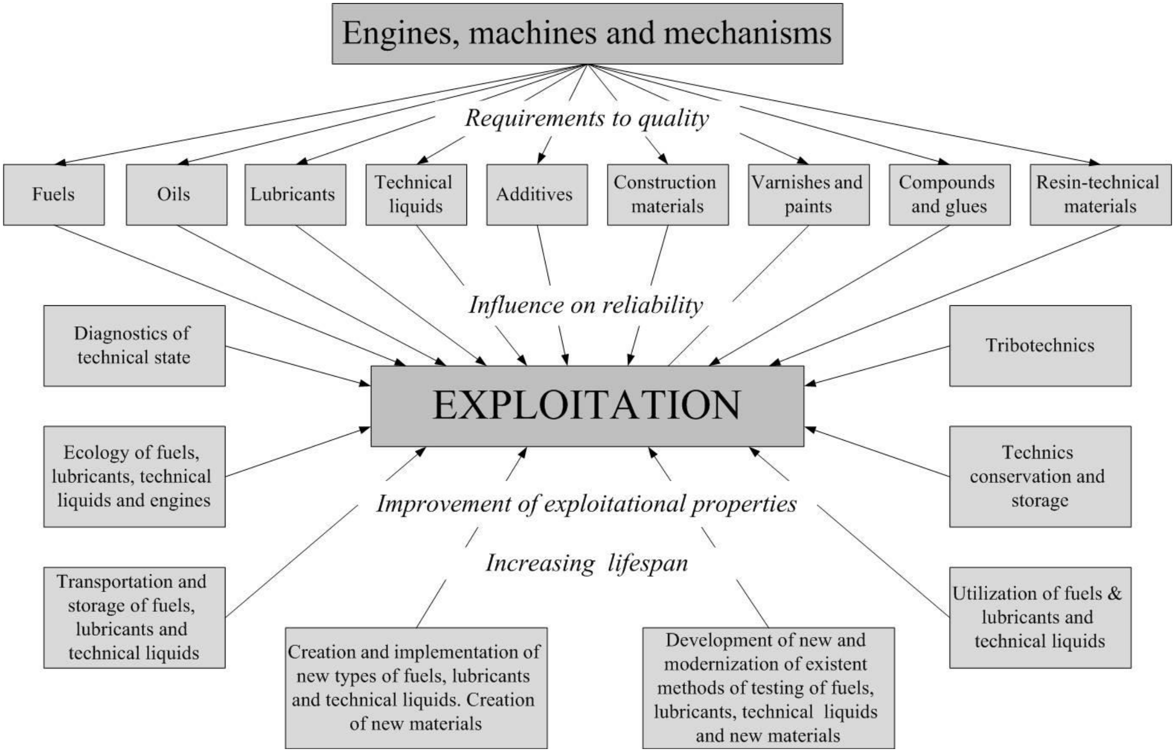


Fig. 1.5. Generalized universal model of the chemmotological system

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. To the certain extent it is an applied embodiment of systems theory in which the term «system» is used in a special way, referring to the way of thinking to explain coherent links (Fig. 1.6, 1.7) between elements of the system, synergy and emergence. Here, the «system» expresses not only the essence, but also related to the nature of the object, emphasizes the class properties interesting point of view from here diversity of definitions and a huge number of possible ways of the system decomposition and release of subsystems.

These viewpoints can be seen in Fig. 1.6, which illustrates the integrated interdisciplinarity of Chemmotology, Chemmotology system itself, it's hierarchy, Chemmotological coherent Interconnections, Structure, Nature, Synergy* and Emergence**.

It is clearly shown here how the interaction of elements and coherent processes on the example of an aircraft engine result in synergistic and emergent effects such as Ecological Compatibility, Efficiency, Reliability and Durability of the equipment.

Currently, consideration of problems of Chemmotology beyond a systematic approach to knowledge is not possible. This is qualitatively higher than just a substantive way of knowing.

**(Synergies is cumulative effect of the interaction of two or more factors, characterized by the fact that their effect is much greater than the effect of each individual component in the form of a simple sum).*

***«Emergence is quality, property of the system, which is not inherent in its elements separately, but instead rises by combining these elements into a single, integrated system».*

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. For example, refiners produce gasoline, diesel and other motor fuel, for further use in engines.

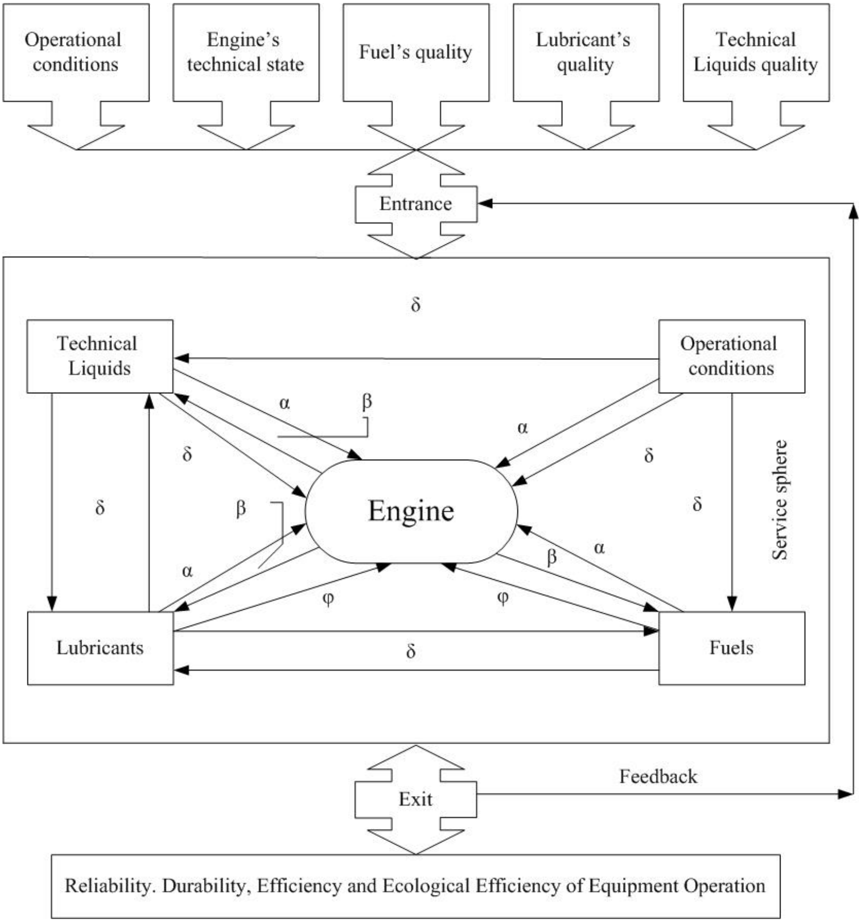


Fig. 1.6. Chemmotological model of «engine – fuel – lubricants – technical liquids» system functioning during equipment operation:

a – influence of fuels, lubricants and technical liquids on working characteristics of engine; b – requirements to fuels, lubricants and technical liquids quality from the engine side; d – influence of operation conditions on characteristics of engine, quality of fuels, lubricants and technical liquids; j – influence of fuels, lubricants and technical liquids on the engine operation efficiency

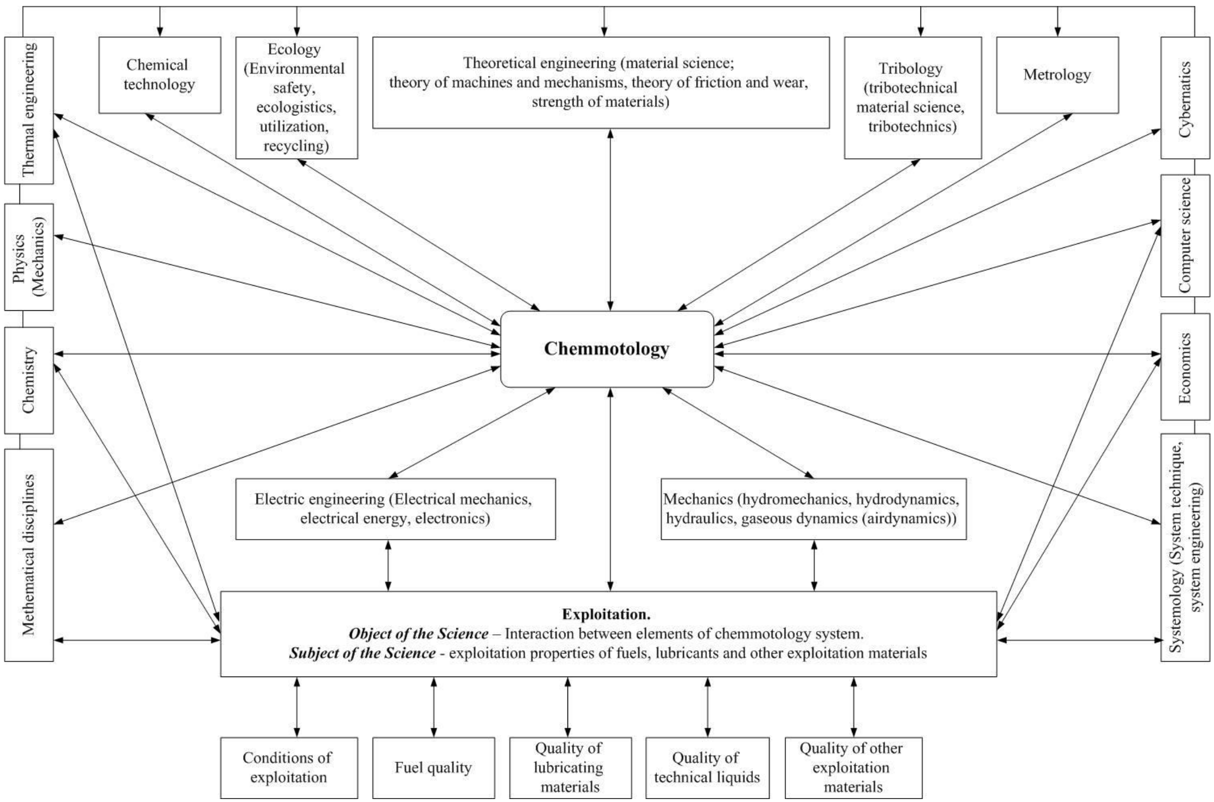


Fig. 1.7a. The phenomenological scheme (model) of Chemmotology

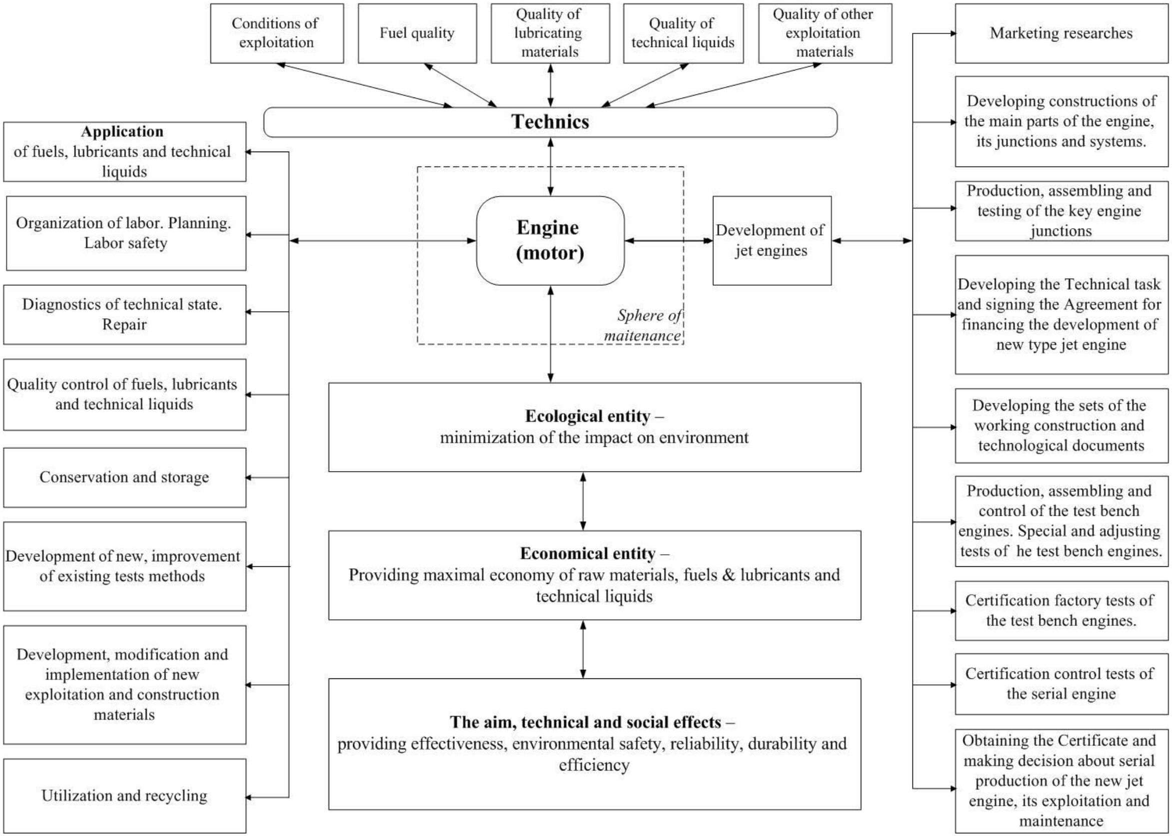


Fig. 1.7 b. The phenomenological scheme (model) of Chemmotology (continuation)

Knowledge of Fuels, Lubricants and Technical liquids implies a clear understanding of the interconnections of indicators that characterise quality with physical, chemical and energy processes that occur during their use in specific conditions, and the relationship with their chemical and group composition.

The absence of such analysis and forecasting makes it impossible to achieve the objectives, technical and social effects. This is another clear evidence of synergy effects in the operation of Chemmotologic system. Quality control of Fuels, Lubricants and Technical liquids plays a special role in Chemmotology on the way from their producer to consumer. As we can see from Fig. 1.6, quality of exploitation materials is included into the parameter of the system itself. Practice has proved that the use of Fuels, Lubricants and Technical liquids with the overestimated indicators on quality (quality level) leads to overcosting in the production sphere, and with underestimated – to cost escalation in mechanical engineering and operation of equipment.

As it is known, consideration of any scientific problem is impossible without a coherent ideological system. Worldview, which selects a particular civilization, defines the whole character of societal activities and its impact on the environment. On this basis, the *environmental essence* of Chemmotology is to minimize the negative impact of Fuels, Lubricants and Technical liquids on ecosystems as far as possible.

The importance of tasks, being solved by the Chemmotology is shown by its role as an applied science: ensuring energy and environmental safety of the country's economy, rational use of conventional and alternative fuels, lubricants and technical liquids in the operation of the modern and advanced equipment.

Quality deterioration of fuels, lubricants and technical liquids is also typical for operational techniques, as a result of evaporation, oxidation, products accumulation, precipitation and wash-out of some additives, mixing fuels, lubricants and technical liquids of different brands et al. The processes of regeneration, quality recovery, utilization and recycling became relevant now (Fig. 1.7).

These arguments allow us to assert that Chemmotologic system «engine-fuel-lubricants-technical liquid» is a management task, in which prescriptive and descriptive methods are applied. Here we can trace Chemmotology coherence with cybernetics (*are shown connections in the top part of Fig. 1.7-a*).

At each stage of engine creation (*see the right side of the underside of Fig. 1.7-b*), operation and application of Fuels and Lubricants also demonstrates the need for decision-making (*see the left side of underside of Fig. 1.7-b*), which eventually is embodied in the synergetic result: to ensure Efficient, Ecological, Reliable and Economical operation of Equipment.

Consequently, the fundamentality of Chemmotology science is the manifestation of the system of methodological characteristics for solving modern engineering problems, improving of technology and development of energy sources for motor vehicles simultaneously. Through applying Chemmotology and practicing its knowledge is possible to achieve significant results of scientific and technical progress in the technology, Petroleum and Gas Industry and Petrochemistry.

The Concept of Chemmotology is the systematic integration of knowledge of engineering, chemical, oil-refining and petrochemical fields of scientific and practical activities to achieve synergistic results in ensuring Reliability, Safety, Durability and Efficiency of equipment.

1.2. Chemmotological Scientific School at the National Aviation University

The bases of Chemmotological scientific and pedagogical school at the National Aviation University started to form at the end of the 1950s when laboratories of tribology under the supervision of Prof. B.I. Kostetzkiy and Prof. N.L. Holego had been organized. In these laboratories, the processes of physical and chemical mechanics of materials under friction were studied with the help of unique equipment; and the recommendations for the increase in longevity, reliability of machines and mechanisms along with improvement of fuels and lubricants quality were based on these research. Many staff members and students, who had taken active part in this research, later became significant scientists and founders of the science (Prof. A.Y. Alyabyev, Prof. V.V. Zaporozhetz, Prof. P.V. Nazarenko, and others).

The studies in the field of theoretical and practical research of hydraulic drives and their elements were started under supervision of Prof. T.M. Bashta at the same time, too. The Department of Details of Machines and Mechanisms (Prof. M.V. Rayko), Department of Aeronautic Engineering (Prof. Z.S. Chernenko), Department of Physics (Prof. A.N. Solovyev), Department of Electrical Engineering (Prof. A.L. Groholskiy), and other subdivision also participated in solving of Chemmotological problems.

The clear orientation of Chemmotological research towards solving problems connected with ensuring working reliability of the aircraft fuel, oil and hydraulic systems appeared in the 1960s. It was at that time that the special scientific group for solving the problems of fuels, lubricants and technical liquids application was created on the initiative of Prof. Alexander Aksenov at the Department of Technical Operation of Aircrafts and Aircraft Engines (Head of the Department – Associate Professor Vasiliy Sukharikov). A range of scientists including V.P. Belyanskiy, V.I. Teryohin, A.A. Litvinov, A.I. Kozachenko, Y.G. Nekipelov, A.E. Borodin, and A.Y. Shepel has participated in the research conducted by this school. The chemmotological scientific field was formalized at the National Aviation University of Ukraine under scientific advisory of the Rector Alexander Aksenov in order to coordinate all research works and analysis of their results.

The activity of the scientific school is inseparable from teaching. An independent Department of Chemistry and Technology of Fuels and Lubricants was created in 1968. It was followed by the creation of the Faculty of Fuels and Lubricant a year after (the head of the department and the first dean was associate professor Alexey Litvinov).

The first group of specialist in the field of testing and use of fuels and lubricants graduated in 1975. All the graduates (around 50 specialists) were in high demand and were hired by different operation companies, research institutes and educational institutes for civil aviation. The majoring Department of Testing and Usage of Fuels and Lubricants created by Professor Litvinov trained specialists in the field aviation Chemmotology. As a result, there was a significant increase in the professional level of fuels and lubricants quality control system.

The phenomenon of scientific and pedagogical school is realized via information supply of the study process under the conditions of integration of science and higher school with the goals of research institute creation. The role of the classic research institute, as first defined by W. Humboldt in the 19th century, is in integration of the study process with fundamental scientific research. The motto of the University of Berlin, founded by William von Humboldt in 1809, was “Devotion to science”.

Information supply being a constituent of integrated scientific supply of the study process is aimed at the creation of organizational and substantial basis of informational and educational environment, which provides the level of society’s informing. In general, scientific and pedagogical schools are the centers of accumulation, concentration and production of scientific and educational information and its application. These centers increase stability, determinancy, predictability and manageability of educational systems and processes. Being open selfmanaging systems these scientific schools are flexible and active in their interaction with external informational environment; they also constantly support and renew the scientific potential of their representatives and followers including students familiarized with science.

V. Vernadskiy, Ukrainian natural philosopher and naturalist, when describing the appearance of scientific schools, noted that “tzar Peter I established the scientific research in Russia, understanding its benefits for the state. And this scientific work had quickly found its place in public minds and didn’t stop during the long decades without government support of the scientific activities. It was formed by the intellectuals of the state, their personal efforts, personal initiative or through the organizations created by them.”

Leading positions in the Chemmotological movement today belong to the department of Chemmotology and the Ukrainian research and training center of Chemmotology and Certification of Fuels, Lubricants and Technical liquids of the National Aviation University. The Ukrainian research and training center of Chemmotology and Certification of Fuels, Lubricants and Technical liquids, created at the National Aviation University, is the successor of the Ukrainian Center of Aviation Chemmotology and Certification of Products (created by Professor Belyanskiy in 1994).

In the modern conditions when requirements for all types of products and services including consulting and educational ones have significantly increased and the conditions of collaboration and relationships between participants of the oil supply system have changed, the Innovative Chemmotological Thought as an Integrated System of Knowledge is gaining an extremely important meaning in the system of information supply.

The main scientific and applied problems being solved by the representatives of the school include the following:

- development of competitive resource- and energy-efficient technologies for storage, transportation of fuels and fuelling;
- development of alternative fuels for vehicles;
- study of physical, chemical and service properties of fuels, lubricants, and technical liquids during conduction of different technological operations;
- development of express methods and methodologies of quality assessment of fuels, lubricants, and technical liquids;
- development of organization, technical and norming activities for preserving the level of quality of fuels, lubricants and technical liquids;
- development of new competitive additives for fuels and lubricants;
- creation of a complex of qualifying tests methods for fuels, lubricants and technical liquids.

The concept of the Chemmotological scientific school development at the National Aviation University is oriented toward the innovative model, the one that allows to collect and multiply the achievements of our staff under the conditions of today's crisis situation in the fuels and lubricants market; the one that lets to increase the level of developments and discoveries and their implementation to the competitive level and in a short term; and also to create the basis for the improvement of working conditions of scientific and pedagogical staff of the Chemmotological school, realization of their scientific and educational programmes, finding and developing talented creative persons among the student youth, and preparation of top qualification specialists.

The goal of the Chemmotological scientific school is stimulation of scientific researches and experimental design works along with training (extension courses) of the specialists in accordance with the international laws and standards for solving actual and prospective problems of Chemmotology, specialists in testing systems, production and usage of fuels, lubricants and technical liquids, for aviation industry in particular, and introduction of energy-efficient technologies.

The strategic goal of the Chemmotological scientific school is the achievement of modern level of research and training of scientific and pedagogical personnel of the highest qualification. The main mission is carrying out of fundamental and applied research, scientific and experimental-design research in accordance with the scientific specializations of the university, notably: Chemmotology, Tribochemistry, Tribology, Environment Protection and Living Safety, certification and quality management, testing, diagnostics, permission for production of fuels, lubricants and technical liquids with the goal to solve priority problems of science and practice.

Social and economic impact of the Chemmotological scientific school comes in the shaping of the highly-educated specialist who could meet the modern level of highly technological production and service in the first place. The role of this kind of specialists is constantly increasing in many countries, since deep knowledge and superior technologies become the new strategic resources. The Chemmotological scientific school of the National Aviation University through stimulation of spreading of knowledge and skills ipso facto ingenuously promotes:

- integration and coordination of researches of creative groups in the field of chemmotology of fuels, lubricants and technical liquids;
- carrying out scientific and experimental-design research;
- training (professional advancement) of personnel for solving chemmotological problems, certification, and quality management in compliance with the international standards;
- development of new materials and products;
- increasing competiveness of products and services at the world level;
- changing the culture (technical in particular), world outlook and modern way of life, etc.

Thus, the Chemmotological scientific and pedagogical school of the National Aviation University influences different sides and spheres of the social life of the university, especially the ones connected with basic training of specialists in the education field, and also with research activities (oriented towards rational use of fuels, oils, greases and technical liquids, for aviation equipment in particular). The school being an important constituent of information supply of educational process through the inclusion of information medium of the university into the global information system. The activity of the school in the structure of the university serves as a joining link between the university and the world scientific environment, global Chemmotology scientists' community. It also ensures the needed level of training of specialists in the field of oil products supply according to the social needs.

Questions for self-contol

1. What does Chemmotology mean?
2. Name the main tasks of Chemmotology.
3. Name the main directions of Chemmotology.
4. Name the main goals of Chemmotology.
5. Describe the universal four-link Chemmotologycal system.
6. Characterise the Chemmotological model of "engine-fuel-lubricants-technical liquids" system.
7. Consider the questions, which are involved in the scientific sphere of Chemmotology science.
8. Which sciences are interconnected to Chemmotology science?
9. Descrie the role of proper condition of fuels and lubricants for mashinery operation.
10. What is the environmental aspect of Chemmotology science?

Chapter 2
CLASSIFICATION OF THE MOTOR FUELS

There are so many products that come from oil, including heating oil, gasoline, jet fuel, kerosene, synthetic fibers etc.

Crude oil is the term for «unprocessed» oil, the stuff that comes out of the ground. It is also known as petroleum. Crude oil is a fossil fuel, meaning that it was made naturally from decaying plants and animals living in ancient seas millions of years ago – most places you can find crude oil were once sea beds. Crude oils vary in color, from clear to tar-black, and in viscosity, from water to almost solid.

Crude oils are such a useful starting point for so many different substances because they contain hydrocarbons. Hydrocarbons are molecules that contain hydrogen and carbon and come in various lengths and structures, from straight chains to branching chains to rings.

It is accepted to distinguish the following fractions of petroleum: petroleum (or oil) fraction, that is boiling away in the range of 30–205 ^{o}C, is called Petrol, in the range of 120–240 ^{o}C – Ligroin (naphtha), 150–315 ^{o}C – Kerosene, 150–360 ^{o}C – Diesel, 230–360 ^{o}C – Gas oil, 300–400 ^{o}C – Straw distillate.

A **motor fuel** is a fuel that is used to provide power to motor vehicles. The generalized interpretation of fuel is as follows. **Fuel** – a combustible substance (firewood, coal, oil, gas, etc.), which is used for the production of heat energy (heat).

As a result of the oil processing, a wide range of commercial products is obtained. These products differ in chemical and fractional composition, as well as in properties and industrial applications.

In practice petroleum is divided into fractions and groups of hydrocarbon in order to derive various petroleum products. Processes of **Primary** and **Secondary processing of petroleum** are used for this purpose. Main process of primary petroleum processing is primary or **Direct Distillation**. Individual fractions obtained as a result of distillation are called **Distillates**.

The secondary processes of petroleum refining are subdivided on **Thermal** and Thermo-catalytic. Group of thermal processes includes those, at the heart of which is the ability of organic compounds of petroleum to break-up, alter chemically under the influence of high temperatures etc. The following thermal processes are used: **Thermal cracking, Viscosity breaking, Carbonization** and **Pyrolysis.**

Group of thermo-catalytic processes includes those, at the heart of which is the use of various catalysts for acceleration of chemical transformations. Among them: **Catalytic cracking**, **Reforming**, **Platforming**, **Hydrocracking, Hydrogenation, Polymerization, Alkylation, Sulfonation** etc.

As it is known commercial fuels are obtained by compounding fractions of primary and secondary processes of oil processing. Fractional and component compositions of fuels are in direct relation (table 2.4).

Table 2.4

Oil refining processes used for fuels production

Kind of fuel	Boiling range, ^{o}C	Main components
Gasoline	35–200 ^{o}C	Fractions of direct distillation, products of reforming, isomerization, alkylation, volatile hydrocarbons
Jet fuel	150–280 ^{o}C	Hydrotreatment, kerosene-gasoil fraction
Diesel fuel	200–360 ^{o}C	Fractions of direct distillation, hydrotreated gasoil fraction, hydrotreated light gasoil of catalyticcracking
Boiler fuel (fuel oils, hydron)	More than 360 ^{o}C	Residues of direct distillation, gasoils

2.1. Subdivision of petroleum and related materials

The natural materials occur in different locations throughout the Earth. The derived and manufactured materials are obtained by using methods different from those used to obtain the natural materials.

Petroleum is perhaps the most important substance consumed in the modern society. It provides not only raw materials for the ubiquitous plastics and other products, but also fuel for energy, industry, heating, and transportation (table 2.5).

All petroleum crude oils are composed primarily of hydrocarbons of the paraffinic, naphthenic, and aromatic classes. Each class contains a very broad range of molecular weights. Out of the ground, crude oil can be as thin and light-colored as apple cider or as thick and black as melted tar. Thin crude oils have relatively low densities and thus, high API gravities. In the U.S., light crudes are called high-gravity crude oils; conversely, thick and heavy crude oils with relatively high densities are low-gravity crude oils. Outside of the U.S. the terminology “light crude” refers to a low-density crude oil and “heavy crude” to a high-density crude oil.

Table 2.5

Subdivision of Fossil Fuels Into Various Subgroups

Natural Materials	Derived Materials	Manufactured Materials
Natural gas	Saturate	Synthetic crude oil
Petroleum	Aromatic	Distillates
Heavy oil	Resins	Lubricating oils
Bitumen*	Carenes**	Wax
Asphaltite	Carboids**	Residuum
Asphaltoid	Asphaltols***	Asphalt
Ozocerite (natural wax)		Coke
Kerogen		Tar
Coal		Pitch

*Bitumen from tar sand deposits,
** Poducts of petroleum processing,
***Products of coal processing

Refining is the process of converting crude oil into high value products. The most important are transportation fuels: gasoline, jet fuel, and diesel fuel. Other products include liquefied petroleum gas (LPG), heating fuel, lubricating oil, wax, and asphalt. High-gravity crude oils contain more of the lighter products such as gasoline and generally have lower sulfur and nitrogen contents, which makes them easier to refine. However, modern refining processes are capable of turning low-gravity crude oils into high value products. Refining low-gravity crude oils requires more complex and expensive processing equipment, more processing steps, and more energy; therefore, costs more. The price difference between high-gravity and low-gravity crude oils reflects a portion of the refining cost difference.

According to the international standard ISO 8681 all oil products are classified into five major classes with letter index (Table 2.6).

All lubricants can be systematized into four basic groups:

1. Oils, which are liquids at normal conditions.
2. Consistent (plastic) lubricants, which are plastic, grease-like materials.
3. Solid lubricants, which are used both as components to oils and greases, and as independent lubricants.
4. Gaseous materials (spray, carbon dioxide, nitrogen, rare gases).

Table 2.6

Classification of the oil products according to ISO 8681

Class	Product
F	Fuels
L	Lubricants, industrial oils and related products
W	Paraffins
B	Bitumen
S	Solvents and raw materials for chemical industry

ISO 8216.0 defines the common classification of fuels (table 2.7).

Table 2.7

General fuel classification according to ISO 8216.0

Class	Category	Product
F	G	Gaseous fuels. Gaseous fuels of petroleum origin, containing mostly methane and (or) ethane
	L	Liquefied gaseous fuels. Gaseous fuels of petroleum origin, containing mostly methane and (or) ethane
	D	Distillate fuels. Fuel of petroleum origin, except liquefied petroleum gases. Include gasolines, kerosene, gas oil and diesel fuel. Heavy distillates may contain small amount of residues
	R	Residual fuels. Petroleum fuel containing residual fraction of oil distillation
	C	Petroleum coke: solid fuels of petroleum origin, containing mainly hydrocarbons obtained by cracking process

Depending on the application, the following types of petroleum fuels are distinguished:

- Gasolines;
- Jet fuels;
- Diesel fuels;
- Gas turbine fuels;
- Boiler fuels;
- Stove fuels;
- Compressed and liquefied hydrocarbon gases.

For operation of public vehicles gasoline, diesel fuel and hydrocarbon gases in compressed or liquefied form are used (Fig. 2.8).

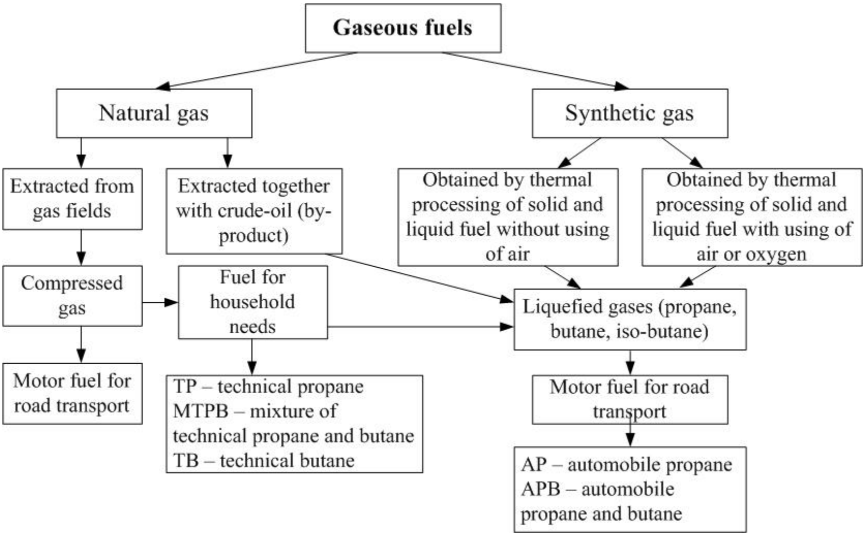


Fig. 2.8. Classification of gaseous fuels

All fuels fall into three general categories based on their physical properties (table 2.8).

Category «A» Fuels – Although the materials used in the construction of the fuel tanks may vary, there does not appear to be any reason why fuel systems for fuels that remain a liquid under normal operating temperatures cannot be evaluated in a similar fashion to conventional gasoline or diesel fuel.

Table 2.8

Classifications of Fuels by Physical Properties

Category	Fuel Type	Examples
A	Fuels with a vapour pressure of less than 1 atmosphere at 20 °C.	Diesel fuel Gasolines Methanol and Ethanol and their blends
B	Fuels with a vapour pressure equal to or greater than 1 atm at 20 °C and which may form a liquid phase on the vehicle.	Propane and Liquefied Petroleum Gas (LPG) Dimethyl ether Liquid natural gas (LNG) Liquid hydrogen
C	Gaseous fuels that do not form a liquid phase on the vehicle.	Methane and natural gas Compressed natural gas (CNG) Ethane Hydrogen Adsorbed gases

Category «B» Fuels – The fuels in category B have many features in common, but there are significant differences between fuels such as LPG and cryogenic systems. In cryogenic systems, significant hazards result from the destruction of the insulation layers that surround the fuel tanks in a «loss of vacuum» incident.

As it is recognized in the existing LPG regulations and test methods, both liquids and vapors will be present and the fuel systems may have complex vaporization and pressure regulation systems external to the fuel tank. Cryogenic systems may operate at near atmospheric or moderate pressures (10 bar). The fuels may have large ratios of thermal expansion compared to container materials and require «stop fill» systems to prevent tank rupture in case when a vehicle is filled cold and then stored in a warm environment. If stored in a sealed container and subject to a fire, these fuels have a high potential. Therefore, the fuel storage systems are usually fitted with a vented pressure relief system. The design of the relief system will be dependent on the fuel, the

anticipated thermal input, and whether it must function in both the gas and liquid phases (as in the case of vehicle rollover).

Category «C» Fuels – These fuels are typically lighter than air, although expanding gas plumes may be chilled and temporarily have a higher density. The gases are typically stored in cylinders rated at 200 to

300 bar and considerable mechanical energy is contained in the compressed gas. Pressures of up to 700 bar are being considered for hydrogen. Because of the high pressure of the stored gas, fuel containers are extremely strong but must be resistant to environmental degradation and be fitted with a thermally activated pressure relief system.

Fuel, in its turn, is divided by four basic features into groups, sorts, brands and types: by **origin** – natural and artificial; by **chemical composition** – hydrocarbon and non-hydrocarbon; by aggregate state – **gaseous, liquid and solid**; by **method of combustion**.

A general classification of motor fuels is presented in Fig. 2.9.

All lubricants can be systematized into four basic groups:

1. Oils, which are liquids at normal conditions.

2. Consistent (plastic) lubricants, which are plastic, grease-like materials.

3. Solid lubricants, which are used both as components to oils and greases, and as independent lubricants.

4. Gaseous materials (spray, carbon dioxide, nitrogen, rare gases).

Classificatiopn of fuels according to the method of combustion is given at Fig. 2.10.

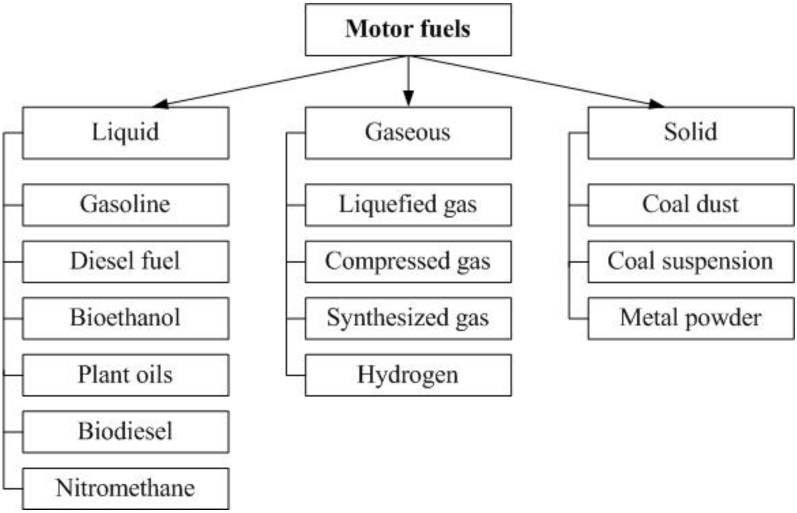
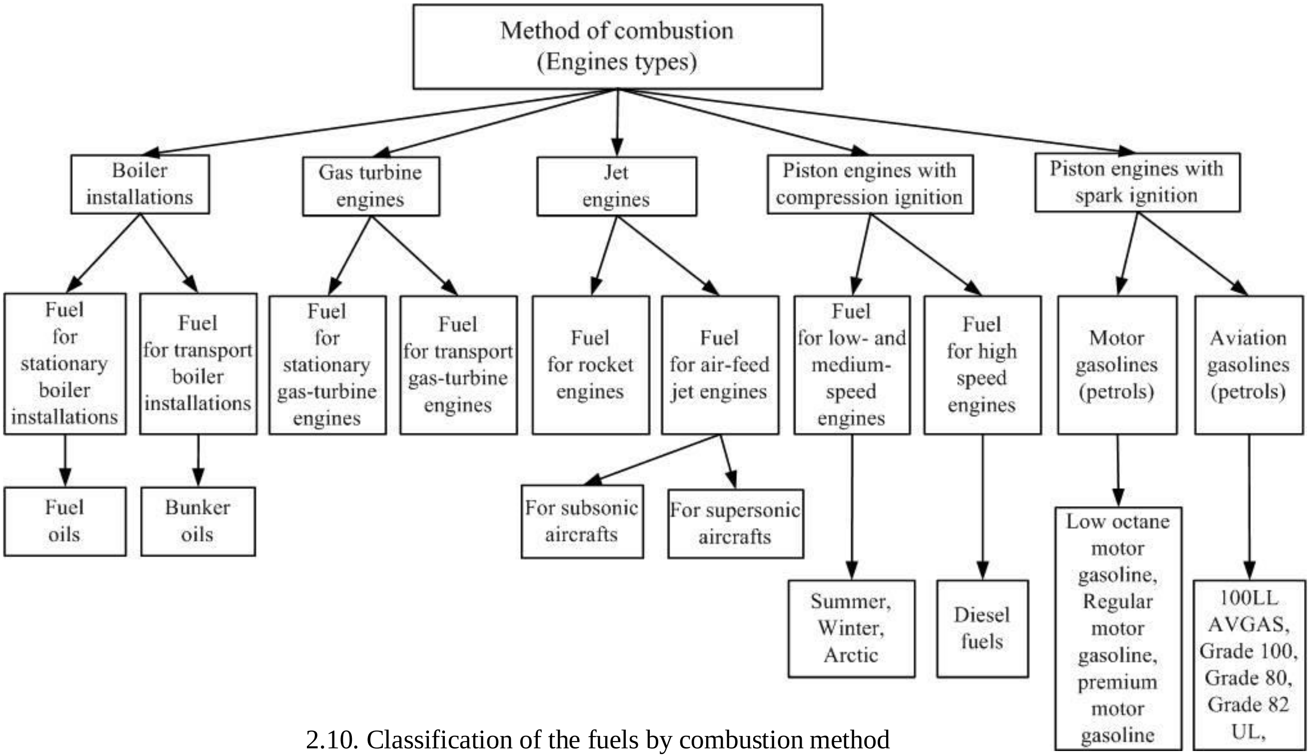


Fig. 2.9. General classification of fuels



2.10. Classification of the fuels by combustion method

2.2. Refining processes

Today's refinery is a complex combination of interdependent processes, the result of a fascinating intertwining of advances in chemistry, engineering, and metallurgy. These processes can be divided into three basic categories:

1. Separation processes. The feed to these processes is separated into two or more components based on a physical property, usually boiling point. These processes do not otherwise change the feedstock. The most common separation process in a refinery is distillation.
2. Upgrading processes. These processes improve the quality of a material by using chemical reactions to remove compounds present in trace amounts that give the material an undesirable quality. Otherwise the bulk properties of the feedstock are not changed. The most commonly used upgrading process for diesel fuel is hydrotreating to remove sulfur.
3. Conversion processes. These processes fundamentally change the molecular structure of the feedstock, usually by "cracking" large molecules into small ones (e.g., catalytic cracking and hydrocracking).

Distillation is by far the most important and widely used separation process in a petroleum refinery. In large part, petroleum products are defined by their boiling range, and distillation is the process used to separate crude oil or other wide boiling range mixtures into products with narrower boiling ranges.

Crude oil is made up of many thousands of components from light gases that boil below ambient temperature, to very heavy materials that cannot be distilled even at temperatures above 550 °C (1000 °F).1 In crude petroleum distillation, hot oil is pumped into a distillation column and the lightest hydrocarbons present, usually propane and butane, rise to the top of the column and are removed. Since gasoline is a little heavier, it does not rise quite so high and is drawn off from the side of the column. Kerosene and diesel, the next heavier products, are drawn off at successively lower points on the column. The products that are obtained directly from crude oil distillation are called straight-run products (e.g., straight-run diesel). The material that is too heavy to vaporize under atmospheric distillation conditions is removed from the bottom of the column (atmospheric bottoms).

The atmospheric bottoms can be fractionated further by a second distillation carried out under reduced pressure. The lower pressure in the distillation column allows some of the heavier components to be vaporized and collected. This process is called vacuum distillation; the overhead product is called vacuum gas oil (VGO), and the bottoms product is called vacuum residue.

Because of the distillation profile of the typical crude, refining by distillation alone has not been able to meet market demand for light fuel products since the early 1900s. It yields too much heavy products and not enough light products. In addition, the quality of light products produced by distillation alone is often poor. The petroleum refiner uses the upgrading and conversion processes to match the barrel to the market.

Upgrading Process Hydroprocessing (hydrogen treating process) is a generic term for a range of processes that use hydrogen with an appropriate catalyst to remove undesired components from a refinery stream. The processes run the gamut from mild conditions that remove reactive compounds like olefins, some sulfur, nitrogen and oxygen compounds (hydrofinishing), to more severe conditions that saturate aromatic rings and remove almost all sulfur and nitrogen compounds (hydrotreating).

Conversion Process Hydrocarbons with higher boiling points (the larger molecules in the distillation bottoms) can be broken down (cracked) into lower boiling hydrocarbons by subjecting them to very high temperatures. The discovery of this process (thermal cracking) offered a way to correct the mismatch between supply and demand. Since 1913, thermal cracking has been used to increase gasoline production. Although by today’s standards, the quality and operation of these earlier cracked products was low, they were sufficient for the engines of the day. Eventually heat was supplemented by a catalyst, transforming thermal cracking into catalytic cracking.

Catalytic cracking produces higher quality products than thermal cracking. There are many variations on catalytic cracking, but fluid catalytic cracking (FCC) is probably the most widely used conversion process, worldwide. Most of the liquid product from FCC eventually goes into gasoline; however, one product stream, light cycle oil (LCO), is often blended into diesel fuel. Before blending, LCO undergoes subsequent hydrotreating to lower sulfur content which makes the LCO more stable and suitable for adding to diesel fuel. To meet the 15 ppm sulfur requirement, LCO undergoes subsequent hydrotreating to lower sulfur content.

Hydrocracking is another major conversion process. It is similar to catalytic cracking because it uses a catalyst, but the reactions take place under a high pressure of hydrogen. The primary feed to the hydrocracking unit is VGO. During hydrocracking, large VGO molecules are cracked into smaller molecules by either cleaving carbon-carbon bonds or by plucking out sulfur and nitrogen atoms from -carbon-sulfur-carbon- and -carbon-nitrogencarbon- molecular linkages. Because of the high hydrogen pressure used in hydrotreating, hydrogen is added to the fragmented molecular ends formed by either cleaving carboncarbon bonds or by extracting sulfur and nitrogen linkage atoms; in addition, rings of some aromatic compounds are saturated with hydrogen during the hydrocracking process. Kerosene and diesel form a large percentage of the product from a hydrocracker. These products are nearly void of sulfur and nitrogen and are enriched in hydrogen.

The VGO obtained from vacuum distillation of the atmospheric bottoms are fed to either the FCC unit or the hydrocracker. The VGO may be hydrotreated to reduce sulfur and nitrogen to the levels that will improve the operation of the FCC process. Previously, the vacuum residual might have been used as a low value, high-sulfur fuel oil for onshore power generation or marine fuel. But to remain competitive, refiners must wring as much high value product as possible from every barrel of crude. As a result, the vacuum residue may be sent to a residue conversion unit, such as a residue cracker, solvent extraction unit, or coker. These units produce additional transportation fuel or gas oil, leaving an irreducible minimum of residue or coke.

A schematic layout of a modern, fully integrated refinery is shown in Fig. 2.11. Crude oil is fed to the distillation column where straight-run naphtha, light and heavy gasoline, chemical naphtha, kerosene, and diesel are separated at atmospheric pressure.

The requirement for unleaded gasoline and the gradual increase of its sales roughly paralleled the gradual phase-down of lead in leaded gasoline. Both these trends increased the need for higher-octane-number components. In response, refiners produced more reformate, FCC gasoline, alkylate, and oxygenates, roughly in this order.

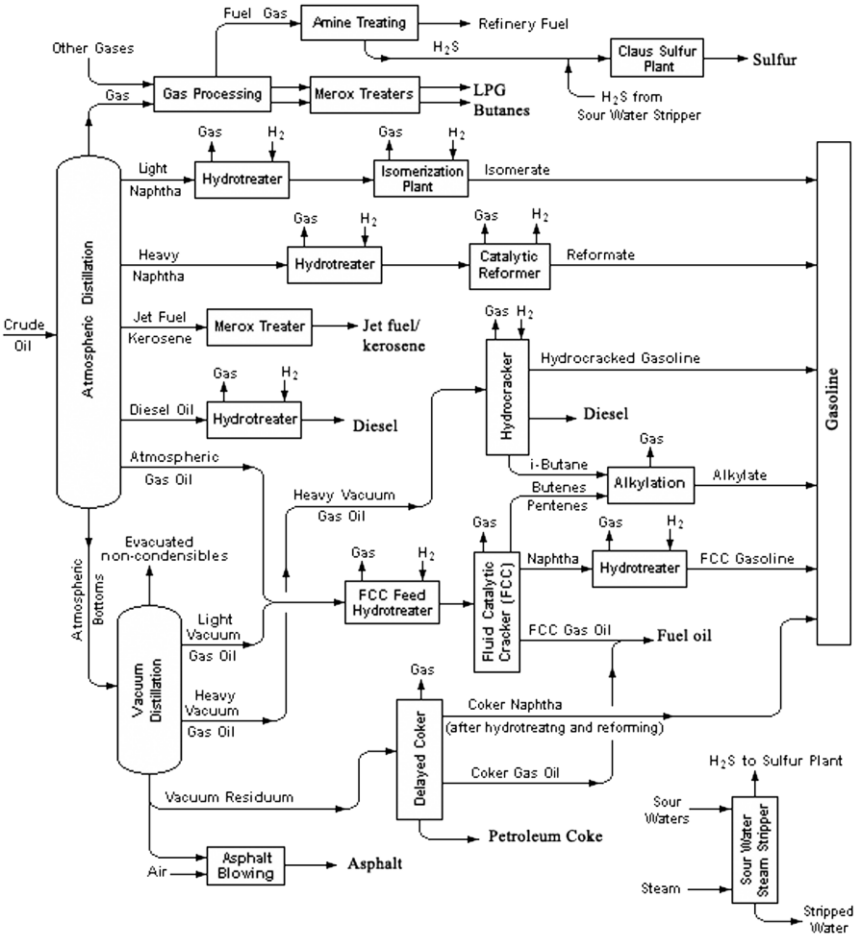


Fig. 2.11. The Modern Refinery Scheme

Later, tighter and tighter vapor pressure limits forced the reduction of the amount of butane that could be added to gasoline in the summer. This resulted in excess butane, and because butane has good octane quality, its reduction further increased the need for higher-octane-number components. A solution for both problems was to use butane to make alkylate. The requirements for oxygenated gasoline helped the octane number shortfall because oxygenates have high octane numbers. The need for oxygenates prompted some refiners to add units to make

MTBE and other ethers. Severe conventional hydrotreating can result in a loss in octane number because of saturation of high-octane-number olefins and aromatics. New versions of hydrotreaters do not cause as much of an octane number loss. New refinery processes for removing sulfur do not involve the use of hydrogen.

2.3. Additives

Most fuels such as gasoline, kerosene (jet fuel), gas oil (diesel fuel) and fuel oil have drawbacks which do not allow their long term storage, make difficult transportation and even use. About 20 properties of fuels can be improved, maintained or imparted new beneficial characteristics by the adding of small amounts of certain chemicals named fuel additives. Fuel additives are added in very small concentrations: from several ppm to several thousands ppm. It is important that additives which improve some properties should not deteriorate other properties of fuels and its quality in general. Fuel additives are organic substances soluble in fuels: antifoams, anti-icing additives, anti-knock additives, antioxidants, antistatic additives, anti-valve seat recession additives, biocides, cetane improvers, combustion chamber deposit modifiers, corrosion inhibitors, demulsifiers, deposit control additives, detergents, diesel fuel stabilizers, drag reducing agents, dyes and markers, leak detector additives, lubricity improvers, metal deactivators, and wax anti-settling additives. Additives to fuel oil also are described: demulsifiers, sludge dispersants, combustion improvers, and additives for prevention oil-ash and cold-end corrosion in boilers. Action of fuel additives, their application, risks and benefits are analysed.

Use of gasoline fuel additives largely reflects developments in engines design and refinery operations, as well the problems occurring during storage and transportation of gasoline. Use of jet fuel additives reflects strict requirements to maintain properties of jet fuel. Use of diesel fuel additives reflects the impact of growing diesel fuel demand and the changing technology of diesel engines. Sometimes additives are divided according to the name of fuel: gasoline, jet fuel, diesel fuel and fuel oil additives. It is conditionally because the same additives (e.g., antioxidants and corrosion inhibitors) can be used in gasoline, jet fuel, and diesel fuel. Situation with aviation fuels (jet fuel and avgas) is unique in that only those additives specifically approved may be added to jet fuel. Before an additive can be approved for use in aviation fuel, it must undergo extensive testing to show both that it is effective and that it does no harm to any other fuel properties. To guard against harmful additive interactions, an additive must be tested at four times its maximum dosage in the presence of other additives before it is approved.

Questions for self-control

1. Describe subdivision of petroleum and related materials.
2. Describe classification chart of recoverable oil resources.
3. Name classes of oil products according to ISO 8681.
4. Which types of petrochemicals are distinguished depending on the application?
5. Name four basic groups of lubricants.
6. Give classification of gaseous fuels.
7. Characterise three basic categories of modern refinery processes?
8. Describe modern refinery scheme.
9. What is the difference between atmospheric and vacuum distillation?
10. What are the main purposes of additives?

Chapter 3.
CHEMMOTOLOGY OF GASOLINES

In May 1876, Nicolaus Otto built the first practical four-stroke-cycle internal combustion engine powered by a liquid fuel. By 1884, he concluded development of his engine with the invention of the first magneto ignition system for low-voltage ignition. The liquid fuel used by Otto became known as gasoline in the United States; elsewhere it may be known as *gasolina, petrol, essence, or benzin (not to be confused with the chemical compound benzene)*.

Gasoline (from French “вenzine”) is one of basic fuel types for the engines of current technics.

About half of world consumption of motor fuels is due to gasoline, which serves as an energy source for the internal combustion engines, in which working mixture is ignited with a spark.

If the petroleum is heated at atmospheric pressure, the lightest petrochemicals evaporate first of all, with the increase of temperature the heaviest petrochemicals start to evaporate. Separate condensation of evaporated products gives different fractions: products evaporating within the range from 30 (35) to 205 (215) °C are considered to be **gasoline** (to compare condensate, which has boiled out at temperatures from 150 to 315 °C, is called **kerosene**, and **diesel** is produced in the range from 150 to 360 °C).

But this method of gasoline production (called straight-run distillation) gives very small amount of gasoline – only 10–15 % of distilled petroleum. This way doesn’t provide the needs of the immense car fleet. Therefore, the biggest share of commercial gasoline (petrol) is produced via so called secondary oil production processes.

Commercial gasoline is a mixture of hydrocarbons, which boil away in the range of temperatures 30 (35) – 200 (215) °C. The element composition of gasoline is formed of 84,0–86,0 % C, 14,0–16,0 % H and 2–3% O.

Gasoline is produced via application of such technological processes as straight-run distillation, catalytic reforming, thermal and catalytic cracking with addition of high-anti-knocking components and additives (Fig.3.12).

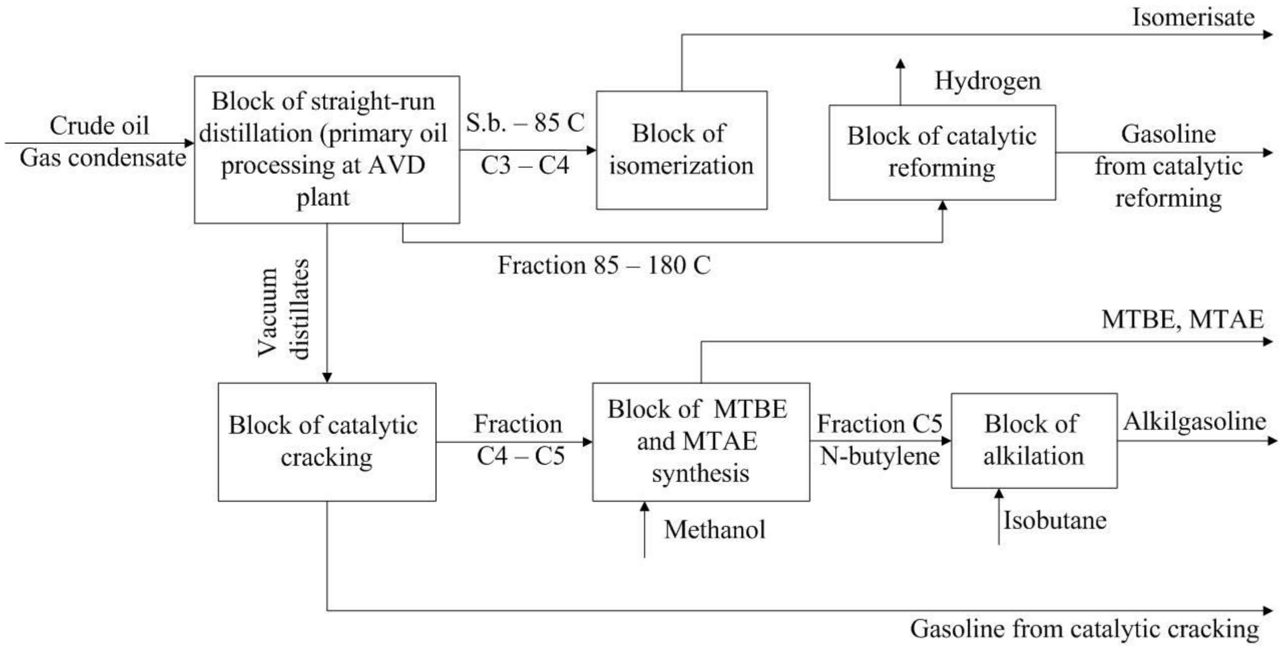


Fig. 3.12. Typical block diagram gasoline production

Gasoline is a mixture of volatile, flammable liquid hydrocarbons derived from petroleum and used as fuel for internal-combustion engines. It is also used as a solvent for oils and fats. Gasoline has become the preferred automobile fuel because of its high energy of combustion and capacity to mix readily with air in a carburetor.

Gasoline is a mixture of hydrocarbons that usually boil below 180 ^{o}C or, at most, below 200 ^{o}C. The hydrocarbon constituents in this boiling range are those that have 4 to 12 carbon atoms in their molecular structure and fall into three general types: paraffins (including the cycloparaffins and branched materials), olefins, and aromatics.

3.1. Composition

There are two ways to describe a material, by its chemical composition and by its properties. Both viewpoints can be instructive.

Gasoline is a complex mixture of hundreds of hydrocarbons that vary by class, including paraffins, olefins, naphthenes, and aromatics. Within each class, hydrocarbons also vary by size. The mixture of hydrocarbons (and oxygenates) in a gasoline determines its physical properties and engine operation characteristics.

Gasoline is manufactured to meet property limits prescribed by specifications and regulations, not to achieve a specific distribution of hydrocarbons by class and size. To varying degrees, property limits define chemical composition. Consider, for example, gasoline volatility. The temperature limits of a distillation profile exclude smaller hydrocarbons with lower boiling points and larger hydrocarbons with higher boiling points. The most common way to characterize the size of a molecule is molecular weight. For a hydrocarbon, an alternate method is by carbon number, that is, the number of carbon atoms in its molecular structure. Butane, for example, has a molecular weight of 58 grams per gram-mole (g/g-mole) and a carbon number of 4 (C_4). Benzene has a molecular weight of 78 g/g-mole and a carbon number of 6 (C_6).

Figure 3.13 shows the carbon number distributions for typical regular unleaded and premium unleaded gasolines. Note that the range of sizes runs from C_4 to C_{12} with the most prevalent size being C_5 for regular and C_8 for premium and the average size being $C_{6\text{-}9}$ for regular and C_7.1 for premium. The average molecular weight of gasoline ranges from 92 to 95. Figure 3.13 shows, as expected, that gasoline's cumulative carbon number distribution parallels the distillation profile.

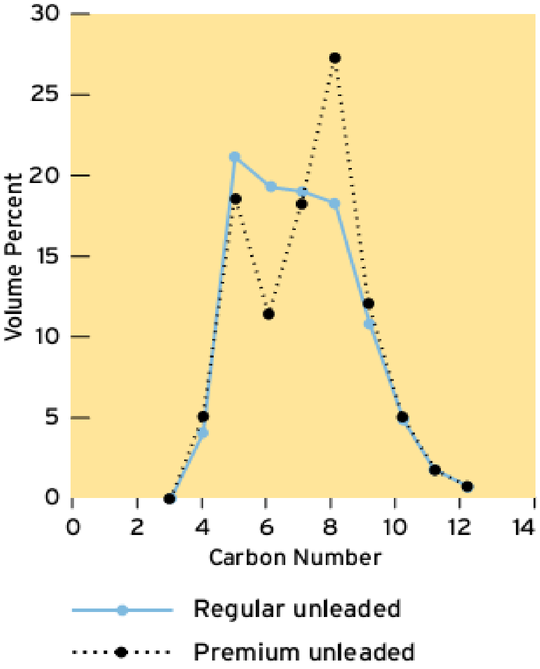
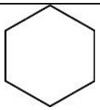
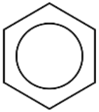
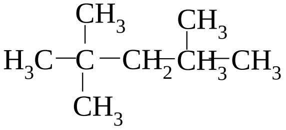
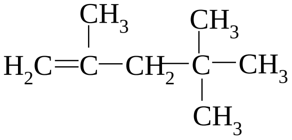
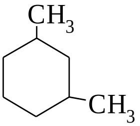
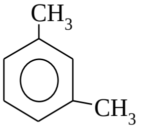


Fig. 3.13. Gasoline Carbone Number Distribution

Octane number is another example of how property limits define chemical limits. Table 3.9 illustrates how Research octane number (RON) varies with class for hydrocarbons of the same carbon number. So, an octane number limit requires greater representation of some classes and less of others. Different isomers of the same hydrocarbon can have different octane numbers.

Table 3.9

Research Octane Number by Hydrocarbon Structure

Compound	n-Hexane	1-Hexene
Formula	C_6H_{14}	C_6H_{12}
Structure	$CH_3(CH_2)_4CH_3$	$H_2C=CH(CH_2)_3CH_3$
RON	25	76
Compound	Cyclo-hexane	Benzene
Formula	C_6H_{12}	C_6H_6
Structure		
RON	83	123 (est.)
Compound	2,2,4-Trimethylpentane (Isooctane)	2,4,4-Trimethyl-1-pentene (Isooctene)
Formula	C_8H_{16}	C_8H_{18}
Structure	 $H_3C-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\overset{CH_3}{CH_3}-CH_3$	 $H_2C=\overset{CH_3}{C}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$
RON	100	106
Compound	Cis 1,3-dimethyl cyclohexane	1,3-Dimethyl benzene
Formula	C_8H_{16}	C_8H_{10}
Structure		
RON	72	118

The RON of isooctane (2,2,4-trimethylpentane) is 100 by definition while the RON of normal octane is estimated to be less than zero. Other properties, such as volatility, also are influenced by isomer structure. With the advent of air pollution regulations throughout the world, property specifications have been supplemented by some composition specifications.

3.2. Blending

Crude oil is fed to the distillation column where straight-run light and heavy gasoline, jet, and diesel are separated at atmospheric pressure. Straight-run jet fuel is usually acceptable as is, straight-run diesel fuel requires further hydrotreatment to remove sulfur, and straightrun gasolines typically require more processing to convert them into gasoline blending components.

Straight-run light gasoline may be isomerized to increase octane number, hydrotreated to convert benzene to cyclohexane so that the final gasoline blend will meet a benzene specification limit, or both. Straight-run heavy gasoline is hydrotreated to remove sulfur and then reformed to improve octane number and generate hydrogen for the hydrotreaters. The bottoms from the atmospheric column are vacuum-distilled to obtain gasoils for FCC or hydrocracker feed. The gasoils are hydrotreated to reduce sulfur and nitrogen to levels that will not interfere with the FCC process. Even though the feed is substantially desulfurized, the FCC product must be sweetened to convert reactive sulfur compounds (mercaptans) to more innocuous ones; otherwise, the gasoline blend will be odorous and unstable.

Despite the diversity and ingenuity of the processes within a modern petroleum refinery, no single stream meets all the requirements of gasoline. Thus, the final step in gasoline manufacture is blending various streams into a finished product. It is not uncommon for finished gasoline to be made up of six or more streams (Fig. 3.12). Sometimes, to provide more flexibility, a stream is distilled into several fractions and each fraction is used as a separate blending component (for example, FCC light and FCC heavy gasoline). Several factors make this flexibility critical: Gasoline specifications (ASTM D4814) and regulations are complex (see Appendix A).

Gasoline Additives. Additives are gasoline-soluble chemicals mixed with gasoline to enhance certain operation characteristics or to provide characteristics not inherent in the gasoline. Typically, they are derived from petroleum-based raw materials and their function and chemistry are highly specialized. They produce the desired effect at the parts-per-million (ppm) concentration range. (One ppm is 0,0001 mass percent or 1mg/kg.)

Oxidation inhibitors, including aromatic amines and hindered phenols, are also called antioxidants. They prevent gasoline components from reacting with oxygen in the air to form peroxides or gums.

Corrosion inhibitors are carboxylic acids and carboxylates. The tank and pipeline facilities of gasoline distribution and marketing systems are constructed primarily of uncoated steel. Corrosion inhibitors help prevent free water in gasoline from rusting or corroding these facilities. Corrosion inhibitors are less important once gasoline is in a vehicle. The metal parts in the fuel systems of today’s vehicles are made of corrosion-resistant alloys or of steel that is covered with a corrosion-resistant coating. More plastic and elastomeric parts are replacing metal parts in fuel systems. In addition, service station systems and operations are designed to help prevent free water from being delivered to vehicle fuel tanks. Silver corrosion inhibitors are substituted thiadiazole.

Combinations of trace amounts of elemental sulfur, hydrogen sulfide, and mercaptans can cause the silver used in vehicle fuel gauge sender units to corrode and fail. Silver corrosion inhibitors, also referred to as filmers, inhibit the corrosion caused by active sulfur compounds. Metal deactivators are chelating agents, that is, chemical compounds that capture specific metal ions. The more active metals such as copper and zinc effectively catalyze the oxidation of gasoline. These metals are not used in most gasoline distribution and vehicle fuel systems, but when they are present, metal deactivators inhibit their catalytic activity.

Demulsifiers are polyglycol derivatives. Demulsifiers improve the water-separating characteristics of gasoline by preventing the formation of stable emulsions.

Antiknock compounds increase the antiknock quality of gasoline. They include materials based on:

- Lead alkyls, such as tetraethyl lead (TEL) and tetramethyl lead (TML);
- Manganese, called methylcyclopentadienyl manganese tricarbonyl (MMT);
- Iron, called ferrocene.

Because only a small amount of additive is needed, using antiknock compounds is a lower-cost method to increase octane number than changing gasoline chemistry.

The gasoline's grades consist of alphabetic and numerical indexes. The alphabetic index specifies a type of an engine, for which gasoline is intended (А – motor gasoline; Б – aviation). Numerical indicates minimum octane number (MON) of gasoline based on a motor method.

The oil refining industry produces many marks of motor gasoline: A-92, A-95, A-98. In the marks of gasoline АИ-80, АИ-92, АИ-95, АИ-98 and АИ-95 the letter "И" means, that ON is determined with the RON.

Different grades of gasoline are colored to be distinguished. Besides, automobile gasolines are subdivided into summer and winter kinds. The summer gasoline should ensure a start-up of a cold engine up to temperature -15°C and absence of vapor locks up to 50°C. The temperature mode of winter gasoline is in limits -25 – -35°C. A -92 gasoline consists of the following components: a gasoline fraction of direct distillation of mineral oil – 0,6 %, reforming – 82,5 %, catalytic cracking – 3,2 %, alkylation – 7,8 %, hydrocarbons up to C4 – 0,4 %, up to C6 – 3,6 %.

For aviation piston engines, according to the ГОСТ 1012, aviation gasoline of two marks: Б-95/130 and Б-91/115 are produced. 130 and 115 refer to the gasoline rating, and 91 and 95 – to the MON.

3.3. Operation properties

When drivers think about gasoline, their thoughts rarely go beyond filling up or checking prices. Because gasoline almost always performs well, drivers forget what a sophisticated product it is. More thought would reveal a demanding set of operation expectations:

- An engine that starts easily when cold, warms up rapidly, and runs smoothly under all conditions.
- An engine that delivers adequate power without knocking.
- A vehicle that provides good fuel economy and generates low emissions.
- A gasoline that does not add to engine deposits or contaminate or corrode a vehicle's fuel system.

Although proper vehicle design and maintenance are necessary, gasoline plays an important role in meeting these expectations.

Driveability describes how an engine starts, warms up, and runs. It is the assessment of a vehicle's response to the use of its accelerator relative to what a driver expects. Driveability problems include hard starting, backfiring, rough idling, poor throttle response, and stalling (at idle, under load, or when decelerating).

The key gasoline characteristic for good driveability is volatility – a gasoline's tendency to vaporize. Volatility is important because liquids and solids don't burn; only vapors burn. When a liquid appears to be burning, actually it is the invisible vapor above its surface that is burning. This rule holds true in the combustion chamber of an engine; gasoline must be vaporized before it can burn. For winter weather, gasoline blenders formulate gasoline to vaporize easily. Gasoline that vaporizes easily allows a cold engine to start quickly and warm up smoothly. Warm-weather gasoline is blended to vaporize less easily to prevent engine vapor lock and other hot fuel handling problems and to control evaporative emissions that contribute to air pollution. It is important to note that there is no single best volatility for gasoline. Volatility must be adjusted for the altitude and seasonal temperature of the location where the gasoline will be used.

Power. The power an engine can produce depends on its design. In general, the more air an engine can process, the more power it can produce. Major design considerations for power are engine displacement, compression ratio, and the presence of a supercharger or turbocharger. Other factors affecting power are the number of valves per cylinder, valve timing, and spark timing. Different grades of gasoline may have small differences in heating value, but they provide comparable power in a given engine as long as their antiknock operation meets the engine's requirement.

Fuel economy is affected by a vehicle's size, weight, aerodynamics, fuel delivery system, engine design, and transmission type. These factors remain constant for a specific vehicle.

There are, however, many variable factors that influence fuel economy. As mentioned, the heating value of gasoline is one. Weather conditions, air conditioner use, road conditions, the route driven, traffic, driving speed, and driving style are others. Fuel economy is also affected by the mechanical condition of the car, including the engine tune, wheel alignment, and tire pressure. Some of these non-gasoline factors have the potential to cause substantial changes in fuel economy.

Many gasolines available around the world contain oxygenates. In engines without closed-loop feedback systems, oxygenated gasoline leans the air-fuel mixture. Fuel leaning can cause some degradation in driveability, depending on an engine's calibration.

Without fuel additives, deposits form throughout an engine's intake system, including the fuel injectors, carburetor, intake manifold, and intake ports and on the intake valves. Deposits can be very deleterious to engine operation, degrading driveability, decreasing power and fuel economy, and increasing emissions.

3.4. Gasoline engine

Gasoline operation and hence quality of an automobile gasoline is determined by its resistance to detonation during service. The antidetonation quality of the fuel limits the power and economy that an engine using that fuel can produce: the higher the antidetonation quality of the fuel, the more the power and efficiency of the engine.

Today, internal combustion engines in cars, trucks, motorcycles, aircraft, construction machinery and many others, most commonly use **a four-stroke cycle**. The four strokes (Fig. 3.14) refer to intake, compression, combustion (power), and exhaust strokes that occur during two crankshaft rotations per working cycle of the gasoline engine and diesel engine.

The cycle begins at top dead center (TDC), when the piston is farthest away from the axis of the crankshaft. A stroke refers to the full travel of the piston from Top Dead Center to Bottom Dead Center (BDC).

Stroke 1 of 4 "Intake": during the intake or induction stroke of the piston, the piston descends from the TDC to the bottom of the cylinder, reducing the pressure inside the cylinder. A mixture of fuel and air is forced by atmospheric (or greater) pressure into the cylinder through the intake port. The intake valve(s) then close.

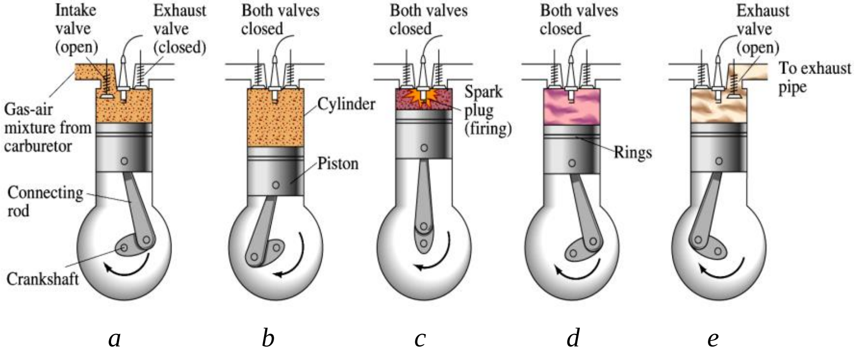


Fig. 3.14. The four strokes of a gasoline engine: *a* – intake; *b* – compression; *c* – ignition; *d* – expansion (power stroke); *e* – exhaust

Stroke 2 of 4 "Compression": With both intake and exhaust valves closed, the piston returns to the TDC compressing the fuel-air mixture. This is known as the compression stroke. The mixture compression is characterized by a compression ratio which is a ratio of the cylinder volume to the volume of compression chamber. For gasolines, compression ratios usually lie within 7–10.

Stroke 3 of 4 "Power": While the piston is at or close to TDC, the compressed air–fuel mixture is ignited, usually by a spark plug (for a gasoline engine) or by the heat and pressure of compression (for a diesel cycle or compression ignition engine). The resulting massive pressure from the combustion of the compressed fuel-air mixture drives the piston back down toward bottom dead center with tremendous force. This is known as the power stroke, which is the main source of the engine's torque and power.

Stroke 4 of 4 "Exhaust": During the exhaust stroke, the piston once again returns to TDC while the exhaust valve is open. This action evacuates the products of combustion from the cylinder by pushing the spent fuel-air mixture through the exhaust valve(s).

For combustion to occur in a cylinder, fuel must be in the vapor state, and burn completely, fuel must have the right mix of air and fuel vapor. The ideal combination, called the stoichiometric mixture, in non-oxygenated gasoline is a ratio of 14.7:1 of air mass to fuel mass. A mixture with less air and more fuel is fuel-rich, and a ratio with more air and less fuel is fuel-lean.

Control of the air-fuel ratio (A/F) is critical to good emissions operation in an engine. Because emission of carbon monoxide (CO) and volatile organic compounds (VOCs) increases under fuel-rich operation and emission of nitrogen oxides (NOx) rises during fuel-lean operation, most modern vehicles are built to maintain stoichiometric A/F.

Under ideal conditions the common internal combustion engine burns the fuel/air mixture in the cylinder in an orderly and controlled fashion. The combustion is started by the spark plug some 10 to 40 crankshaft degrees prior to TDC, depending on many factors including engine speed and load. This ignition advance allows time for the combustion process to develop peak pressure at the ideal time for maximum recovery of work from the expanding gases.

3.5. Detonation and octane numbers

Knocking (also called knock, detonation, spark knock or pinging) in spark-ignition internal combustion engines occurs when combustion of the air/fuel mixture in the cylinder starts off correctly in response to ignition by the spark plug, but one or more pockets of air/fuel mixture explode outside the envelope of the normal combustion front. The fuel-air charge is meant to be ignited by the spark plug only, and at a precise time in the piston's stroke cycle. The peak of the combustion process no longer occurs at the optimum moment for the four-stroke cycle. The speed of flame spreading of detonation is about 1500-2000 m/s comparing to 20-30 m/s for a normal combustion. The pressure of gases increases in leaps and bounds forming the shock waves. The shock wave creates the characteristic metallic "pinging" sound, and cylinder pressure increases dramatically.

Effects of engine knocking range from inconsequential to completely destructive. The detonation of fuels leads to increase in fuel consumption, decrease of power of the engine and its overheating, burnout of pistons and exhausting valves, and fast engine failure.

The inclination of a fuel to detonation is caused by its chemical composition. Normal paraffins have the least desirable knocking characteristics, and these become progressively worse as the molecular weight increases. Iso-paraffins have higher octane numbers than the corresponding normal isomers, and the octane number increases as the degree of branching of the chain is increased. Olefins have markedly higher octane numbers than the related paraffins; naphthenes are usually better than the corresponding normal paraffins but rarely have very high octane numbers; aromatics usually have quite high octane numbers.

The **octane rating (number)** is a measure of the resistance of gasoline and other fuels to autoignition and detonation in spark-ignition internal combustion engines.

Blends of *n*-heptane (ON=0) and *iso*-octane (2,2,4-trimethylpentane) (ON=100) serve as a reference system for gasoline and provide a wide range of quality used as an antiknock scale. The exact blend, which matches the antiknock resistance and compression ratio of the fuel under test, is found, and the percentage of iso-octane in that blend is termed the **octane number of the gasoline**. For example, gasoline with a knocking ability and compression ratio that matches that of a blend of 90 % *iso*-octane and 10 % *n*-heptane has an octane number of 90.

Because some fuels are more knock-resistant than *iso*-octane, the definition has been extended to allow for octane numbers higher than 100. RON of benzene is 101, toluene 111, ethanol 129.

Octane numbers are obtained by two test procedures; those obtained by the first method are called motor octane numbers (indicative of high-speed performance) GOST 511 or ASTM D 2700; and those obtained by the second method are called research octane numbers (indicative of normal road performance) GOST 8226 or ASTM D 2699.

There are two laboratory test methods used to measure the octane number of a gasoline. One method yields the **Research octane number (RON)**; the other results in the **Motor octane number (MON)**. RON correlates best low-speed, mild-knocking conditions; MON correlates best high-speed and high-temperature knocking conditions and with part-throttle operation. For a given gasoline, RON is always greater than MON. The difference between the two indicates the **sensitivity of the gasoline** to changes in operating conditions. The larger the difference, the more sensitive the gasoline is.

3.6. Aviation gasoline

Aviation gasoline (Avgas) is a form of motor gasoline that has been especially prepared for use for aviation piston engines. It has an octane number suited to the engine, a freezing point of mines 60 ^oC, and a distillation range usually within the limits of 30 ^oC to 180 ^oC compared to 1 ^oC to 200 ^oC for automobile gasoline. The narrower boiling range ensures better distribution of the vaporized fuel through the more complicated induction systems of aircraft engines.

Aircraft operates at altitudes at which the prevailing pressure is less than the pressure at the surface of the earth (pressure at 6 km is twice less than the pressure at the surface of the earth). Thus, the vapor pressure of aviation gasoline must be limited to reduce boiling in the tanks, fuel lines, and carburetors. Thus, aviation gasoline does not usually contain the gaseous hydrocarbons (butanes) that give automobile gasoline the higher vapor pressures.

An aircraft piston engine produces power by converting chemical energy stored in the fuel into mechanical energy. Since space is at a premium in most aircraft, the amount of energy contained in a given quantity of fuel is important.

The energy content of avgas can be measured; it is the heat released (also called the heat of combustion) when a known quantity of fuel is burned under specific conditions. The amount of heat released depends on whether the water formed during combustion remains as a vapor or is condensed to a liquid. If the water is condensed to the liquid phase, giving up its heat of vaporization in the process, the energy released is called the gross energy content. The net energy content is lower because the water remains in its gaseous phase (water vapor). Since engines exhaust water as vapor, net energy content is the appropriate value for comparing fuels (see Appendix D).

Because the energy content of individual hydrocarbons can differ, fuels with different compositions may have different energy contents. But the gravimetric energy content of avgas doesn’t vary much – typically, only a few percent. The energy content variation is small because the avgas specifications tightly constrain its chemical composition.

The amount of power generated by a specific engine depends more on its design than on the fuel used. In general, the more air an engine can process, the more power it can produce. Therefore, major design considerations for power include engine cylinder size (displacement), engine compression ratio, and whether the incoming air is pressurized (supercharged or turbocharged).

Knock Resistance

Knock-free engine operation is essential to smooth, reliable engine operation. Octane number and operation number are measures of the ability of avgas to resist knocking as it burns in the combustion chamber (see sidebar).

Two laboratory engine tests are used to measure the antiknock operation of Avgas:

1. One measures operation at a lower fuel-air ratio (lean-mixture condition) that simulates cruising;
2. The other at higher fuel-air ratios (rich-mixture conditions) that simulate take-off, where two tests are required because knock-free operation in the lean fuel-extra power is needed.

Air ratio regime does not guarantee knock-free operation in the rich regime in some engines.

The octane number scale is defined by two pure chemical reference fuels: normal heptane (*n*-heptane) with an octane number of zero, and isooctane (2,2,4-trimethylpentane) with an octane number of 100.The octane number of a blend of these two compounds is equal to the volume percentage of isooctane it contains. Isooctane also defines 100 on the operation number scale. The operation number scale above 100 is defined by mixtures of isooctane and TEL.

The result from either test is called an octane number if it has a value of 100 or less, and operation number if it has a value greater than 100.

The rich-mixture operation number scale is constructed to be approximately linear in maximum engine power output. Numbers above 100 indicate the additional knock-limited power, relative to isooctane, provided by an avgas with that rating. For example, an avgas with a operation number of 130 delivers about 130 percent of the knock-limited power available from isooctane.

Engine and fuel are interdependent components of a single system. Each engine is designed and certified for fuel with a specific minimum antiknock operation. Using a fuel with a lower anti-knock operation will produce less knock-limited power and possibly damage the engine under severe knock conditions. Use of a fuel with a higher antiknock operation is not harmful, but provides no benefit.

3.7. Environmental effects

When fuel is burned with the correct amount of air in a gasoline-powered engine, the gases that are left are predominantly water vapor, carbon dioxide, and nitrogen. All of these gases are benign, although carbon dioxide is a greenhouse gas (GHG). Deviations from ideal combustion lead to the production of some VOCs, CO, NO_X and particulate matter.

Smog is the common term for the forms of air pollution involving haze and oxidants, such as ozone. Vehicle emissions are a significant source of smog precursors. That is why the new legislation controls the type and amount of emissions, regulating the construction of vehicles and the quality (composition) of the fuel. For example, today a new-model passenger car emits less than 1 percent of the volatile organic compounds (VOCs), less than 5 % of the carbon monoxide, and) emitted only about 7 % of the oxides of nitrogen (NO_X) by a vehicle built before emission controls were implemented.

Volatile organic compounds (VOCs). The importance of VOCs stems from their role in forming ozone. Most hydrocarbon (HC) emissions are VOCs, which explains why so much effort is directed toward reducing HC emissions from vehicles and other source categories. VOCs include such toxic substances as benzene, polycyclic aromatic hydrocarbons, and aldehydes (formed during the combustion).

The vast majority of gasoline is burned before combustion gases exit the engine in a properly operating vehicle, but a small fraction, typically 1 to 5 %, escapes the combustion chamber unburned. These VOC emissions consist primarily of unburned hydrocarbons, but partially burned oxygen-containing compounds such as aldehydes are also present in small amounts. Most are removed by a vehicle's catalytic converter. The quantity of exhaust VOC emissions is influenced by many factors, including engine design, controls, and condition;

operating temperature; A/F; fuel system deposits; and catalytic converter operation. If a vehicle has a malfunctioning component that inhibits proper ignition or combustion, such as a bad spark plug, VOC emissions can be many times higher than normal.

Evaporative VOC emissions differ from exhaust VOC emissions in that evaporative emissions contain no combustion products. Because evaporative VOC emissions originate largely from gasoline vapor, their composition is weighted heavily toward the lowest boiling components of gasoline.

Gasoline vapor escapes from a typical vehicle at various points, including the fuel tank, carbuerator (on vehicles that use them), and intake manifold. In addition, liquid gasoline can permeate plastic fuel tanks and elastomeric fuel hoses, and the permeation effects are greater with ethanol-blended gasoline. Liquid gasoline can also leak or seep from fuel system components or connections.

Carbon Monoxide. CO is formed when carbon in fuel is not burned completely. The highest ambient levels generally occur during the colder months, when atmospheric temperature inversions are more common, trapping CO emissions near the surface of the earth under a layer of warmer air. On-road gasoline vehicles are responsible for about 55 percent of man-made CO emissions.

Over the last decade, the auto industry has made remarkable advances in tightly controlling air-fuel ratio, which reduces CO emissions. This, combined with continuing refinements in catalyst technology that cleans up pollutants from engine exhaust, has helped to drastically reduce CO emissions from today's cars.

Nitrogen Oxides. NO_X form when fuel is burned at high temperatures. On-road gasoline vehicles generate about 19 percent of man-made NO_X emissions.

Changes in gasoline properties and composition can help reduce vehicle emissions. Certain gasoline modifications are very effective at enabling vehicle emission control systems to perform at their optimum levels.

Sulfur. Sulfur in fuel becomes sulfur oxides in exhaust that temporarily poison the three-way catalyst. Reducing gasoline's sulfur content increases converter efficiency and decreases VOC, CO, NOx, and toxics emissions. Although gasoline engines are not a major source of SO_2, a criteria pollutant, reducing gasoline sulfur content also reduces the direct emission of this pollutant.

Vapor Pressure. Decreasing the vapor pressure of gasoline reduces evaporative VOC emissions and, to a lesser extent, can reduce exhaust VOC and CO.

Oxygenates. In older cars, adding oxygenates to gasoline has the same effect as increasing the amount of combustion air. Oxygenated gasolines add more oxygen to a combustion chamber, make combustion more complete, and help reduce formation of carbon monoxide. Oxygenates also tend to reduce exhaust VOC emissions somewhat, but they increase aldehyde emissions and tend to increase NOx emissions in many vehicles.

Aromatics. Decreasing the total aromatics content of gasoline may reduce CO and exhaust VOC emissions, but the effects are variable and complex, probably because the aromatic compounds in gasoline are so diverse. Decreasing aromatics content reduces benzene in vehicle exhaust emissions because larger aromatic molecules are partially converted to benzene during combustion or in the catalytic converter.

Benzene. Decreasing the benzene content of gasoline reduces the amount of benzene in both evaporative and exhaust VOC emissions.

Distillation Profile Temperatures. Gasoline containing significant amounts of high-temperature boiling components tends to generate high VOC exhaust emissions. High-temperature boiling components are more difficult to vaporize, especially in a cold engine, making complete combustion more difficult. Thus, placing limits on the distillation profile of gasoline can help lower VOC emissions.

Questions for self-control

1. What does gasoline mean?
2. What is aviation gasoline?
3. Name main stages of gasoline blending.
4. Name operation properties of automobile gasoline.
5. What does four-stroke automobile engine cycle mean?
6. What gasoline additives do you know?
7. How we can improve anti-knocking characteristics of gasoline?
8. What kinds of anti-knock additives do you know?
9. Describe ecological effects of gasoline.
10. Name the composition of exhaust gases, forming in a result of gasoline combustion.

Chapter 4.
CHEMMOTOLOGY OF JET FUELS

Jet engines (JE) became highly popular in modern aviation. JE are related to heat engines with continuously flowing working process.

Fuel comes to combustion chamber without any breaks and combustion process goes constantly. External ignition is necessary only at the moment when engine starts.

External ignition is used for engine start only. Air that necessary for fuel combustion also comes to JE combustion chamber constantly. It comes to chamber compressed and heated by compressor. Gaseous products of combustion come out of chamber and move to turbine, where part of heat energy transforms into mechanical work of turbine wheel rotation. Its axle makes compressor rotor moving as well as fuel and lubrication pumps. After the turbine, products of fuel combustion in a form of gaseous stream come through jet pipe, expand there and create a jet thrust, due to what the aircraft flies.

Production of jet fuels is one of the leading directions in oil processing industry in the world. First of all, it is connected with increasing number of aircrafts all the world.

Today according to the data of World Airfleet, there are about 2 thousand of airlines in the world.

According to the forecast of International Air Transport Association the world aircraft fleet will increase up to 35 thousand before year 2025.

Fuel in JEs moves from aircraft tanks under low pressure (0,02–0,03 MPa) with a help of booster pump through the system of fine filtration filters to the main fuel regulatory pump of high pressure (0,8–1,0 MPa). Moving through nozzles with the help of regulatory pump of high pressure, fuel is dispersed to combustion chambers into heated and highly turbulent air stream that provides increasing of fuel evaporation surface and uniform distribution of its vapors in all the volume of engine combustion chamber. Fuel goes to chamber without disturbances and thus, the process of fuel combustion goes constantly. External ignition is necessary during engine start only.

Air that is necessary for fuel combustion also comes to JE combustion chamber constantly. It comes to chamber compressed and heated by compressor.

Commercial jet fuels are obtained by compounding of fractions of primary, secondary processing of oil and purification of obtained fractions in proportions that provide requirements of exhausted standard.

Main requirements to jet fuels are formed by:

- International Air Transport Association – IATA;
- American Society of Test Materials – ASTM;
- English specification (DERD);
- «Check List».

The most widespread jet fuel has international name Aviation turbine Fuel (AVTUR) – jet fuel for gas-turbine engines.

Fuel with wide fractional composition that includes gasoline fraction except kerosene is designated as AVTAG, where letter G (gasoline) means presence of gasoline.

Fuel of more narrow fractional composition is called AVCAT (table 4.10).

Table 4.10

Designation of jet fuels

IATA recommendation			
Designation	Name	ASTM, DERD, «Check List»	Mlitary specification of the USA
AVTUR	Aviation Turbine Fuel — Kerosine Type	Jet A (AVTUR-40)	—
		Jet A-1 (AVTUR-50)	JP-7, JP-8
AVTAG	Aviation Turbine Fuel — Wide Cut	Jet B	JP-4
AVCAT	Aviation Turbine Fuel — High Flash Point — Kerosine Type	AVCAT-48	JP-5

According to IATA recommendations these fuels are called correspondingly: kerosene type, wide cut, high flash.

Except international designations foreign fuels have grades defined by the national, industrial and company specifications.

All jet fuels are divided into two subgroups: straight-run distillation and thermally stable. Each group can include 2–3 grades of fuel of various fractional composition:

- wide fractional composition;
- easily flashing kerosene (ligroin-kerosene);
- heavy fractional composition (kerosene-gasoil) with increased flash point.

Depending on the oil nature, distillates used for jet fuels production are divided according to their fractional and chemical composition. Jet fuel of grade T-1 is produced from low-sulfur oil with boing temperature 140–280 °C. Jet fuel of grade TC-1 is produced usually from sulfur oils that boil in a range 140–250 °C, as well as T-2 – fuel of wide fractional composition (60–280 °C), that is considered as reserve fuel.

Previously low-sulfur oils of naphtenic origin were used for production of jet fuel of grade T-5, that was used for supersonic aviation with boiling range 195–315 °C. Because of low thermal stability this fuel was not popularized and now it is not produced

Jet propulsion can be traced back to the 1st century B.C. when an Egyptian, Hero, is credited with inventing a toy that used jets of steam to spin a sphere. Sixteen centuries later, Leonardo da Vinci sketched a device that used a flux of hot gas to do mechanical work. By the 17th century, inventors were beginning to develop simple turbine systems to operate machinery. The development of a turbine engine for aircraft began independently in Germany and Britain in the 1930s. In Germany, Hans von Ohain designed the engine that powered the first jet flight in 1939. Germany deployed the jet-powered Messerschmitt 262 late in the World War II. In Britain, Frank Whittle obtained a patent for a turbine engine in 1930. An aircraft powered by an engine he had designed first flew in 1941. The first British jet fighter, the Gloster Meteor, also flew late in the World War II.

Illuminating kerosene, produced for wick lamps, was used to fuel the first turbine engines. Since the engines were thought to be relatively insensitive to fuel properties, kerosene was chosen mainly because of availability; the war effort required every drop of gasoline. After the World War II, the U.S. Air Force started using “wide-cut” fuel, which, essentially, is a hydrocarbon mixture spanning the gasoline and kerosene boiling ranges. Again, the choice was driven by considerations of availability: it was assumed that a wide-cut fuel would be available in larger volumes than either gasoline or kerosene alone, especially in time of war. However, compared to a kerosene-type fuel, wide-cut jet fuel was found to have operational disadvantages due to its higher volatility:

- greater losses due to evaporation at high altitudes;
- greater risk of fire during handling on the ground;
- crashes of planes fuelled with wide-cut fuel were less survivable.

Jet fuel is a type of aviation fuel designed for the use in the aircraft powered by the JEs. Unlike piston engines, JEs use a continuous gas stream, the motion of the aircraft being the result of the force associated with the kinetic energy of the exhaust gases. The chemical characteristics relating to auto-ignition do not have any particular involvement here. The important properties of the jet fuel are linked rather to preparation of the fuel-air mixture, flame radiation, and potential formation of carbon deposits. Moreover, considering the high altitudes encountered, it is evident that the jet fuel must remain fluid at very low temperatures. Finally, under special conditions, particularly for supersonic aircraft, a high thermal stability is required.

For optimum combustion, the fuel should vaporize rapidly and mix intimately with the air. Even though the design of the injection system and combustion chamber play a very important role, properties such as volatility, surface tension, and fuel viscosity also affect the quality of atomization and penetration of the fuel.

Modern fuels for civil aviation should meet a number of requirements related to efficiency, reliability and durability of the aviation mechanics. Special attention is paid now to the environmental safety of jet fuels.

Reliable and long-term operation of an aircraft is guaranteed, when JF has certain fractional composition that provides stable combustion process at all regimes of JE operation and doesn’t cause formation of vapour locks in fuel system during high-altitude flights; when fuel and its combustion products don’t make harm to details of JE and fuel system; and also, in case when fuel provide stable operation of JE in a wide range of external conditions (temperature, pressure, humidity, etc.).

Efficient operation of an aircraft is guaranteed in case, when fuel has low cost, high heat of combustion and high density. It should also have chemical and group composition that provides maximally complete combustion process and low evaporability in case of high-altitude flights and long-term storage.

Considering the environmental safety of jet fuels, it is necessary to mention, that JFs have to cause minimal negative effect on environment during all stages of its exploitation (manufacturing, transportation, storage, aircraft fuelling etc). Special attention is paid to emissions of exhaust gases into atmosphere, its volumes and chemical composition. Moreover, jet fuels have to be safe and not to influence negatively on human organisms.

However, the real jet fuels usually do not possess the whole complex of desired properties. Moreover, improving of certain fuel properties during manufacturing may cause worsening of other properties. That’s why the main tasks during jet fuels production are to reach the desired properties, which provide satisfaction of the most important requirements to jet fuels.

Among the general technical requirements for jet fuels are the following:

- high level of volatility that provides reliable flammability and completeness of fuel 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 the JE,
- absence of negative impact on metal and non-metal parts of the engine fuel system, equipment for storage and transportation of fuel,
- good lubricating properties, which eliminate excessive wearing of friction parts of fuel assemblies,
- 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, the minimum content of sulphur compounds, which lead to the formation of ecologically harmful products in a result of fuel combustion.

4.1. Composition

Aviation turbine fuel is a light petroleum distillate that is available in several forms suitable for use in various types of JEs. It is a complex mixture of hundreds of liquid hydrocarbons. The range of their sizes (molecular weights or carbon numbers) is restricted by the distillation, freezing point, and sometimes naphthalenes and smoke point requirements for the product.

Typical hydrocarbon chain lengths characterizing jet fuels range from C5 to C16. Modern analytical techniques are not powerful enough to separate all the individual molecular species present in jet fuel, so we don’t know how many there are, but a good guess is a thousand or more. Aviation fuels consist primarily of straight and branched alkanes and cycloalkanes. Aromatic hydrocarbons are limited to 20 % to 25 % of the total mixture because they produce smoke when burned. A maximum of 5 % alkenes is specified for some jet fuels. The approximate distribution by chemical classes: straight chain alkanes (32 %), branched alkanes (31 %), cycloalkanes (16 %), and aromatic hydrocarbons (21 %).

Boiling point and **density** increase with carbon number for compounds in the same class. On a volume basis, the order is reversed, with paraffins having the lowest energy content per unit volume and aromatics the highest. The same relationship holds for fuels. Lighter (less dense) fuels, like gasoline, have higher energy content on a weight basis, whereas heavier (more dense) fuels, like diesel, have higher energy content on a volume basis. Viscosity is related more to carbon number than to hydrocarbon class. For a given carbon number, naphthenes generally have slightly higher viscosity than paraffins or aromatics.

For mixtures, the values of some properties are weighted averages of the property’s values for all the individual components. Properties that obey this relationship are called bulk properties. Density is a bulk property; to a first approximation, the density of a mixture is the volume average of the densities of all the components. The values of other properties are determined by individual components present in small, or trace amounts (less than 1000 ppm, and often less than 100 ppm), and are not reflective of the bulk composition of the mixture. Table 4.11 shows which of the important jet fuel properties are bulk properties, and which depend on the presence or absence of trace components.

The trace components may be present in the hydrocarbon base fuel as manufactured or come from another source, such as additives or contaminants.

Table 4.11

Relationship of Jet Fuel Properties to Composition

Property	Relation to Composition
Energy content	Bulk
Combustion characteristics	Bulk
Distillation range	Bulk
Density	Bulk
Fluidity	Bulk
Lubricity	Trace
Stability	Trace
Corrosiveness	Trace
Cleanness	Trace
Electrical conductivity	Trace

Freezing point also increases with carbon number within each class, but it is strongly influenced by molecular shape. The compounds, such as normal paraffins and unsubstituted aromatics, freeze (crystallize) at much higher temperatures than other compounds with the same carbon number, because they have a geometry, that allows them to pack together easily into a crystalline structure. *Normal paraffins* have poor volumetric energy contents and very poor low-temperature flow properties. *Aromatics* have very good volumetric energy contents but poor combustion quality and low-temperature flow properties. *Iso-paraffins* and *naphthenes* are intermediate, with these properties falling between those of normal paraffins and aromatics.

Nitrogen- and/or **sulfur-containing compounds, organic acids,** and reactive **alkenes** present in extremely small amounts have a great influence on thermal stability of jet fuels. Instability involves the formation of peroxides and hydroperoxides, soluble gums, and, most critically, insoluble material that may either coat surfaces or form particulates.

Water can occur in three different forms in jet fuel: dissolved in the fuel, as a separate liquid phase (free water), and as a fuel-water emulsion. Some amount of dissolved water is present in all fuels. This dissolved water is not a problem; free water or water emulsion are potentially hazardous and must be avoided. During any flight the temperature of the fuel in the tanks will decrease due to the low temperatures in the upper atmosphere. This will cause dissolved water in the fuel to precipitate out and since the water is denser than fuel it will drop to the bottom of the tank. As it is no longer in solution this water can freeze, blocking fuel inlet pipes. Since it is impractical to remove all water from fuel, fuel heaters are usually used on commercial aircraft to prevent water freezing in the fuel.

Additives are fuel-soluble chemicals added in small amounts to enhance or maintain properties important to fuel operation or fuel handling. All jet fuel specifications list approved additives along with allowed concentrations. Main additives are:

1. *Fuel system icing inhibitors* work by combining with any free water that forms and lowering the freezing point of the mixture so that no ice crystals are formed.
2. *Antioxidants* work by interrupting chain of oxidizing reactions between oxygen dissolved in fuels and reactive compounds, preventing the formation of peroxides, soluble gums, or insoluble particulates. Peroxides can attack elastomeric fuel system parts, gums can lead to engine deposits, and particulates can plug fuel filters.
3. *Metal deactivators* are chemical compounds that form stable complexes with specific metal ions. More active metals, like copper and zinc, are effective catalysts for oxidation reactions, and degrade fuel thermal stability.
4. *Corrosion inhibitors* prevent free water and oxygen in the jet fuel from rusting or corroding the steel tanks and pipelines of the jet fuel distribution system.
5. *Lubricity additives* are used to compensate for the poor lubricity of severely hydrotreated jet fuel.
6. *Electrical-conductivity additives (static dissipator additives).*
7. *Biocides* are designed to kill microorganisms, which include bacteria and fungi.

4.2. Types of Fuel

The jet fuel produced by a refinery may be all straight-run or hydroprocessed product, or it may be a blend of straight-run, hydroprocessed, and/or hydrocracked product. Small amounts of heavy gasoline components also may be added. Straight-run kerosene from low-sulfur crude oil may meet all the jet fuel specification properties. But straight-run kerosene is normally upgraded by Merox treating (mercaptan oxidation), clay treating, or hydrotreating before it can be sold as jet fuel.

Gasoline-type (wide-cut) jet fuel includes all light hydrocarbon oils for use in aviation turbine power units, which are distilled between 100 ^{o}C and 250 ^{o}C. It is obtained by blending kerosene and gasoline in such a way that the aromatic content does not exceed 25 % in volume. Wide-cut jet fuel has a carbon number distribution between about 5 and 15. Additives can be included to improve fuel stability and combustibility.

Kerosene-type jet fuel is a medium distillate product that is used for aviation turbine power units. It has the same distillation characteristics and flash point as kerosene (between 150 ^{o}C and 300 ^{o}C, but not generally above 250 ^{o}C). Kerosene-type jet fuel has a carbon number distribution between about 8 and 16 carbon numbers. In addition, it has particular specifications (such as freezing point) that are established by the International Air Transport Association (IATA).

Grades and Specifications

In Ukraine and Russia jet fuels of grades PT, TC-1, T-l, T-2 are used in aviation, and grades T-6, T-8B are used in supersonic aircraft. About 20 grades of fuels were created over the time of aviation development.

The **TC-1** fuel is a straight-run distillate (kerosene fraction) of sulfuric oil which boils within the limits of 140–250 °C. It is produced by blending hydrogenated and straight-run distillate feedstocks. The disadvantage of this fuel is rather low stability at high temperatures.

The **PT** fuel can be obtained by straight-run distillation, by blending straight-run distillates and hydrogenated fractions and by hydrorefining straight-run distillates of petroleum with the high content of sulfur, it boils in the range of 135–280 °C. The PT fuel is universal, as it can be applied on aircrafts, flying with a supersonic velocity of flight up to M=1,5 (M – Mach number equal to the relation of an airplane speed to sonic speed (331,8 m/s at 273 K and atmospheric pressure)). Under working conditions both grades of jet fuels, TC-1 and PT, are interchangeable. Requirements to fuels of grades TC-1 and PT are shown in table 4.12.

Outside former communist areas, there are currently two main grades of turbine fuel in use in civil commercial aviation: Jet A-1 and Jet A, both are kerosene type fuels. There is another grade of jet fuel, Jet B which is a wide cut kerosene (a blend of gasoline and kerosene) but it is rarely used except in very cold climates (table 4.13). Military gas turbine fuels include JP-4, JP-5, and JP-8.

Jet A-1 is a kerosene grade of fuel suitable for most turbine engine aircraft. It is produced to a stringent internationally agreed standard, has a flash point above 38°C and a freeze point maximum of -47 °C.

Table 4.12

Requirements to jet fuels of grades TC-1 and PT

Parameter	Units of measu-rement	Norm for grades	
		PT	TC-1
		ГСТУ 320.00149943.007-97	ГСТУ 320.00149943.011-99
1	*2*	*3*	*4*
Density at 20, °C	kg/m^3	>775	>775
Distillation temperature: - initial boiling point - 10 % recovered - 50 % recovered - 90 % recovered - 98 % recovered	°C	reported 175 225 270 280	reported 175 225 270 280
Kinematic viscosity at - 20 °C - -40 °C	mm^2/sec	>1,25 <16	>1,25 <16
Net heat of combustion	kJ/kg	>43100	<43120
Smoke point	mm	>25	>25
Acidity, total	mg KOH/100g	0,2 – 0,7	<0,7
Iodine value	g I_2/100 g	0,5	3,5

1	*2*	*3*	*4*
Flash point	°C	>30	>28
Freezing point	°C	< -55	< -55
Thermal stability in static conditions: - deposit	mg/100 cm^3 fuel	<6	<18
Aromatics, m/m	%	<22	<22
Existent gums	mg/100 cm^3 fuel	<4	<5
Sulfur, total, m/m	%	<0,1	<0,25
Sulfur, mercaptan, m/m	%	<0,001	<0,003
Hydrogen sulfide	Absence		
Copper strip, 3 h at 100 °C	Resist		
Ash content	%	<0,003	<0,003
Thermal stability in dynamic conditions at 150–180 °C: - filter pressure drop during 5 h - tube deposits - critical temperature	kPa points °C	<10 <2 -	- - >115
Interaction with water: - state of fuel-water interface, - state of separated phases	points	<1 -	<1 -
Specific electrical conductivity - at temperature of fuelling - at 20 °C,	pS/m	>50 <600	>50 <600
Mechanical admixtures and water content	Absence		
Water soluble basic compounds content	Absence		
Water soluble acids and bases	Absence		
Soaps of naphthenic acids	Absence		
Naphthalenes content, m/m	%	<1,5	<3
Anti-wear properties in conditions of sliding friction at device УПС-01, criteria of anti-wear properties	-	-	>95
High-temperature corrosion, loss of sample mass during test at 120 °C - at copper - at bronze ВБ23НЦ	g/m^2	3,0 2,5	15 2,5

Jet A is a similar kerosene type of fuel, produced to an ASTM specification and normally only available in the USA It has the same flash point as Jet A-1, but a higher freeze point maximum (-40 °C).

Jet B is a distillate covering the naphtha and kerosene fractions. It can be used as an alternative to Jet A-1 but because it is more difficult to handle (higher flammability), there is only significant demand in very cold climates where its better cold weather performance is important.

Table 4.13

Requirements to jet fuel of grade Jet A-1

Parameter	Units of measurement	Values for standards		
		Def Stan 91-91	ASTM D 1655	ASTM D 7566
1	*2*	*3*	*4*	*5*
Density at *15*, °C	kg/m^3	775–840	775–840	775–840
Distillation temperature:				
- 10% recovered, t	°C	205	205	205
- 50% recovered, t		report	report	report
- 90% recovered, t		report	report	report
- final boiling point		300	300	300
Distillation residue	%	<1,5	<1,5	<1,5
Distillation loss	%	<1,5	<1,5	<1,5
Refining components, at point of manufacture:			-	-
- Nonhydroprocessed components		report		
- Hydroprocessed components	% v/v	report		
- Severely hydroprocessed components		report		
- Synthetic components		report		
Kinematic viscosity at -20 °C	mm^2/sec	<8	<8	<8
Net heat of combustion	MJ/kg	>42,8	>42,8	>42,8
Smoke point, or	mm	>25	>25	>25
Smoke point	mm	>19	>18	>18
and naphtalenes	%	<3 (v/v)	<3 (v/v)	<3 (v/v)
Acidity, total	mg KOH/g	<0,015	<0.1	<0.1
Flash point,	°C	>38	>38	>38
Freezing point,	°C	<– 47	<– 47	<– 47

1	*2*	*3*	*4*	*5*
Thermal stability (2,5 h at control temperature of *260* °C min): Filter pressure drop Tube deposits less than	mm Hg	<25 <3	<25 <3	<25 <3
Aromatics, v/v	%	<25 (v/v)	<25 (v/v)	<25 (v/v)
Existent gums	mg/100 mL	<7	<7	<7
Sulfur, mercaptan, mass	%	<0,003	<0,003	<0,003
Sulfur, total, mass Doctor test	%	<0,3 negative	<0,3 -	<0.3 -
Sulfur, mercaptan, mass	%	<0,003	<0,003	<0,003
Copper strip, 2 h at 100 °C	Class	<No. 1	<No. 1	<No. 1
Microseparometer, rating Without electrical conductivity additive With electrical conductivity additive	mg/l	>85 >70	>85 >70	>85 >70
Specific electrical conductivity at 20 °C,	pS/m	50–600	-	-
Particulate contamination, at point of manufacture		<1,0	-	-
Lubricity: Wear Scar Diameter	mm	0,85	0,85	0,85

4.3. Operation properties

Since the primary function of jet fuel is to power an aircraft, energy content and combustion quality are key fuel operation properties. Other significant operation properties are stability, lubricity, fluidity, volatility, non-corrosiveness, and cleanness. Besides providing a source of energy, fuel is also used as a hydraulic fluid in engine control systems and as a coolant for certain fuel system components.

Energy content. An aircraft turbine engine generates power by converting chemical energy stored in the fuel into a combination of mechanical energy and heat. Since space is at a premium in most aircraft, the amount of energy contained in a given quantity of fuel is important.

The energy content of jet fuel can be measured: it is the heat released (also called the heat of combustion) when a known quantity of fuel is burned under specific conditions. Energy content can be expressed either gravimetrically (energy per unit mass of fuel) or volumetrically (energy per unit volume of fuel). The International Metric (SI) units are megajoules per kilogram (MJ/kg) and megajoules per liter (MJ/L). Generally, less dense jet fuels have higher gravimetric energy content, and more dense jet fuels have higher volumetric energy content.

Combustion Characteristics. In a JE, small carbonaceous particles are formed early in the combustion process. These particles continue to burn as they pass through the flame and are completely consumed under suitable conditions. But these particles become incandescent under the high temperature and pressure conditions of the combustion section. Absorption of this infrared radiation by the combustor walls augments the normal heat received by heat transfer from the combustion gases. High combustor wall temperatures or hot spots can lead to cracks and premature engine failures.

If these carbonaceous particles are not completely consumed by the flame, they can also be harmful if they impinge on turbine blades and stators, causing erosion. Carbon deposits can also plug the holes in the combustor wall that supply dilution air to the combustion section, disrupting the flow pattern of the combustion products.

Fuels with high aromatics content, and especially fuels with high naphthalenes content, form more of these carbonaceous particles. Since these carbonaceous particles are potentially harmful, both the total aromatic content and the total naphthalenes content of jet fuel are controlled.

Carbon particles that are not completely consumed are responsible for the visible smoke that some engines emit. Smoke formation is determined mainly by engine design and operating conditions, although for a given design, fuel composition can influence emissions. Better fuel and air mixing results in more complete combustion and, thus, less carbon formation. Newer engines emit considerably less smoke because of design changes that improved mixing.

Stability. A stable fuel is one which properties remain unchanged. Factors that can lead to deleterious changes in fuel properties include time (storage stability) and exposure to high temperatures in the engine (thermal stability).

Storage Stability. Instability of jet fuel during storage is generally not a problem, because most fuel is used within weeks or months of its manufacture. Storage stability is an issue for the military, which often store fuel for emergency use. And it can be an issue at small airports that don't use a lot of fuel. Jet fuel that has been properly manufactured, stored, and handled should remain stable for at least one year. Jet fuel subjected to longer storage or to improper storage or handling should be tested to be sure it meets all applicable specification requirements before use.

Being among the most reactive substances, fuel components cause instability, thus, storage stability is influenced by fuel composition. It is also influenced by storage conditions; instability reactions occur faster and to a greater extent at higher ambient temperatures. Antioxidants may be added to fuel to improve its storage stability.

Thermal Stability. Thermal stability is one of the most important jet fuel properties because the fuel serves as a heat exchange medium in the engine and airframe. Jet fuel is used to remove heat from engine oil, hydraulic fluid, and air conditioning equipment. The resulting heating of the fuel accelerates the reactions that lead to gum and particulate formation.

These gums and particles may deposit:

- on fuel filters, increasing the pressure drop across the filter and reducing fuel flow;
- in fuel injector nozzles, disrupting the spray pattern, which may lead to hot spots in the combustion chamber;
- in the main engine control, interfering with fuel flow and engine system control;
- on heat exchangers, reducing heat transfer efficiency and fuel flow.

These deposits may lead to operational problems and increased maintenance cost. Antioxidants that are used to improve fuel storage stability are not generally effective in improving thermal stability.

Engine problems related to inadequate fuel thermal stability typically become evident only after hundreds or thousands of hours of operation. The long time and large volume of fuel consumed make it impractical to test fuel thermal stability under conditions identical to those that exist in engines. Instead, the fuel is subjected to more severe conditions in a bench test in order to be able to see a measurable effect in a reasonable period of time.

Lubricity. Lubricity is the ability to reduce friction between solid surfaces in relative motion, so it is a measure of a material's effectiveness as a lubricant. Jet fuel must possess a certain degree of lubricity, because JEs rely on the fuel to lubricate some moving parts in fuel pumps and flow control units.

The lubrication mechanism is a combination of hydrodynamic lubrication and boundary lubrication. In hydrodynamic lubrication, a layer of the liquid lubricant prevents the opposing moving surfaces from contacting each other. Higher viscosity liquids provide more hydrodynamic lubrication than lower viscosity liquids. While jet fuel specifications do not include an explicit lower limit on viscosity, the distillation specification serves as a surrogate limit. JEs are designed to work with jet fuels within the normal viscosity range, and therefore, typical jet fuels provide adequate hydrodynamic lubrication.

When close position of interacting details squeeze out most of the liquid layer that provides hydrodynamic lubrication, boundary lubrication becomes important. Now, small areas of the opposing surfaces are in contact. Boundary lubricants are compounds that form a protective anti-wear layer by adhering to the metal surfaces.

Straight-run jet fuels are good boundary lubricants. This is not due to the hydrocarbons that constitute the bulk of the fuel, but is attributed to trace amounts of certain oxygen-, nitrogen-, and sulfur-containing compounds. Evidence for the role of trace quantities is the fact that adding as little as 10 ppm of a lubricity enhancing additive to a poor lubricity fuel can make it acceptable.

The naturally occurring compounds that provide jet fuel with its natural lubricity can be removed by hydrotreating – the refining process used to reduce sulfur and aromatic content. However, low sulfur or aromatics levels in jet fuel are not, per se, signs of inadequate lubricity. The boundary lubricity of jet fuel cannot be predicted from bulk physical or chemical properties. It can only be measured in a specially designed test apparatus. Fuels with similar sulfur and aromatics content can have different lubricity.

Fluidity. Fluidity is a general term that deals with the ability of a substance to flow, but it is not a defined physical property. Viscosity and freezing point are the physical properties used to quantitatively characterize the fluidity of jet fuel.

Jet fuel is exposed to very low temperatures both at altitude – especially on polar routes in winter-time – and on the ground at locations subjected to cold weather extremes. The fuel must retain its fluidity at these low temperatures or fuel flow to the engines will be reduced or even stop.

Viscosity is a measure of a liquid's resistance to the flow under pressure, generated either by gravity or mechanical source. “Thin” liquids, like water or gasoline, have low viscosities; “thick” liquids, like sugar syrup or motor oil, have higher viscosities. The viscosity of a liquid increases as its temperature decreases.

Jet fuel at high pressure is injected into the combustion section of the turbine engine through nozzles. This system is designed to produce a fine spray of fuel droplets that evaporate quickly as they mix with air. The spray pattern and droplet size are influenced by fuel viscosity. If it is too high, an engine can be difficult to relight in flight. For this reason, jet fuel specifications place an upper limit on viscosity.

Fuel viscosity also influences the pressure drop in the fuel system lines. Higher viscosities result in higher line pressure drops, requiring the fuel pump to work harder to maintain a constant fuel flow rate. Fuel viscosity also influences the operation of the fuel system control unit.

Freezing Point. Because it is a mixture of many hundreds of individual hydrocarbons, each with its own freezing point, jet fuel does not become solid at one temperature the way water does. As the fuel is cooled, the hydrocarbon components with the highest freezing points solidify first, forming wax crystals. Further cooling causes hydrocarbons with lower freezing points to solidify. Thus, the fuel changes from a homogenous liquid, to a liquid containing a few hydrocarbon (wax) crystals, to a slush of fuel and hydrocarbon crystals, and, finally, to a near-solid block of hydrocarbons. The freezing point of jet fuel is defined as the temperature at which the last wax crystal melts, when warming a fuel that has previously been cooled until wax crystals form. Thus the freezing point of fuel is well above the temperature at which it completely solidifies.

The primary criterion for fuel system operation is pumpability – the ability to move fuel from the fuel tank to the engine. Pumpability is influenced both by fuel fluidity and fuel system design.

Volatility. Volatility is a fuel's tendency to vaporize. Two physical properties are used to characterize fuel volatility: vapor pressure and distillation profile. A more volatile fuel has a higher vapor pressure and lower initial distillation temperatures.

Volatility is important because the fuel must vaporize before it can burn. However, too high volatility can result in evaporative losses or fuel system vapor lock.

Volatility is one of the major differences between kerosene-type and wide-cut jet fuel. Kerosene-type jet fuel is relatively non-volatile. Wide-cut jet fuel is better suited for cold weather applications because it has a lower viscosity and freezing point than kerosene-type jet fuel. In such applications, evaporative losses are less of a concern.

Non-corrosiveness. Jet fuel contacts a variety of materials during distribution and use. It is essential that the fuel not corrode any of these materials, especially those in aircraft fuel systems. Typically, fuel tanks are aluminum, but fuel systems also contain steel and other metals. Fuel tanks may also have sealants or coatings, and elastomers are used in other sections of the fuel system. Engine and airframe manufacturers conduct extensive fuel compatibility testing before approving a material for fuel system use.

Corrosive compounds potentially present in jet fuel include organic acids and mercaptans. The specifications limit these classes of compounds. By-products of microbial growth also can be corrosive.

Contamination from trace amounts of sodium, potassium, and other alkali metals in the fuel can cause corrosion in the turbine section of the engine.

Cleanness. Fuel cleanliness means the absence of solid particulates and free water. Particulates – rust, dirt, etc. – can plug fuel filters and increase fuel pump wear. Water, in addition to not burning in an engine, will freeze at the low temperatures encountered in high altitude flights. The resulting ice may plug fuel filters and otherwise impede fuel flow. Water in the fuel also may facilitate the corrosion of some metals and the growth of microorganisms.

Safety properties. Jet fuel can be hazardous if not handled properly. First, and foremost, it ignites easily and it burns rapidly. Second, exposure to jet fuel liquid or vapor should be limited. Anyone planning to handle jet fuel should obtain and read the Material Safety Data Sheet (MSDS) issued by the supplier.

Liquid doesn't burn; only vapor burns. And vapor doesn't always burn – the mixture of vapor and air must be within the flammable range. Mixtures with insufficient vapor (below the lower flammability limit) or too much vapor (above the upper flammability limit) will not burn. For kerosene-type jet fuel, the lower and upper flammability limits are 0,6 volume percent vapor in air and 4,7 volume percent vapor in air, respectively. For wide-cut jet fuel, the lower and upper flammability limits are 1,3 volume percent vapor in air and 8,0 volume percent vapor in air, respectively.

In most circumstances, the hydrocarbon vapor-air mixture in an enclosed space over kerosene-type jet fuel will not be in the flammable range; the mixture will be below the lower flammability limit. However, high ambient temperature can heat the fuel enough to bring the vapor space into the flammable range. The flash point of a fuel is the lower flammability temperature of the fuel under the specific test conditions. However, this is not necessarily the lower flammability temperature under other conditions, such as in an aircraft fuel tank.

For the more volatile wide-cut fuel, the hydrocarbon vapor-air mixture in an enclosed space may be in the flammable range. The upper flammability temperature limit depends on the vapor pressure of the fuel. A fuel with a vapor pressure of 18 kPa will have an upper flammability temperature limit of approximately 18 °C.

However, in the absence of specific information to the contrary, any jet fuel handling situation should be considered potentially hazardous and the appropriate safety measures observed.

Flash Point. The flash point is the lowest temperature at which the vapors above a flammable liquid will ignite on the application of an ignition source. At the flash point temperature, just enough liquid has vaporized to bring the vapor-air space over the liquid above the lower flammability limit. The flash point is a function of the specific test conditions under which it is measured. The flash point of wide-cut jet fuel is below 0 °C and is not typically measured or controlled. The minimum flash point of Jet A and Jet A-1 kerosene-type fuel is 38 °C.

Electrical Conductivity. Static electrical charge can be generated when dissimilar surfaces move across each other, for example, when fuel moves through a pipe, hose, valve, or fine filter. The rate at which the static charge dissipates is proportional to the liquid's ability to conduct electricity (electrical conductivity). Pure hydrocarbons are essentially non-conductors. While jet fuel is composed of hydrocarbons, it is a slightly better conductor because it contains trace amounts of ionizable compounds, e.g., water, phenols, and naphthenic acids.

Filtering or rapidly pumping a liquid that is a relatively poor electrical conductor, like jet fuel, can result in a static charge being created much faster than it dissipates. When the accumulated charge exceeds the ionization potential of the air above the liquid, it can discharge from the liquid surface as a spark. The energy of the spark can initiate an explosion if the liquid is flammable and the composition of vapor and air in the vicinity is in the flammable range.

To prevent explosions triggered by a static discharge, well designed fuel handling systems use bonding and grounding (or earthing), and account pumping rate limits, and time for charge dissipation (relaxation time), before the fuel is exposed to air. Military jet fuels and international Jet A-1 require the use of an additive to increase the electrical conductivity of the fuel. Conductivity improving additives are also called anti-static additives or static dissipator additives. Use of an additive reduces the hazard of the charge accumulation for handling situations that are less than optimum. The additive does not prevent charge generation; rather it increases the rate of charge dissipation by increasing fuel conductivity (see Appendix E).

Microbial growth. Jet fuel is sterile when it is first produced because of the high refinery processing temperatures. But it quickly becomes contaminated with microorganisms that are always present in air and water. Microorganisms found in fuels include bacteria and fungi (yeasts and molds). The solids formed by microbial growth are very effective at plugging fuel filters. Some microorganisms also generate acidic by-products that can accelerate metal corrosion.

Since most microorganisms need free water to grow, microbial growth is usually concentrated at the fuel-water interface, when one exists. Some organisms need air to grow (aerobic organisms), while others grow only in the absence of air (anaerobic organisms). In addition to food (fuel) and water, microorganisms also need certain elemental nutrients. Jet fuel can supply most of these; phosphorus is the only one which concentration might be low enough to limit microbial growth. Higher ambient temperatures also favour microbial growth.

The best approach to handling the problem of microbial contamination is prevention. And the most important preventive step is keeping the amount of free water in fuel storage tanks and aircraft fuel tanks as low as possible.

When microorganisms reach problem levels in aircraft fuel tanks, approved biocides may be used under controlled conditions. But biocides have their limits. A biocide may not work if a heavy biofilm has accumulated on the surface of the tank or other equipment, because then it doesn't reach the organisms living deep within the biofilm. In such cases, the tank must be drained and mechanically cleaned.

And even if the biocide effectively stops microbial growth, it still may be necessary to remove the accumulated biomass to avoid filter plugging. Since biocides are toxic, any water bottoms that contain biocides must be disposed of appropriately.

4.4. Microbiological damage of aviation jet fuels

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.

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.

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 requires a risk-based approach in aviation fuel supply.

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:

- 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:

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.

Aviation fuels, fuel storage systems, fuel handling equipment and aircraft fuel tanks can become contaminated by microbiological organisms (microbes). Microbes cause degradation of fuel quality and severe damage to equipment; they also lead to blockages in fuel filters and fuel lines. In cases of confirmed microbial contamination, considerable period of time is often required for remedial treatment, this can lead to interruptions in supply and violation of both fuelling and aircraft operations. Microbial contamination in fuel and fuel systems is very real, serious and costly issue, which has potential to impact directly on the safety of aviation operations (Fig. 4.15, table 4.14).

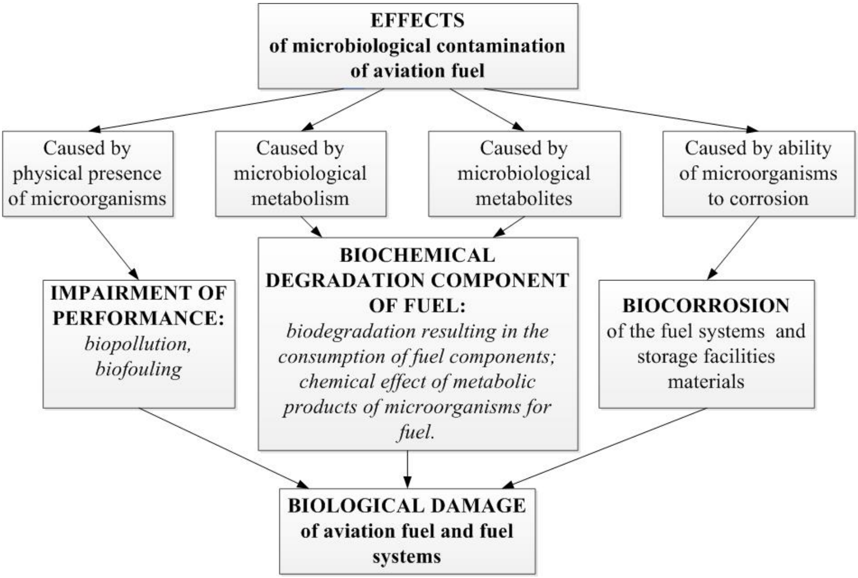


Fig. 4.15 The risks and consequences of microbial contamination of aviation fuels

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 factors. 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.

Water is essential for the growth of microbes. Therefore, it is critical that fuel systems are kept as dry as possible by frequent draining of any accumulated water. The fundamental method for assessing the presence of microbiological growth in the storage tanks and filters is the daily clear and bright test on the sump sample. The presence of discoloured water, a lacy interface between the fuel and water layers or organic debris in the fuel or water layer are all the indications of likely microbiological activity, requiring immediate investigation and appropriate expert advice.

Table 4.14

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

The following industry regulation documents provide detailed information on testing, control and remedial strategies:

- IATA Guidance Material on Microbiological Contamination in Aircraft Fuel Tanks;
- ASTM D6469;

- EI Guidelines for the investigation of the microbial content of petroleum fuels and for the implementation of avoidance and remedial strategies;
- SAE AS 6401;
- JIG 1, 2 and 3;
- API RP 1595.

4.4.1 Microbiological growth

Statistics indicate that 30 % all technological equipment corrosion damage is caused by processes involving microorganisms. As a result of biological corrosion pipelines, underground equipment, steel storage reservoirs for petroleum products, and aircraft fuel tanks are damaged, early clogging of ground and aircraft fuel filters, as well as blocage of fuel quantity indication sensors occur.

Today it is known 200 species of microorganisms, including 30 families that can use hydrocarbons as sole source of carbon and energy (table 4.15). These include bacteria, yeast and fungi.

Table 4.15

The main microorganisms, that cause biocontamination of fuels

Type of microorganism	Species
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 aeruginosa, Serratia marcescens
Yeasts	Candida sp, Candida famata, Candida guilliermondii, Candida lipolytica, Rhodotorula sp.

The main microorganisms that cause fuel biodamage are bacteria of Pseudomonas, Micrococcus, Mycobacterium genera and fungi of Cladosporium, Aspergillus, Penicillum, Alternaria genera etc. The most frequently detected bacteria in oil are *Pseudomonas aerugenosa* and fungi *Cladosporium resinae* ("kerosene fungus").

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.

The 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. Today this group classified as fungi *Monascus floridanus,* which is inherent in the ability to develop rapidly in the aviation fuel. Fungi have some morphological, physiological and genetic features, good with which they occupy the dominant position among organisms causing biological damage.

Most bacteria and fungi are chemo-organotrophic heterotrophs. Fungi reproduce with spores, which may be dormant for a long time, and therefore they are undetected in fuel. Under suitable conditions favourable for their development, spores germinate, fungi multiply, and fuel is significantly contaminated. Microbiological contaminations by *Cladosporium resinae* consist of fibers in the form of strands, which reach considerable length and form the interwoven layer. Since the size of spores is very small (2–3 µm) and aviation fuel supply companies provide maximum filtering capacity of 3–5 µm, it is clear that filtering systems can't remove spores from the fuel. Therefore, fuel is often contaminated with microscopic fungi during transportation, storage, preparation for delivery, as well as in the aircraft tanks.

In the completely dry fuel the development and growth of microorganisms are depressed. However, it is impossible to get rid of the moisture completely under the real condition of fuels usage and storage. Significant factors contributing to the active microorganisms' development are medium of pH, the presence of some elements (carbon, phosphorus, potassium, nitrogen, sulfur, and iron), ambient temperature. Spores actively grow under 25–35 °C, although they can grow at temperatures ranging from plus 5 to 45 °C. It is proved that the spores remain alive for several hours at the temperature of -40 °C.

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. 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. 4.16). The greatest value of biomass is defined for the *Hormoconis resinae* isolated from the tank of the aircraft.

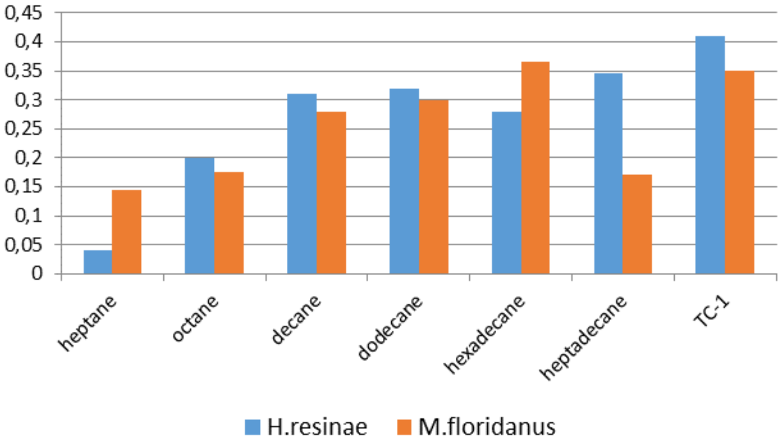


Fig. 4.16. Biomass of active destructors after a month growth in hydrocarbons

The ability to grow potential destructors for various hydrocarbons was studied. Micromycetes grow on all tested liquid hydrocarbons, except for hexane. 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 ($C_{16}H_{34}$).

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. 4.17). 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.

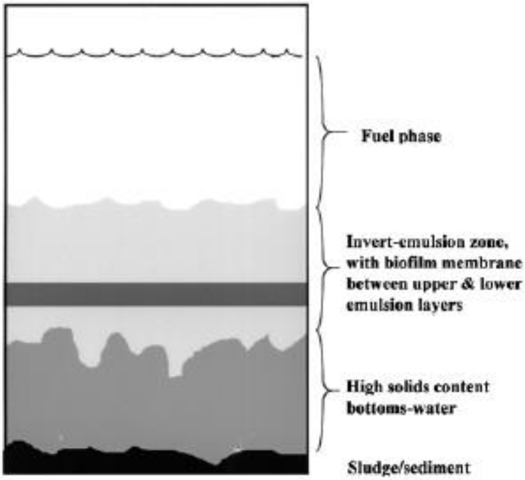


Fig. 4.17. Schematic of fuel tank bottom sample with significant microbial contamination and biodeterioration

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.

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. 4.18.

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 to 35 °C, with growth optimal between 25 °C and 35 °C.

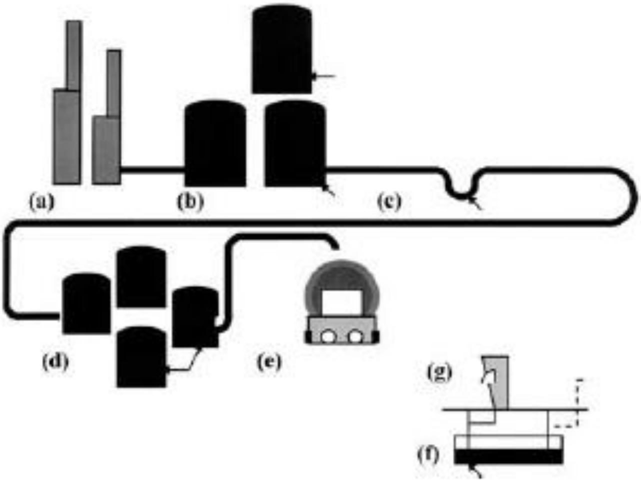


Fig. 4.18. Fuel supply scheme (arrows indicate sites where water and biologicals tend to accumulate): *a)* – refinery distillation towers, *(b)* – refinery product tanks, *(c)* – fuel transportation pipeline (low points in pipeline trap water), *(d)* – distribution terminal tanks, *(e)* – commercial dispensing rack and tank truck, *(f)* – retail/fleet underground storage tank, *(g)* – retail/fleet dispensing system.

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 4.16).

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.

Table 4.16

The growth of fungi in fuel at positive temperatures (in points)

Fungi	The time of 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,
3 – mucus formation,
4 - the formation of small clots,
5 - the formation of large clots.

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.

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:

– *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 consequence is appearance of accidents and emergency landings.

The changing the acidity of fuel is an important consequence of the proliferation of microorganisms (Fig. 4.19). 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.

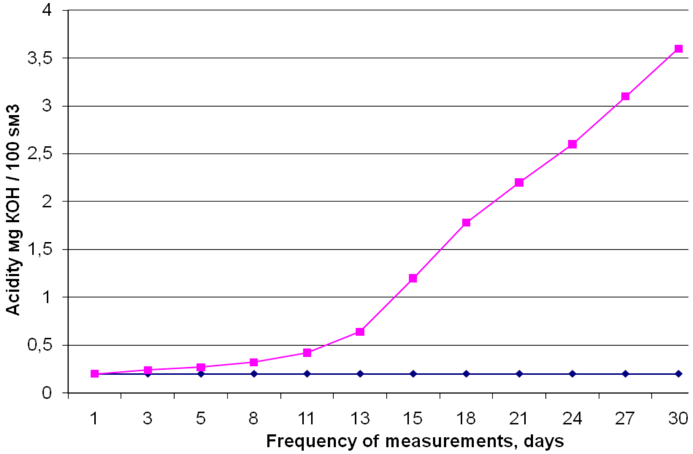


Fig. 4.19. Change jet fuel acidity under the influence of microbiological contamination

🟥 - 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. It is necessary to replace petroleum hydrocarbons alternative raw materials. 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 are 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.

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.

The list of samples and results of their tests is presented in table 4.17. The results of research have shown that fuel for JEs 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 JEs 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. 4.20). 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.

Table 4.17

List of samples for research and test results

Sample	The test result
Clean jet fuel TC-1	
Clean jet fuel Jet A-1	
Jet fuel TC-1 with microbiological pollution	
Jet fuel Jet A-1 with microbiological pollution	

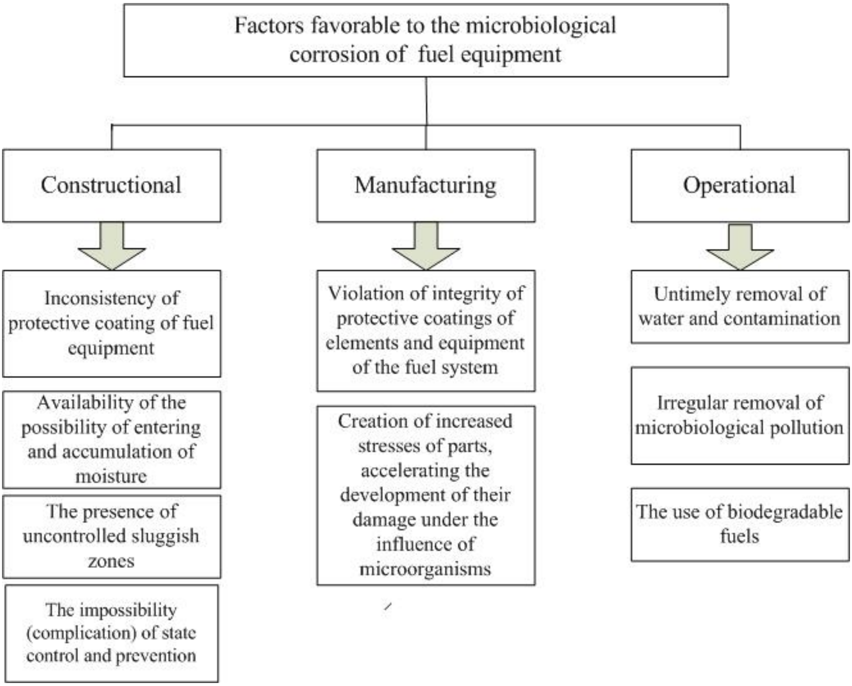


Fig. 4.20. The causes of microbiological corrosion.

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.

One of the most serious consequences of fuel tanks microbiological contamination is corrosion of enforstment wing set. The funguses attach to the horizontal surfaces of fuel tanks, and multiply, forming the threaded layer. As a result, there are areas with different aeration, where corrosion is intensified. While growing fungus produce organic acids (mostly citric acid), as a result the acidity of the water at the tank bottom decreases (pH 2,5–4,5). This reduces the surface tension, increases diffusion rate at the interface between fuel and water and fungi growth is facilitated. Interweaved mycelium layer can move in the liquid volume during aircraft fuelling, leading to the clogging of filters, sensors, etc.

Statistics of materials biological damage show that fuels and lubricants are very actively attacked by microbiological factor (Fig. 4.21).

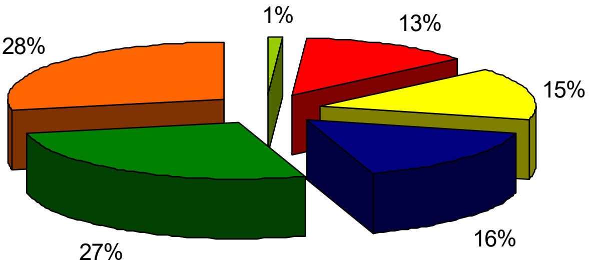


Fig. 4.21. Statistics of materials biological damage: 27 % – fuels and lubricants; 16 % – lacquer and paint coating; 28 % – polymers; 13 % – metals and alloys; 1 % – glass; 15 % – other materials

Moreover, contamination by *Cladosporium resinae* affecting on polyurethanes can make them permeable after 4-6 weeks; there is a risk of cavities formation in the metal substrate and intercrystalline separation of structural metal development (table 4.18).

There are the following features of fuel biodamage:

1. Accumulation of sludge (water with a variety of contaminants, including bacterial mucus) at the bottom of fuel tanks and reservoirs;
2. Deterioration of fuel conditioning, including stable water-oil emulsions, acidification, color and smell changes, contamination with mycelium and mucus particles;
3. Mycelium and bacteria colonies segregation on the inner walls of the fuel systems, tanks, pipelines and filters clogging with sediments;
4. Metal corrosion of the bottoms, where water sludge is accumulated, especially at the interface between fuel and water;
5. Destruction or delaminating of protective coatings under the clusters of microorganisms colonies, destruction of seals and hermetics by metabolites.

Table 4.18

Organisms living conditions

Energy source	Electron donor	Carbon source	Mode of existence	Example
Red-ox reactions	Inorganic substances	CO_2	Chemo-lytho-autotrophs	Nitrophilic bacteria, thionic bacteria, hydrogen bacteria, acidophilic bacteria
		Organic substances	Chemo-lytho-heterotrophs	Methane forming archibacteria, hydrogen bacteria
	Organic substances	CO_2	Chemo-organo-autotrophs	Facultative methylotrophs oxidizing formic acid (HCOOH)
		Organic substances	Chemo-organo-heterotrophs	Mostly prokaryotes, most bacteria, animals, fungi
Light	Inorganic substances	CO_2	Photo-lytho-autotrophs	Cyanobacteria, purple and green bacteria, algae, blue-green, higher plants
		Organic substances	Photo-lytho-heterotrophs	Cyanobacteria, purple and green bacteria
	Organic substances	CO_2	Photo-organo-autotrophs	Purple bacteria
		Organic substances	Photo-organo-heterotrophs	Purple and green bacteria, halobacteria, cianobacteria

4.4.2. Protection of aviation fuels from biological damage

There are many ways to prevent biological contamination of fuels. Actions for prevention of fuels microbial contamination may be classified as active and passive. Aviation fuel supply companies’ operational activity aimed at reducing preconditions for the intensive development of microbiological fuel contamination is referred to as passive; and adding biocides (antimicrobial additives) to the fuel is referred to as active.

One of prevention 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. 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).

Operational protective activities include: compliance with the requirements to the safe storage of fuels, preventing contact with water and atmospheric moisture, timely drying and water (sludge) removal from reservoirs, filters, bottom of reservoirs, fuel ground and aircraft tanks; timely cleaning of fuels storage technological equipment, filtration. Usage of filters with the openings equal 1–2 microns gives good results in cleaning and decontamination of the fuel, although their usage in pipeline injection sections is problematic because of considerable price.

Chemical methods of protection should not affect the power characteristics of fuel. Therefore, some biocides that are used, for example, to protect polymer and other materials against biodamage do not fit to protect the fuel.

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.

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.

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.

Biocide additives may be soluble in fuels, and water cushion and destroy microorganisms in both phases.

Many biocide products have been tested abroad that meet the above requirements, there are the following: ethyleneglycol monometyl ether and Biofora F.

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 JEs 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.

The additive BioborJF is the most common aviation biocide in the world. It is microbiocide and designed to eliminate fungi, algae and other microorganisms, damaging fuel systems. It was initially developed in the United States in 1963; nowadays BioborJF is produced by Hammonds Industries, Inc in Houston, Texas.

Biobor's active ingredients are: 2,2'-oxybis (4,4 6-trimethyl-1,3,2-dioxaborinane) and 2,2'-(methyltrimethylenedioxy) bis-(4-methyl 1-1,3,2-dioxaborinane). Biobor JF is designed primarily for diesel and jet fuel, but can be used in any hydrocarbon based fuel. JF can also be used as a wood preservative.

BioborJF concentration in any fuel that is required to achieve sterilization effect is 270 ppm, and then the concentration should be reduced to 135 ppm for prevention of reinfection. The additive introduction into the fuel is carried out through the dosing-metering gauge; if it is absent, the manual mixing is allowed. It is possible to introduce the additive during the aircraft fuelling directly into the tanks of small capacity. Time additions should coincide with the filling of the tank in half for ensuring additive uniform mixing.

Two aspects prevent widespread usage of the last additive in our country. Firstly, the biocide BioborJF addition directly into the fuel at aircraft filling is not regulated by national standard and guidance documents, although it could be used as sterilization material for washing the fuel tanks or fuel storage reserviors during periodic maintenance operations. The second aspect is the high cost of BioborJF.

BioforJF 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 content in these tanks is reduced.

There is well-known anti-water 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 JEs, 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.

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 %.

Due to increasing the range of biocide additives, there were studied bactericidal activity of such compounds dimethyl-dialkyl-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 JE.

During the study of these compounds has been established 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.

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-dialkyl-ammonium chloride. Simultaneously, this additive is an effective anti-static additive in concentration of 0,003 %, increases conductivity and reduces oil electrification during their motion.

It is set that the antiwater-crystallization additive PFA-55MB has high bactericidal effect for JEs. 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 JEs. This additive is the most widespread abroad.

It was found that 8-hydroxyquinoline and disalicildenpropandiamin in addition to fuel for JEs 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-diaminopropane or hexamethyldiamine, 0,12 % ethylendiamine, 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.

There is also known multifunctional additive IPOD (isopropyloctadecylamine).

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 %.

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.

The additive Kathon ® FP 1,5 is also used for biocide fuel treatment, which has received numerous approvals from leading manufacturers of aircraft engines and sailplanes; IATA has recommend it for the application in the aircraft fuel systems in accordance with the MIL-S-53 021.

Kathon FP 1.5 is registered with the EPA as a fuel biocide, and is used very successfully worldwide. Unlike BioborJF, it is served through the regular dosing devices, its feeding directly into the fuel tank is not allowed. It destroys the contamination quickly and efficiently, the time of action is from 12 to 24 hours. It is also economically efficient for fuel sterilization: additive expenditure is 1 gallon per 10 000 gallon of fuel.

4.4.3. Methods for fuels microbial contamination detection

Regular sludge removal is used as the main precautions for all aircraft fuel tanks. If you suspect that a control sample has bioconyamination (turbidity, color changing, presence of hydrogen sulfide odor, presence of mucus) it should be tested. Practice has shown that in areas with the highest risk of fuel infection the frequency of testing for microbiological contamination presence should be not less than once a month.

In industry there are patented methods and instruments for determining this contamination, such as MicrobMonitor 2, Hum Bug Detector, Bug Alert, Bug Check sets, the electronic meter HMB IV, etc. For example, when MicrobMonitor 2 is used, test results are available after three days and do not require further decoding.

4.5. Aviation fuel specifications

Product specifications represent the mechanism by which producers and users of a product identify and control the properties necessary for satisfactory and reliable operation.

Two organizations have taken the lead role in setting and maintaining specifications for civil aviation jet fuel: American Society for Testing and Materials (ASTM) and the United Kingdom Ministry of Defence (MOD). The specifications issued by these two organizations are very similar but not identical. Many other countries issue their own national specifications for jet fuel; these are very nearly or completely identical to either the ASTM or MOD specifications.

In the Commonwealth of Independent States (CIS) and parts of the Eastern Europe, jet fuel is covered by GOST specifications.

American Society for Testing and Materials ASTM is made up of many committees. Subcommittee J of the Committee D-2, Petroleum Products and Lubricants, is responsible for aviation fuel specifications. ASTM is a consensus standards organization. This ensures that the viewpoints of the large number of groups that are affected by and/or interested in the specifications are considered. These groups include:

- Individual refiners;
- Petroleum refining organizations;
- Petroleum marketing organizations;
- Additive and equipment suppliers;
- Aircraft and airframe manufacturers;
- Aircraft engine manufacturers;
- Governmental regulatory agencies, like the Federal Aviation Administration (FAA);
- Special-interest groups and consultants.

4.6. Aviation turbine engines

By the end of the World War II, the aircraft piston engine was a fully developed power plant that was undergoing only incremental improvement. The introduction of the gas turbine engine paved the way for quantum leaps in aircraft operation. It enabled man to break the sound barrier and to routinely fly nonstop halfway around the world in a matter of hours. This chapter gives a brief overview of today's aircraft turbine engines.

The principle of turbines operation is conceptually simple: they convert the kinetic energy of moving fluid into mechanical energy by using the motion of the fluid to turn a rotor. The rotor, in turn, is connected to a device that does useful work. The moving fluid could be water, steam, air, or hot gases. Turbines driven by steam are widely used for electrical power generation.

An aircraft gas turbine engine generates hot, pressurized gas by burning fuel in a confined space. The gas, in the process of escaping from the engine, drives a turbine that, in turn, drives the compressor that compresses the air entering the engine. The hot compressed gas leaves the engine at high velocity, generating the thrust that pushes the aircraft forward. The aircraft turbine engine is sometimes called a reaction engine because it exemplifies Newton's Third Law, which states: for every action there is an equal but opposite reaction. In this case, the action is the expulsion of the hot exhaust gas from the rear of the engine. The reaction is the thrust imparted to the engine – thrust that the engine transmits to the rest of the airframe.

Gas turbine engines consist of three sections, each with a different function: compression section, combustion section, and turbine section. The compression section draws in and compresses ambient air and delivers the compressed air to the combustion section.

There are two basic types of compressors: axial and centrifugal. In an axial compressor, air moves essentially parallel to the long axis of the engine as it passes through the compressor. In a centrifugal compressor, air is slung radially outward into a chamber, the diffuser that redirects it to the combustion chamber.

Modern commercial engines often have two or three sets of compressors that work in series to achieve the desired degree of compression. At the end of the compression section, the air has a pressure of 30 to 35 atmospheres and a temperature of 550 °C (1020 °F) to 625 °C (1160 °F).

In the combustion section, fuel is continuously injected into the compressed air through a set of nozzles. The fuel evaporates as it mixes with the hot air, and then burns. The hot combustion gases are then forced into the turbine section by the high pressure at the outlet of the compressor. A more in-depth discussion of combustion is included below.

The turbine section contains a series of pairs of stator vanes and rotor blades. The vanes and blades are basically just extremely sophisticated airfoils. Stator vanes are stationary and accelerate the gas flow to push on the rotor blades. The rotors are connected to the compressor by a shaft. The push of the moving combustion gases against the rotor blades turns the turbine and, hence, the compressor.

Finally, the hot mixture of combustion gases and air is accelerated through a nozzle at the rear of the engine. It is this exhaust stream that produces the thrust that drives the aircraft.

The combination of a turbine, the compressor it drives, and the connecting shaft is called a spool. An engine with two compressors will also have two independent turbines. The high-pressure compressor driven by the high-pressure turbine is the inner spool. The low-pressure compressor driven by the low-pressure turbine is the outer spool. The shafts of the two spools are concentric and rotate independently of each other at different speeds.

Engine Control Systems. Besides providing the source of energy needed to power flight, fuel is also used to control various engine parameters. The main engine control meters fuel to the engine based on throttle demand coming from the cockpit, and also controls various engine operating parameters.

Fuel is used as a hydraulic fluid to transmit pressure signals in the control and to position engine devices, such as compressor stator vane position or compressor air bleed valve position, to achieve desired operating conditions.

Fuel is also used as a coolant or a heat sink in the engine.

Engine Types. The earliest turbine engines had a single spool and were called turbojet engines. Turbojet engines perform well at high altitudes and high airspeeds, but are less efficient at low altitudes and low airspeeds.

Virtually all modern aircraft turbine engines are turbofan engines (Fig. 4.22).

A turbofan engine uses a turbojet as a core, but has a large fan mounted in front of the compressor section. This fan is visible in the front of a commercial airline JE. The fan, which, like the compressors, is driven by a turbine, acts like a propeller; it pushes air to create thrust. It differs from a conventional propeller in that it has lots of wide blades spaced closely together and is surrounded by a tight cowling. The fan may be 8–12 feet in diameter, more than twice the diameter of the core turbojet engine. Some of the air driven by the fan goes into the core while the rest goes around the outside of the core. This bypass air provides most of the thrust in high-bypass turbofan engines, perhaps 85 %, while the hot exhaust gases provide only about 15 %.

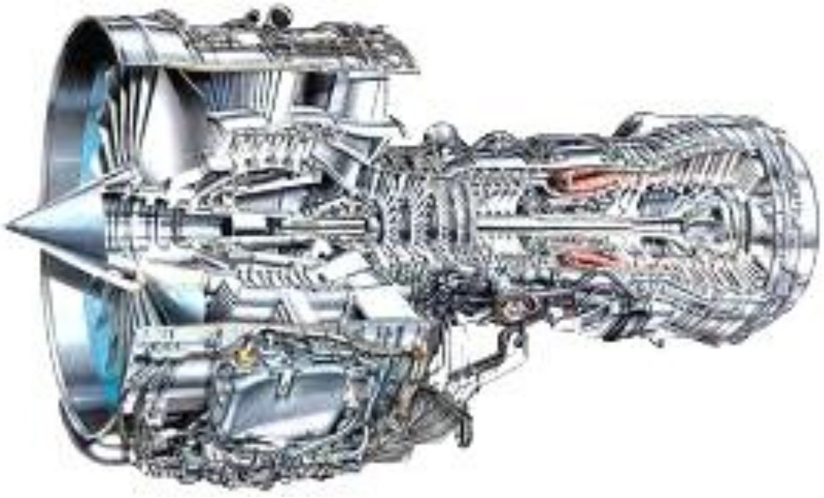


Fig. 4.22. Cutaway drawing of a commercial turbofan engine

Propellers are more efficient than turbojet engines at low altitudes and airspeeds. Turbofans combine the best features of both systems. Turbofans also are quieter than turbojets because the bypass air partially buffers the noise of the hot exhaust gases. A turboshaft is the third major type of aircraft turbine engine. A turboshaft uses a turbojet engine, but the exhaust gases drive a low-pressure turbine, which connects to a gearbox. If the gearbox drives a propeller, then the engine is called a turboprop. The gearbox can also be connected to electric generators, pumping devices, or, in helicopters, a rotor. In these applications the engine is known as a turboshaft.

Combustion in the engine combustion, or burning, is a series of rapid oxidation reactions that release heat and, usually, light. Carbon dioxide and water are the final products of complete combustion. Combustion occurs in the gas phase; solids or liquids do not burn because there is not enough oxygen present in the condensed phase to support combustion. When solids or liquids appear to burn, it is really volatile components that have vaporized from the surface and mixed with air that are burning. A source of energy is needed to initiate combustion, but once combustion is established, it will continue as long as fuel and oxygen (air) are present in the required proportions. Turbine engines have igniters to initiate combustion at startup. After this, combustion is sustained by the continuous injection of fuel into the flame. But this is an oversimplification.

Continuous combustion requires a stable flame, which, in turn, requires matching the fuel and airflow rates to the flame propagation rate. Hydrocarbon flame propagation rates are fairly slow, ranging from about 0,5 m/sec for a static mixture, to about 10 to 30 m/sec under turbulent flow conditions. Flame in the combustion zone is stable only if its propagation velocity is greater than the velocity of the primary air. Otherwise, the flame would blow out and stable combustion would be impossible.

In the combustion section, airflow is divided so that only a portion enters the primary combustion zone around the fuel nozzle. This portion of the total airflow, made up of dome air and primary air, is approximately enough for stoichiometric combustion of the fuel. A portion of the diverted air is used to cool the combustor liner. The remaining air is called dilution air and enters around the outside of the combustion chamber to cool and further mix the hot gases before they reach the turbine blades. Fig. 4.23 shows a schematic diagram of airflow in the combustion section.

The velocity of the air exiting the compressor section, about 150 m/sec, is much too high to support continuous combustion. This velocity is reduced to approximately 25 m/sec near the fuel nozzle by increasing the cross-sectional area at the entrance to the combustion section and diverting the secondary and dilution air around the primary combustion zone. Fuel is fed into combustion chamber through injectors under a pressure of about 50 kg/cm^2 (700 psi). Under these conditions, fuel discharges from the nozzle with a velocity of about 30 m/sec, forming a jet of finely atomized fuel. Thus, the velocity of the fuel spray, the velocity of the primary air, and the propagation velocity of a turbulent flame are closely matched. This allows the formation of a stable flame under very difficult conditions.

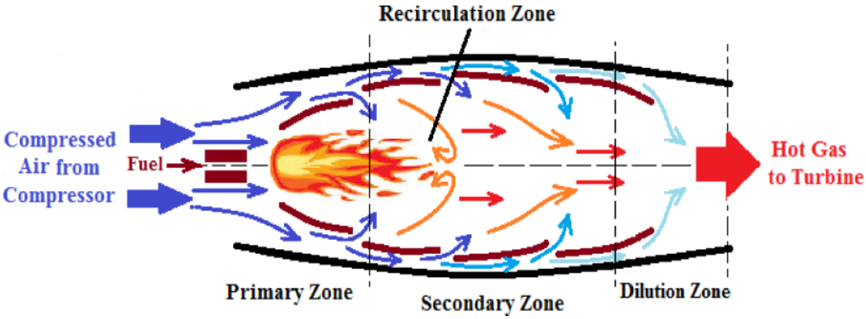


Fig. 4.23. Schematic Diagram of Airflow in the Combustion Section

The highest flame temperatures, about 2050 °C (3725 °F), are found in the primary combustion zone in the region where the fuel-air ratio is near stoichiometric. The introduction of dilution air, coupled with the liner cooling air, reduces the temperature to about 1500 °C (2730 °F) at the entrance to the turbine section.

Fuel Tanks. Commercial aircraft store fuel in their wings. Fig. 4.24 shows the arrangement of fuel tanks in a Boeing 747-400. There are two main tanks and one reserve tank in each wing along with a center wing tank in the fuselage. Some 747-400s also have an additional fuel tank in the tail horizontal stabilizer. Each main tank has a pump that supplies fuel to a manifold that feeds the engines. A Boeing 747-400 fully loaded with 216,389 l of fuel is carrying about 175,275 kg at a fuel density of 0,810 g/ml. The Airbus A380 holds about 310,000 l of fuel.

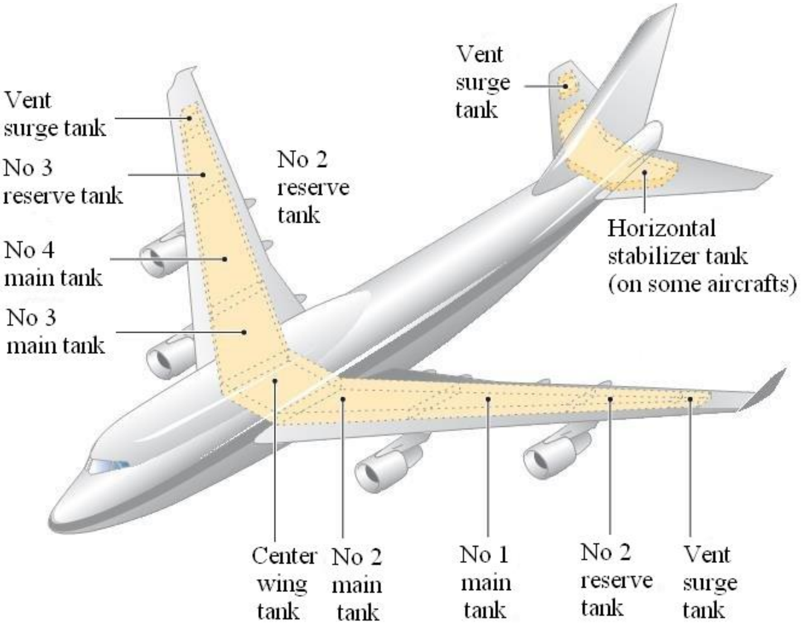


Fig. 4.24. Boeing 747-400 Fuel Tank Arrangement

4.7. Environmental effects

Aircraft engine emissions have not received as much attention in recent years as emissions from other energy sources. This is because aviation only contributes a small proportion of emissions compared to ground vehicles and stationary sources.

4.7.1. Aircraft emission

The main products of jet fuels combustion are CO_2 and H_2O. Fuels production is connected with extraction of fossil fuels from Earth's interior and it leads to increase of total CO_2 amount in the atmosphere. As a result we observe intensification of the global greenhouse effect on our planet. According to the data presented by UNEP (United Nations Environment Programme) about ¾ of all anthropogenic emission of CO_2 during last 20 years became a result of extraction and combustion of crude oil, coal and natural gas. Today CO_2 concentration in the atmosphere is about 400 ppm (0,04 %). With a current place of development CO_2 concentration may reach 500 ppm (0,05 %) in 2050.

Such rapid increase of CO_2 in the atmosphere is connected to active development of the aviation industry. Today the overall volume of passenger air traffic increases annually by 4–5 %. According to the data presented by COMAC (Commercial Aircraft Corporation of China) today the world passenger air fleet counts 18202 aircrafts. According to the forecasts the number of aircrafts will increase in two times till 2031 and will count about 31 thousand units. Enlargement of air fleet and number of flights consequently leads to increasing of jet fuels consumption. Today about 5,5 thousand barrels of jet fuel is produced and used every day. During the 10 year period (1992–2002) the level of JF consumption has risen by 21 %. At the same time IEA (International Energy Agency) states that the share of CO_2 produced by air transport is about 2 % (Fig. 4.25) and may reach 3 % in the nearest future.

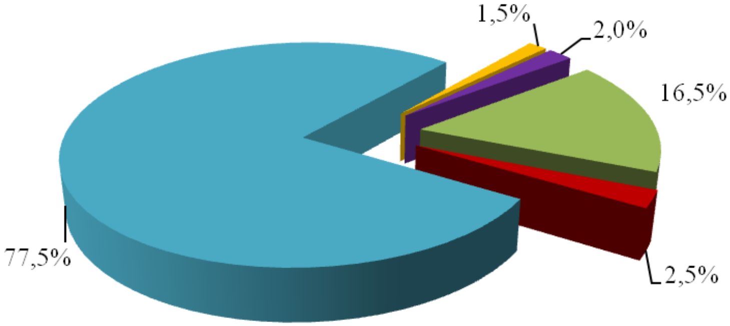


Fig. 4.25. The share of CO_2 emissions from air transport comparing to other kind of transport: 1.5 % – international aviation, 2 % – international marine transport, 16.5 % – motor transport, 2.5 % – other kinds of transport, 77.5 % – other energy sources

Except CO_2 aircraft’s emissions contain number of substances, which negatively influence on environment. Generally, aircrafts exhaust gases contain about 200 pollutants including CO_2, SO_x, CH_4, CO, PM (soot), NO_x, unburned hydrocarbons etc (Fig. 4.26).

In addition, emissions of NO_x cause an indirect effect on climate change by causing changes in O_3 and CH_4 concentrations through chemical reactions. O_3 concentration is increased and CH_4 decreased, with a net warming effect. This effect has complex dependencies on altitude, season, and latitude. Oxides of nitrogen have a lifetime of weeks in the atmosphere. A further impact of aviation emissions at altitude on climate change arises as a result of water vapor and particulate matter emissions, which under particular meteorological conditions can persist for hours and can spread into cirrus clouds. Contrails and aviation-induced cirrus clouds are believed to cause a net warming effect. However, both their formation and their climate impact are presently not well understood in several respects, and the level of scientific understanding of this phenomenon is still evolving. Finally, smaller effects on climate change are associated with particulate and water vapor emissions.

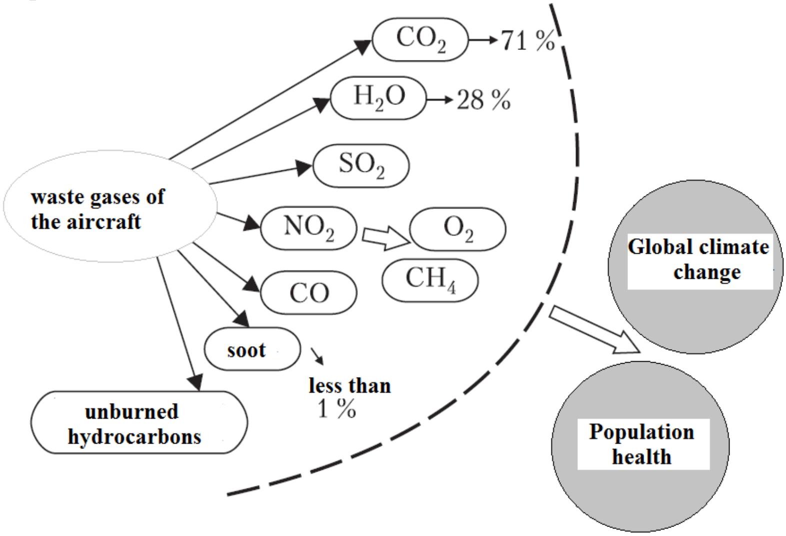


Fig. 4.26. Average composition of aircrafts' exhaust gases

When hydrocarbons are completely combusted, the products are carbon dioxide and water. However, when jet fuel is burned, other emissions including sulfur oxides, nitrogen oxides, unburned hydrocarbons, and particulates (soot) are formed. This is due to both trace amounts of sulfur and nitrogen in the fuel and also engine design and operating conditions.

The ICAO has established limits for emissions of nitrogen oxides, carbon monoxide, unburned hydrocarbons, and smoke from commercial

JEs. These limits were established for a defined landing and take-off cycle (LTO) to limit emissions near ground level, but they also indirectly limit emissions at altitude.

Carbon dioxide is a GHG and is implicated in climate change. Its emissions are directly related to the amount of fuel consumed and can be reduced by increasing efficiency of the engines and airframe. Aviation emissions of CO_2 are somewhat between 2 and 3 % of total carbon dioxide emissions.

Water vapor is the other major product of combustion. Emissions at ground level are not an issue, but water vapor emissions at cruise altitude can lead to formation of contrails and aviation-induced cirrus clouds. The effect of these contrails and clouds is uncertain, but they are thought to contribute to climate change.

Sulfur oxides are the result of combustion of sulfur containing compounds in the fuel, and thus are proportional to fuel sulfur content. SO_x emissions are thought to contribute to aerosols and particulate formation.

Nitrogen oxides are mainly formed from oxidation of atmospheric nitrogen at the very high temperatures found in the combustor. Any fuel bound nitrogen will also result in NO_x formation. NO_x emissions are a concern because they contribute to the formation of ozone near ground level.

Particulates and unburned hydrocarbons are the result of incomplete combustion. If present in high enough concentration, these particulates will be visible as smoke or soot coming out of the engine. Particulates at ground level can contribute to haze and smog formation and can be harmful if inhaled.

Generalizing the global approaches and challenges to lowering global CO_2 emissions from a commercial aircraft we can assume that the following ways can be implemented:

- Reduce the energy required to fly the aircraft by reducing its weight and/or drag,
- Improve the efficiency with which the energy is converted from fuel into thrust—in other words, improve the propulsion system efficiency,
- Reduce the carbon intensity of the energy required—in other words, reduce the net amount of carbon that is emitted into the

atmosphere for each joule of energy that is generated. This includes total life-cycle carbon emissions during production of the fuel.

The last point is strongly connected with implementation of alternative JFs. Other words, production and use of alternative JFs is one of the most promising measures to reduce carbon dioxide emissions. This idea includes closed life-cycle of carbon dioxide starting from the process of fuel production to its combustion.

For the far future electric aircraft, this would also include carbon emissions produced by the source of electricity, either on the ground (for battery-powered aircraft) or on the aircraft (for generator-equipped electric aircraft).

4.7.2. Airline fuel supply systems safety enhancement

Safety issues have lately become one of the priority tasks for the air traffic quality provision. Attention is paid to all constituents of this process: antiterrorist and anti hi-jacking defense of airlines, support of sanitary, epidemic and emergency safety of passengers and cargoes, and also technical and environmental safety of flights and airports.

The main sources of environmental threat within an airport are buildings and structures of aircraft technical maintenance, ancillary facilities (warehouses, garages, heating plants and etc.), hangars, runways, fuel storages and fuel supply systems (FSS). All the above mentioned sources affect the environment via air emissions and household and industrial wastewaters discharges and only FSS storages bring specific contamination with light petroleum products and lubricating materials to the environment. This pollution is concentrated mainly in the area adjoining to the airports.

The principal reason of environmental pollution caused by FSS storages is the loss of hydrocarbon materials, which takes place during transport operations and exploitation of imperfect equipment. The volumes of possible losses are limited with regulations and on the whole depend on the period of year, type of works and type of the equipment used in the given production processes, fuel composition and ways of its delivery to the storage. Considerable amount of FSS is lost as a result of violation of technical regulations for tanks loading operations, in the process of fuel transport, storage in reservoirs, reservoirs cleaning and unloading. These losses can be avoided by the means of installing closed fuel vapors circulation systems, strict fulfillment of technical safety rules, and timely technical maintenance. Apart from exploitation losses, certain amounts of fuel stored in the reservoirs are lost as a result of crippling, contributing to soils, underground and superficial waters pollution, as well as indirect atmosphere pollution. The installation of modern reservoir equipment and safe double-wall reservoirs takes probability and potential consequences of such losses to the minimum. Nevertheless, if there is a pipeline 20 km long, which transports 10000 t of kerosene per month, it releases to the environment 0,35 t at the ejection point, 0,22 t at the main and 0,23 t at the intermediate pumping station and 0,075 at the delivery point, this means 0,875 t of kerosene lost within the regulatory framework.

However, the linear part of any FSS service, which is used for pumping fuel over the airport territory from the points of reception from cisterns or petroleum storage depot main pipelines to the airplanes via filling machines, turns to be one of the basic sources of pollution. The losses take place through leakages and vapors on the pump stations and piping system. The use of metallic compressions and pumping by the “pump in a pump” method allow shortening the losses by more than 60 %. The FSS losses occur directly in the pipeline linear part through the compression of bolts and compensates, as a result of failures, and also through the openings of isolation, which arise up under the influence of corrosion. The systematic failures caused by the reduction of thickness and perforation of pipeline walls are characteristic during the exploitation period. Although the losses of FSS through the openings are insignificant in separate areas of pipelines, the overall volumes may reach 50 % general losses for the whole pipeline. Research shows that the second factor among the reasons of pipeline failures is corrosion and defects of structures and materials – 15 and 18 % accordingly, after external influences (50 % common amount) followed by soil changes and errors of exploitation, which give only 5–6 % failures. Therefore, definition of crippling reasons and conditions, determination of leakage points, their estimation and localization are the most important tasks on the way to airport pipeline systems environmental and technical safety enhancement.

A range of factors influences the permeability of pipelines. Metallic pipelines of airports are laid underground in isolating sleeves, therefore seasonal soil temperature and humidity changes influence them adversely. The pipeline surface expands under the influence of heating and diminishes when cooling. It results in the origin of pipeline material fatigue, which is displayed especially strongly in the places of welds and knees. The additional pressure is created by twisting and bends related to the change of external environment (slides, washing away etc.). Soil acidity and alkalinity also adversely affect the condition of pipe insulation and results in formation of insignificant cracks, which creates conditions for the pipeline contacts with the surrounding soil and leads to the corrosion of pipe walls in the place of contact.

All the above mentioned factors cause cracks and openings formation, where intensive tensions, fatigue and corrosion are present, and let the working body (petroleum product, kerosene, oils) get into the environment. Parent metal break, dent with the break of pipe wall, through corrosive openings, local crack, parent metal circular crack, pipeline walls thinning, flange joint screw-bolts break are basic damages of pipelines linear part.

The study of underground pipelines exploitation conditions showed that their destruction was the result of joint action of corrosive environment and repeated-variable loadings with relatively small frequency of recurrence. There are two types of loadings typical for pipelines: static (single) and small-cycle (repeated-static). Destruction due to the small-cycle loading starts with formation of fatigue cracks in the areas of tensions concentration. As a rule, it takes place along the defects location (on welds and adjoining areas).

One of the reasons of corrosive destructions under the deflection mode is the weld defects, caused by improper welding technology. The most widespread concentrators of tensions are: spills, penetrations and welds strengthening. It is set during researches, that the internal defects of welding diminish durability of welded connections by the factor of 3 and superficial defects – almost by one order. Working life reduction both at presence of internal and external defects takes place due to shortened period of cracks development.

The experiments show that the possible loss of fuel through the corrosion induced openings can account for 0,39 l/year for pipelines older than 3 years and 0,1 l/year for those which are less than 3 years old per each km of a pipeline. However, the study dealt with the pipelines not older than 8 years, whereas pipeline systems of many airports are much older. In order to avoid significant environmental harm and losses of valuable material it is necessary to conduct periodic control of pipelines condition and remove the detected defects. The pipeline walls integrity control is carried out by the means of non-destructive control methods, which perform remote diagnostics without violation of the pipe integrity.

Visual control is the simplest and cheapest method of damage location. Oil spots appear on the ground surface in the place of pipeline break. However, if this break is old, and pipeline diameter and pressure are considerable, the fuel spill can take considerable area and the exact localization of the break is impossible.

One of perspective control techniques is thermal nondestructive control. Pipeline, which lies underground and transports any material with the temperature different from soil temperature, is the source of heat. It forms some temperature anomaly on the soil surface, which is registered by special devices (thermal imagers, radiometers). A lot of defects in pipelines (sources, obstructions, insulation openings) are also heat sources, which give additional temperature rises. The use of special methods of temperature field analysis allows interpreting the underlying structure of the controlled object and identification of thermal sources.

It is set, that the temperature rise on the surface of soil above any pipeline, caused by fuel flowing in it, can make a few degrees difference, and the temperature anomaly created by leakage can reach 2–3 times higher values, that is enough to define pipeline position and its defects, and also determine their parameters. Following the defect localization and its nature determination it is possible to define the amount of fuel, leaking out of the pipeline.

Using remote electromagnetic measuring it is possible to determine the current losses and transitional resistance of pipeline isolating coverage, which are the parameters of insulation integrity. All measurements of this kind are based on testing magnetic field strength, which appears as a result of the current flowing within the underground pipeline. The analysis of the current distribution enables determination of the locations with damaged insulation cover, as the testing current is lost at the point of any defect.

The acoustic methods of non-destructive control of pipelines are very popular as a result of being easy to do and highly applicable to different tasks, including pipelines impermeability control. There are 2 approaches to the use of acoustic methods of pipelines diagnostics. The first is the use of ultrasound to control welds and structural elements of pipelines, which are assembled, and the second is the location of defects by the sound of liquid leaking out of a pipeline. Two detectors are set in two accessible places of a pipeline so that the suspected damaged area was situated in between. Effluents flowing out create stochastic noises. They are passed to the detectors by the pipeline. Correlation of these signals and difference between two values of time delay give the place of defect localization.

Ambient (air and soil) temperature, soil humidity, presence of mechanical and electromagnetic interference sources, depth of pipelines affects accuracy of control techniques and possibility of their application. Therefore, it is necessary to consider specific conditions in order to recommend research method for a certain air enterprise. On the whole, it is necessary to accept that the acoustic and electromagnetic methods of control can be applied after determination and taking into account the existent background noise level in the area of airports; the use of thermal methods is impossible, when temperature of soil is similar to the temperature of transported fuel.

Data obtained during pipelines defects detection are used to estimate remaining resource and its durability prolongation. The procedure of pipeline capacity and remaining life estimation at presence of cracks or crack-like defects involves successive implementation of the following stages:

1. Determination of the area deformation mode.
2. Approximation of initial crack-like defects to the database of calculated defect analogues.
3. Calculation of maximum (destroying) values of tensions and/or deformations relevant to the specific defect.
4. Calculation of the defect critical sizes for the current deformation mode.
5. Evaluation of the construction durability under the current combination of defects.
6. Calculation and experimental prognosis of defects development rate.
7. Calculation of the remaining resource of the pipeline structure.

This way the remaining pipeline working resource evaluation for the area with corrosive defects includes such stages:

- calculation of wall thinning;

- evaluation of the mean corrosion rate;
- evaluation of the remaining life.

Similar algorithms are developed for pipelines with the defects of crimps, dents, cracks. It is necessary to note that the calculation of capacity and evaluation of residual working resource of pipelines with cracks are quite complicated task, which includes calculation of tensions maximum values, determination of defects critical sizes, evaluation of reliability factors under the set sizes of defects and finally evaluation of its resource. Based on the total results of the analysis the following variants of decisions are made: prolongation of exploitation without the change of the mode till the complete running out of the remaining working resource or till the next date of inspection; exploitation under the lowered working pressure; interruption of exploitation to conduct repair or replace defected area.

Questions for self-control

1. What types of jet fuels do you know?
2. Characterize hydrocarbon composition of jet fuels.
3. Name modern types of jet fuels.
4. What is the difference between kerosene-type jet fuel and gasoline-type jet fuel?
5. Name jet fuel operation properties.
6. What additives to jet fuel do you know?
7. Name main aviation fuel specifications.
8. What are the reasons for microbial growth in jet fuel?
9. Describe ecological effects of jet fuels.
10. Describe the principle of JE operation.

Chapter 5.
CHEMMOTOLOGY OF DIESEL FUELS

Diesel fuel keeps the world economy moving. From consumer goods moved around the world, to the generation of electric power, to increased efficiency on farms, diesel fuel plays a vital role in strengthening the global economy and the standards of living. Classification of fuels for diesel engines is represented in table 5.19.

Table 5.19

Classification of fuels for diesel engines

Engine	Application area	Kind of Fuel
High-speed (n >1500 min^{-1})	Automobiles, diesel locomotives, small-displacement river and sea vessels, stationary devices	Fuel for high-speed diesel engines, low-viscosity marine ship fuel
Medium-speed (n =250–1500 min^{-1})	Small-displacement river and sea vessels, stationary devices	Medium-viscosity marine ship fuel
Slow-speed (n < 1500 min^{-1})	High-displacement river and sea vessels	High-viscosity Marine ship fuel, bunker fuel

Diesel fuel contains about 85,5–86,0% of C, 12,5–13% of H and 1–2% of O.

5.1. Production of diesel fuel

Diesel fuel is made from petroleum. The diesel fuel produced by a refinery is a blend of all the appropriate available streams: straight-run product, FCC light cycle oil, and hydrocracked gas oil. The straight-run diesel may be acceptable as it is, or may need minor upgrading for use in diesel fuel prepared for off-road use. EN 590 European standard diesel fuels are being produced and used in the European Union (EU) since 1996. To meet the 15 ppm sulfur limit, all the streams used to prepare diesel fuel need hydrotreating to lower the sulfur concentration.

The refiner must blend the available streams to meet all operation, regulatory, economic, and inventory requirements. Sophisticated computer programs have been developed to optimize all aspects of refinery operation, including the final blending step. Refineries are optimized for overall performance, not just for the production of diesel fuel. The refiner really has limited control over the detailed composition of the final diesel blend. It is determined primarily by the composition of the crude oil feed, which is usually selected based on considerations of availability and cost. While the chemical reactions that occur in the conversion processes involve compositional changes, they are not specific enough to allow for much tailoring of the products. Yet, despite these limitations, refineries daily produce large volumes of on-test products.

Hydrocarbon compounds. Hydrocarbons are organic compounds composed entirely of carbon and hydrogen atoms. There are four major classes of hydrocarbons: paraffins, naphthenes, olefins, and aromatics. Each class is a family of individual hydrocarbon molecules that share a common structural feature, but differ in size (number of carbon atoms) or geometry. The classes also differ in the ratio of hydrogen to carbon atoms and in the way the carbon atoms are bonded to each other.

Paraffins have the general formula C_nH_{2n+2}, where “n” is the number of carbon atoms (carbon number) in the molecule. There are two subclasses of paraffins: normal paraffins and isoparaffins.

Normal paraffins have carbon atoms linked to form chain-like molecules, with each carbon – except those at the ends – bonded to two others, one on either side.

Isoparaffins have a similar carbon backbone, but they also have one or more carbons branching off from the backbone. Normal decane and 2,4-dimethyloctane have the same chemical formula, $C_{10}H_{22}$, but different chemical and physical properties. Compounds like this, with the same chemical formula, but a different arrangement of atoms, are called structural isomers.

Naphthenes have some of their carbon atoms arranged in a ring. The naphthenes in diesel fuel have rings of five or six carbons. Sometimes two or more rings are fused together, with some carbons shared by adjacent rings. Naphthenes with one ring have the general formula C_nH_{2n}.

Olefins are similar to paraffins, but have fewer hydrogen atoms and contain at least one double bond between a pair of carbon atoms. Olefins rarely occur in crude oil; they are formed by certain refinery processes. Like paraffins, olefins with four or more carbons can exist as structural isomers. Olefins with one double bond have the general formula CnH2n, the same as naphthenes.

Aromatics. As with naphthenes, some of the carbon atoms in aromatics are arranged in a ring, but they are joined by aromatic bonds, not the single bonds found in naphthenes. Aromatic hydrocarbon rings contain six carbon atoms. Benzene is the simplest aromatic compound. The benzene structure was originally conceptualized as two equivalent structures with alternating single and double bonds. Each structure continually transformed itself into the other as the double bonds flipped back and forth between different pairs of carbon atoms. Now, we know that all the carbon to carbon bonds in benzene are equivalent. The shorthand representation of benzene is a hexagon with a circle inside representing the aromatic bonds. One-ring aromatics have the general formula C_nH_{2n-6}.

Polycyclic aromatics are compounds with two or more aromatic rings. These rings are fused together, with some carbons being shared by adjacent rings. Paraffins and naphthenes are classified as saturated hydrocarbons because no more hydrogen can be added to them without breaking the carbon backbone. Aromatics and olefins are classified as unsaturated hydrocarbons. They contain carbon to carbon double bonds or aromatic bonds that can be converted to single bonds by adding hydrogen atoms to the adjacent carbons. When straight-chain olefins are saturated with hydrogen, they become paraffins. When aromatics are completely saturated with hydrogen, they become naphthenes; when they are partially saturated, they become cyclic olefins.

Some molecules contain structural features characteristic of two or more hydrocarbon classes. For example, a molecule could contain an aromatic ring, a naphthenic ring, and a paraffinic chain. How should this molecule be classified? Chemists have established a hierarchy of hydrocarbon structural features, with aromatics at the top, followed by olefins, naphthenes, and paraffins. A compound with features of more than one class is placed in the class highest in the hierarchy. So, in our example, the molecule is classified as an aromatic.

Other compounds. While carbon and hydrogen are the predominant elements in crude oil, small amounts of sulfur, nitrogen, and oxygen are also present. These elements are called heteroatoms (“other” atoms). Molecules containing heteroatoms are not classified as hydrocarbons. Typical examples found in diesel fuel include dibenzothiophene and carbazole. Although these compounds are present in small amounts, they play a large role in determining certain fuel properties.

5.2. Operation properties

Several operating characteristics influence engine operation, and their relative importance depends on engine type and duty cycle (for example, truck, passenger car, stationary generator, marine vessel, etc.). These characteristics are:

- Starting ease;
- Low noise;
- Low wear (high lubricity);
- Long filter life (stability and fuel cleanliness);
- Sufficient power;
- Good fuel economy;
- Low temperature operability;
- Low emissions.

Engine design has the greatest impact on most of these characteristics. However, because the focus of this publication is fuel, this chapter discusses how these characteristics are affected by fuel properties (see Appendixes B, C).

Starting. Leaks and heat loss reduce the pressure and temperature of the fuel/air mixture at the end of the compression stroke. Thus, a cold diesel engine is more difficult to start and the mixture more difficult to ignite when compared to a hot diesel engine. Engines are equipped with start-assist systems that increase the air temperature to aid ignition. These controls in the diesel engine can also decrease starting engine noise, white smoke, and cranking time.

Diesel fuel that readily burns, or has good ignition quality, improves cold start operation. The cetane number of the fuel defines its ignition quality. It is believed that fuels with minimum cetane number requirement of 40 provide adequate operation in modern diesel engines. The minimum cetane number in Europe is 51. Some researchers claim that a number of modern engines can benefit from a higher cetane number when starting in very cold climates. Smoothness of operation, misfire, smoke emissions, noise, and ease of starting are all dependent on the ignition quality of the fuel. At temperatures below freezing, starting aids may be necessary regardless of the cetane number.

Power is determined by the engine design. Diesel engines are rated at the brake horse-power developed at the smoke limit. For a given engine, varying fuel properties within specification range does not alter power significantly.

The ***noise*** produced by a diesel engine is a combination of combustion and mechanical noise. Fuel properties can affect combustion noise directly. In a diesel engine, fuel ignites spontaneously shortly after injection begins. During this delay, the fuel is vaporizing and mixing with the air in the combustion chamber. Combustion causes a rapid heat release and a rapid rise of combustion chamber pressure. The rapid rise in pressure is responsible for the knock that is very audible in some diesel engines.

By increasing the cetane number of the fuel, the knock intensity is decreased by the shortened ignition delay. Fuels with high cetane numbers ignite before most of the fuel is injected into the combustion chamber. The rates of heat release and pressure rise are then controlled primarily by the rate of injection and fuel-air mixing, and smoother engine operation results.

A recent development is the common rail electronic fuel injection system. The use of a common rail allows engine manufacturers to reduce exhaust emissions and, especially, to lower engine noise.

Fuel economy. Here again, engine design is more important than fuel properties. However, for a given engine used for a particular duty, fuel economy is related to the heating value of the fuel. The fuel economy standard is expressed as volume used per unit distance – liters per 100 kilometer. Therefore, the relevant units for heating value are heat per volume (kilojoules per liter/cubic meter). Heating value per volume is directly proportional to density when other fuel properties are unchanged.

Lubricity. The less-processed diesel fuels of the past were good boundary lubricants. This was not caused by the hydrocarbons that constitute the bulk of the fuel, but was attributed to trace amounts of oxygen- and nitrogen-containing compounds and certain classes of aromatic compounds. Evidence for the role of trace quantities is the fact that the lubricity of a fuel can be restored with the addition of as little as 10 parts per million (ppm) of an additive.

Lubricity enhancing compounds are naturally present in diesel fuel derived from petroleum crude by distillation. They can be altered or changed by hydrotreating, the process used to reduce sulfur and aromatic contents. However, lowering sulfur or aromatics, per se, does not necessarily lower fuel lubricity.

Cleanness. Inadequate lubricity is not the only cause of wear in diesel engine fuel systems. Diesel fuel can cause abrasive wear of the fuel system and the piston rings if it is contaminated with abrasive inorganic particles. Fuel injectors and fuel injection pumps are particularly susceptible to wear because the high liquid pressures they generate require extremely close tolerances between parts moving relative to one another.

Acidity. Organic acids in diesel fuel can also cause corrosive wear of the fuel system. While this may be a significant wear mechanism for high sulfur diesel, it is less significant for low sulfur diesel because hydrotreating to reduce sulfur also destroys organic acids. With the introduction of biodiesel fuel, there is some indication that organic acids could potentially increase.

Low-temperature operability is an issue with middle distillate fuels, because they contain straight and branched chain hydrocarbons (paraffin waxes) that become solid at ambient winter temperatures in colder geographic areas. Wax formation can also be exacerbated by blends of biodiesel with conventional diesel fuel. Wax may plug the fuel filter or completely gel the fuel, making it impossible for the fuel system to deliver fuel to the engine.

Engine design changes to address this problem include locating the fuel pump and filter where they will receive the most heat from the engine. The practice of pumping more fuel to the injectors than the engine requires is also beneficial because the warmed excess fuel is circulated back to the tank. While the primary purpose of this recycle is to cool the injectors, it also heats the fuel in the fuel tank.

Sometimes operators may allow diesel equipment to idle in cold weather rather than turning the engine off, when it is not in use. This practice is no longer allowed in certain regions. In some cases the cost of the fuel may be less than the cost of winterizing the engine; vehicles designed for low-temperature operation are usually equipped with heated fuel tanks, insulated fuel lines, and heated fuel filters.

In a refinery, there are a number of approaches to improve a fuel's low-temperature operability, such as:

1. Manufacture it from less waxy crudes.
2. Manufacture it to a lower distillation end point. (This excludes higher boiling waxy components with higher melting points.)
3. Dilute it with a fuel with lower wax content.
4. Treat it with a low-temperature operability additive.

Additives are used to improve low-temperature filterability and lower the pour point. When they work, additives have several advantages over dilution: they are readily available in most areas of the world, treatment cost is less, and the treatment does not lower fuel density (thus heating value and fuel economy are not affected).

Fuel stability – filter life. Unstable diesel fuels can form soluble gums or insoluble organic particulates. Both gums and particulates may contribute to injector deposits, and particulates can clog fuel filters. The formation of gums and particulates may occur gradually during long-term storage or quickly during fuel system recirculation caused by fuel heating.

Storage stability of diesel fuel has been studied extensively because of governmental and military interest in fuel reserves. However, long-term (at ambient temperatures) storage stability is of little concern to the average user, because most diesel fuel is consumed within a few weeks of manufacture. Thermal (high-temperature) stability, on the other hand, is a necessary requirement for diesel fuel to function effectively as a heat transfer fluid. Thermal stability may become more important because diesel engine manufacturers expect future injector designs to employ higher pressures to achieve better combustion and lower emissions. The change will subject the fuel to higher temperatures and/or longer injector residence times.

Low sulfur diesel fuels tend to be more stable than their high sulfur predecessors because hydrotreating to remove sulfur also tends to destroy the precursors of insoluble organic particulates. However, hydrotreating also tends to destroy naturally occurring antioxidants. It may be necessary for the refiner to treat some low sulfur diesel fuels with a stabilizer to prevent the formation of peroxides that are the precursors of soluble gums.

Smoke. The fuel system of a diesel engine is designed and calibrated so that it does not inject more fuel than the engine can consume completely through combustion. If an excess of fuel exists, the engine will be unable to consume it completely, and incomplete combustion will produce black smoke. The point at which smoke production begins is known as the smoke limit. Most countries set standards for exhaust smoke from high-speed, heavy-duty engines.

Smoke that appears after engine warm-up is an indication of maintenance or adjustment problems. A restricted air filter may limit the amount of air, or a worn injector may introduce too much fuel. Other causes may be miscalibrated fuel pumps or maladjusted injection timing. Changes made to fuel pump calibration and injection timing to increase the power of an engine can lead to increased emissions.

Fuel can indirectly lead to smoking by degrading injector operation over time, when:

1. Gums in the fuel are deposited on the injectors, causing sticking, which interferes with fuel metering.
2. Petroleum residue or inorganic salts in the fuel result in injector tip deposits that prevent the injector from creating the desired fuel spray pattern. (Some low-speed, large diesel engines are designed to burn fuel containing large amounts of petroleum residue. These are typically used in marine and power generation applications.)
3. Abrasive contaminants or organic acids in the fuel, or inadequate fuel lubricity cause excessive abrasive or corrosive injector wear.

5.3. Diesel engine

Diesel engines have long been the workhorse of industry. Due to it high torque output, durability, exceptional fuel economy and ability to provide power under a wide range of conditions, diesels are the dominant engines used in applications such as trucking, construction, farming, and mining. They are also extensively used for stationary power generation and marine propulsion and in passenger vehicles in many regions of the world. Because of significant improvements in diesel engine operation, injection technology, and exhaust after treatment devices, particulate matter and nitrogen oxides emissions have been reduced such that diesels are poised to achieve future emissions standards.

Diesel engines are similar to gasoline engines in many ways. Both are internal combustion engines and most versions of them use a four-stroke cycle. There are four fundamental differences:

- The conventional gasoline engine injects fuel into the air as it is drawn into a cylinder. The diesel engine draws air into a cylinder and injects fuel after the air has been compressed.
- The gasoline engine ignites the fuel-air mixture with a spark. The diesel engine relies on high temperature alone for ignition. Diesel engines are often referred to as compression-ignition engines because this high temperature is the result of compressing air above the piston as it travels upward.
- The power output of a gasoline engine is controlled by a throttle, which varies the amount of fuel-air mixture drawn into a cylinder. A diesel engine does not throttle the intake air. It controls the power output by varying the amount of fuel injected into the air, thereby, varying the fuel-air ratio. This is one of the primary reasons that diesel engines are more fuel efficient than spark-ignition gasoline engines.
- A conventional gasoline engine runs stoichiometrically – the F/A ratio is fixed so that there is just enough air to burn all the fuel. A diesel engine runs lean – there is always more air than is needed to burn the fuel.

The main advantage of a diesel engine is its high thermal efficiency. Diesel engines can achieve thermal efficiencies in excess of 50 %. The best conventional gasoline engines are approximately from 30 to 33 % efficient, and then only at wide throttle openings. As a result, diesel engines have better fuel economy than gasoline engines.

By far the most common type of diesel engine used today has reciprocating pistons and uses a four-stroke operating cycle (Fig. 5.27).

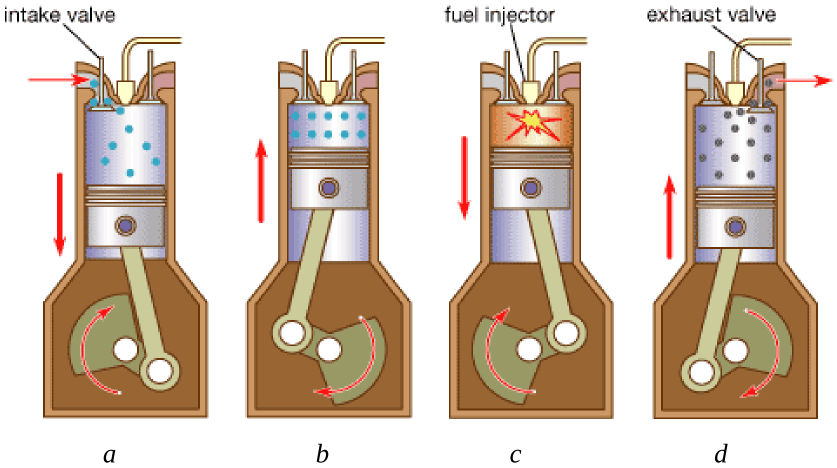


Fig. 5.27. Four strokes of a diesel engine: *a* – intake; *b* – compression; *c* – power; *d* – exhaust

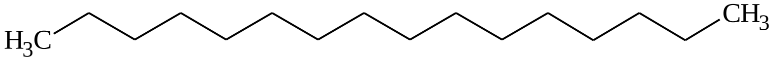
In the first stroke (intake stroke), the intake valve opens while the piston moves down from its highest position in the cylinder (closest to the cylinder head) to its lowest position. This draws air into the cylinder in the process. In the second stroke (compression stroke), the intake valve closes and the piston moves back up the cylinder. This compresses the air and, consequently, heats it to a high temperature, typically in excess of 540°. Near the end of the compression stroke, fuel is injected into the cylinder. After a short delay, the fuel ignites spontaneously, a process called autoignition. The hot gases produced by combustion of the fuel further increase the pressure in the cylinder, forcing the piston down (expansion stroke or power stroke); the combustion energy is transformed into mechanical energy. The exhaust valve opens when the piston is again near its lowest position, so that as the piston once more moves to its highest position (exhaust stroke), most of the burned gases are forced out of the cylinder.

5.4. Cetane number

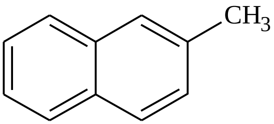
Cetane number or CN is a measurement of the combustion quality of diesel fuel during compression ignition. Cetane number is actually a measure of a fuel's ignition delay; the time period between the start of injection and start of combustion (ignition) of the fuel. In a particular diesel engine, higher cetane fuels will have shorter ignition delay periods than lower cetane fuels.

Generally, diesel engines run well with a CN from 40 to 55. Fuels with higher cetane number which have shorter ignition delays provide more time for the fuel combustion process to be completed. Hence, higher speed diesels operate more effectively with higher cetane number fuels. There is no operation or emission advantage when the CN is raised past approximately 55; after this point, the fuel's operation hits a plateau.

Cetane (n-hexadecane) CH_3-$(CH_2)_{14}$-CH_3 is an un-branched open chain alkane molecule that ignites very easily under compression, so it was assigned a cetane number of 100, while alpha-methylnaphthalene was assigned a cetane number of 0. These hydrocarbons are the primary reference for the method of determination of fuels cetane number (Fig. 5.28).



n-Hexadecane (cetane), cetane number = 100



1-Methylnaphthalene, cetane number = 0

Fig. 5.28. Chemical structure of n-hexadecane and 1-methylnaphthalene

All other hydrocarbons in diesel fuel are indexed to cetane as to how well they ignite under compression. The cetane number therefore measures how quickly the fuel starts to burn (auto-ignites) under diesel engine conditions. Since there are hundreds of components in diesel fuel, with each having a different cetane quality, the overall cetane number of the diesel is the average cetane quality of all the components. There is very little actual cetane in diesel fuel.

The **cetane number** of a fuel is defined as the volume percent of n-hexadecane in a blend of n-hexadecane and 1-methylnaphthalene that gives the same ignition delay period as the test sample. For example, a fuel with a cetane number of 40 will perform the same in the engine as a blend of 40 % n-hexadecane and 60 % 1-methylnaphthalene.

To measure the cetane number properly is rather difficult, as it requires burning the fuel in a special, hard-to-find, diesel engine called a Cooperative Fuel Research (CFR) engine, under standard test conditions. The operator of the CFR engine uses a hand-wheel to increase the pressure within the cylinder of the engine until the time between fuel injection and ignition is 2,407 ms. The resulting cetane number is then calculated by determining which mixture of cetane (hexadecane) and alpha-methylnaphthalene will result in the same ignition delay.

5.5. Additives for diesel fuel

5.5.1 Operation properties improvement

Cetane Number Improvers (Diesel Ignition Improvers) raise the cetane number of the fuel. Within a certain range, a higher number can reduce combustion noise and smoke and enhance ease of starting the engine in cold climates. The magnitude of the benefit varies among engine designs and operating modes, ranging from no effect to readily perceptible improvement.

2-Ethylhexyl nitrate (EHN) is the most widely used cetane number improver. It is also called octyl nitrate. EHN is thermally unstable and decomposes rapidly at the high temperatures in the combustion chamber. The products of decomposition help initiate fuel combustion and thus shorten the ignition delay period from that of the fuel without the additive.

The increase in cetane number from a given concentration of EHN varies from one fuel to another. It is greater for a fuel whose natural cetane number is already relatively high. The incremental increase gets smaller as more EHN is added, so there is little benefit to exceeding a certain concentration. EHN typically is used in the concentration range from 0,05 to 0,4 % mass and may yield a three to eight cetane number benefit. A disadvantage of EHN is that it decreases the thermal stability of some diesel fuels. This can be compensated for by the use of thermal stability additives.

Di-tertiary butyl peroxide (DTBP) is another additive, which is used commercially as a diesel cetane improver; it is a less effective cetane number improver than EHN. However, DTBP does not degrade thermal stability of most diesel fuels, and it does not contain nitrogen (which may be important for meeting some reformulated diesel fuel regulatory requirements).

Other alkyl nitrates, as well as ether nitrates, peroxides, and some nitroso compounds, have also been found to be effective cetane number improvers, but most are not used commercially. The effects of these other cetane number improvers on other fuel properties, such as thermal stability, is not fully known.

Injector Cleanliness Additives. Fuel and/or crankcase lubricant can form deposits in the nozzle area of injectors – the area exposed to high cylinder temperatures. The extent of deposit formation varies with engine design, fuel composition, lubricant composition, and operating conditions. Excessive deposits may upset the injector spray pattern which, in turn, may hinder the fuel-air mixing process. In some engines, this may result in decreased fuel economy and increased emissions.

Ashless polymeric detergent additives can clean up fuel injector deposits and/or keep injectors clean. These additives are composed of a polar group that bonds to deposits and deposit precursors, and a non-polar group that dissolves in the fuel. Thus, the additive can redissolve deposits that already have formed and reduce the opportunity for deposit precursors to form deposits. Detergent additives typically are used in the concentration range of 50 to 300 ppm.

Lubricity Additives are used to compensate for the lower lubricity of severely hydrotreated diesel fuels. They contain a polar group that is attracted to metal surfaces that causes the additive to form a thin surface film. The film acts as a boundary lubricant when two metal surfaces come in contact.

Three additive chemistries, mono acids, amides, and esters, are commonly used. Monoacids are more effective, therefore lower concentrations are used (10 to 50 ppm). Since esters and amides have lower polarity, they require a higher concentration range from 50 to 250 ppm.

Smoke Suppressants. Some organometallic compounds act as combustion catalysts. Adding these compounds to fuel can reduce the black smoke emissions that result from incomplete combustion. Such benefits are most significant when used with older technology engines which are significant smoke producers.

Smoke suppressants based on other metals, e.g., iron, cerium, or platinum, continue to see limited use in some parts of the world, where the emissions reduction benefits may outweigh the potential health hazards of exposure to these materials. Use of metallic fuel additives is not currently allowed in the U.S., Japan, and certain other countries.

5.5.2. Fuel Handling Additives

Antifoam Additives. Some diesel fuels tend to foam as they are pumped into vehicle tanks. The foaming can interfere with filling the tank completely or result in a spill. Most antifoam additives are organosilicone compounds and are typically used at concentrations of 10 ppm or lower.

De-Icing Additives. Free water in diesel fuel freezes at low temperatures. The resulting ice crystals can plug fuel lines or filters, blocking fuel flow. Low molecular weight alcohols or glycols can be added to diesel fuel to prevent ice formation. The alcohols/glycols preferentially dissolve in the free water giving the resulting mixture a lower freezing point than that of pure water.

Low-Temperature Operability Additives. There are additives that can lower a diesel fuel's pour point (gel point) or cloud point or improve its cold flow properties. Most of these additives are polymers that interact with the wax crystals that form in diesel fuel when it is cooled below the cloud point. The polymers mitigate the effect of wax crystals on fuel flow by modifying their size, shape, and/or degree of agglomeration. The polymer-wax interactions are fairly specific; a particular additive generally will not perform equally well in all fuels.

The additives can be broken down into three idealized groups:

- specialized additives for narrow boiling range fuels;
- general purpose additives;
- specialized additives for high final boiling point fuels.

To be effective, the additives must be blended into the fuel before any wax has formed, i.e., when the fuel is above its cloud point. The best additive and treat rate for a particular fuel cannot be predicted; it must be determined experimentally. Some cloud point depressant additives also provide lubricity improvements.

Conductivity Additives. When fuel is pumped from one tank to another (in a refinery, terminal, or fuelling station), especially when pumped through a filter, a small amount of static electric charge is generated. Normally, this charge is quickly dissipated and does not pose a problem. However, if the conductivity of the fuel is low, the fuel may act as an insulator allowing a significant amount of charge to accumulate. Static discharge may then occur posing a potential risk of fire hazard. Typically, the lower-sulfur diesel fuels have lower conductivity.

In order to prevent static charge accumulation, anti-static additives can be used to improve the electrical conductivity of fuel. Anti-static additives are available in both metallic and non-metallic chemistries, and are typically used at concentrations of 10 ppm or less.

Drag Reducing Additives. Pipeline companies sometimes use drag reducing additives to increase the volume of product they can deliver. These high molecular weight polymers change the turbulent flow characteristics of fluids flowing in a pipeline, which can increase the maximum flow rate from 20 to 40 %. Drag reducing additives are typically used in concentrations below 15 ppm. When the added product passes through a pump, the additive is broken down (sheared) into smaller molecules that have minimal effect on product performance in engines at normal operating temperatures.

Fuel Stability Additives. Fuel instability results in the formation of gums that can lead to injector deposits or particulates that can plug fuel filters or the fuel injection system. The need for a stability additive varies widely from one fuel to another. It depends on how the fuel was made – the crude oil source and the refinery processing and blending. Stability additives typically work by blocking one step in a multi-step reaction pathway. Because of the complex chemistry involved, an additive that is effective in one fuel may not work as well in another.

If a fuel needs to be stabilized, it should be tested to select an effective additive and treat rate. Best results are obtained when the additive is added immediately after the fuel is manufactured. S15 diesel fuels will probably be more thermally stable, but may be prone to peroxide formation during storage.

Antioxidants. One mode of fuel instability is oxidation. Oxidation takes place when oxygen, in the small amount of dissolved air, attacks reactive compounds in the fuel. This initial attack sets off complex chain reactions.

Antioxidants work by interrupting the chain reactions. Hindered phenols and certain amines, such as phenylenediamine, are the most commonly used antioxidants. They typically are used in the concentration range from 10 to 80 ppm.

Stabilizers. Acid-base reactions are another mode of fuel instability. The stabilizers used to prevent these reactions typically are strongly basic amines and are used in the concentration range from 50 to 150 ppm. They react with weakly acidic compounds to form products that remain dissolved in the fuel and do not react further.

Metal Deactivators. When trace amounts of certain metals, especially copper and iron, are dissolved in diesel fuel, they catalyze (accelerate) the reactions involved in fuel instability. Metal deactivators tie up (chelate) these metals and neutralize their catalytic effect. They are typically used in the concentration range from 1 to 15 ppm.

Dispersants. Multi-component fuel stabilizer packages may contain a dispersant. The dispersant doesn't prevent the fuel instability reactions; however, it does disperse the particulates that form preventing them from clustering into aggregates large enough to plug fuel filters or injectors. Dispersants typically are used in the concentration range from 15 to 100 ppm.

5.5.3. Contaminant Control

This class of additives mainly is used to deal with problems in distribution and storage systems.

Biocides. The high temperatures involved in refinery processing effectively sterilize diesel fuel. However, the fuel may quickly become contaminated if exposed to microorganisms present in air or water. These microorganisms include bacteria and fungi (yeasts and molds).

Because most microorganisms need free water to grow, microbial growth is usually concentrated at the fuel-water interface, when one exists. In addition to the fuel and water, they also need certain elemental nutrients in order to grow. Of these nutrients, phosphorous is the only one whose concentration might be low enough in a fuel system to limit microbial growth. Higher ambient temperatures also promote growth. Some organisms need air to grow (aerobic), while others only grow in the absence of air (anaerobic).

The time available for growth is also important. A few, or even a few thousand, organisms don't pose a problem. Only when the colony has had time to grow much larger will it have produced enough acidic by-products to accelerate tank corrosion or enough biomass (microbial slime) to plug filters. Although growth can occur in working fuel tanks, static tanks, where fuel is being stored for an extended period of time, are a much better growth environment when water is present.

Biocides can be used when microorganisms reach problem levels. The best choice is an additive that dissolves in both fuel and water to attack the microbes in both phases. Biocides typically are used in the concentration range from 200 to 600 ppm.

A biocide may not work if a heavy biofilm has accumulated on the surface of the tank or other equipment, because it may not be able to penetrate to the organisms living deep within the film. In such cases, the tank must be drained and mechanically cleaned.

Even if the biocide effectively stops microbial growth, it still may be necessary to remove the accumulated biomass to avoid filter plugging. Any water bottoms that contain biocides must be disposed of appropriately because biocides are toxic.

The best approach to microbial contamination is prevention. The most important preventative step is keeping the amount of water in a fuel storage tank as low as possible, preferably at zero.

De-emulsifiers. Normally, hydrocarbons and water separate rapidly and cleanly. However, if the fuel contains polar compounds that behave like surfactants and if free water is present, the fuel and water can form an emulsion. Any operation which subjects the mixture to high shear forces (such as pumping the fuel) can stabilize the emulsion. De-emulsifiers are surfactants that break up emulsions and allow the fuel and water to separate. De-emulsifiers typically are used in the concentration range from 5 to 30 ppm.

Corrosion Inhibitors. Most petroleum pipes and tanks are made of steel and the most common type of corrosion is the formation of rust in the presence of water. Over time severe rusting can eat holes in steel walls, and create leaks. More immediately, the fuel is contaminated by rust particles, which can plug fuel filters or increase fuel pump and injector wear.

Corrosion inhibitors are compounds that attach to metal surfaces and form a protective barrier that prevents attack by corrosive agents. They typically are used in the concentration range from 5 to 15 ppm.

5.6. Environmental effects

Exhaust emissions are the Achilles' heel of diesel engines. Diesel exhaust tends to be high in nitrogen oxides (NO_x) and particulates, both visible (smoke) and invisible. Both NO_x and particulates are significant environmental pollutants. Unlike the exhaust of gasoline engines, diesel exhaust contains much less unburned or partially burned hydrocarbons and carbon monoxide.

Diesel exhausts of NO_x and particulate matter (PM) are linked by the nature of diesel combustion. Efforts to reduce PM by increasing combustion efficiency lead to higher combustion temperatures, thus, higher NO_x emissions. Lowering NO_x formation by lowering combustion temperature leads to less complete combustion and, thus, higher PM emissions. The challenge for diesel engine designers is to reduce emissions of NO_x and PM simultaneously.

The sulfur content of diesel fuel affects PM emissions because some of it in the fuel is converted to sulfate particulates in the exhaust. The fraction converted to PM varies from one engine to another, but reducing sulfur decreases PM linearly (up to a point – sulfur is not the only source of PM) in almost all engines. For this reason, and to enable some exhaust after treatment devices, the European Union limited diesel sulfur content to 10 ppm in 2009. At the moment, it is allowed in Ukraine to use diesel fuel with sulfur content being as high as 50 ppm.

Hydrocarbon emissions can be either unburned or partially burned fuel molecules and can come from several sources. At ignition, some of the vaporized fuel will already be in a region that is too lean for it to burn and, unless it burns later in the cycle, this fuel will be emitted. The cylinder walls and “crevice” regions around the top of the piston edge and above the rings are much cooler than the combustion gases and tend to quench flames as they encroach. Thus, fuel at the cylinder wall can contribute to HC emissions. Fuel that does not vaporize during a cold start makes up the white smoke seen under this condition. A small amount of fuel can also dissolve in the thin film of lubricating oil on the cylinder wall, be desorbed in the expansion stroke, and then emitted. However, since diesel engines operate at an overall lean fuel-air ratio, they tend to emit low levels of hydrocarbons.

Carbon monoxide CO is a result of incomplete combustion. It mostly forms in regions of the cylinder that are too fuel-rich to support complete combustion; although, it may also originate at the lean limit of combustible fuel-air mixtures. If temperatures are high enough, the CO can further react with oxygen to form CO_2. Because diesel engines have excess oxygen, CO emissions are generally low.

A modern diesel engine that has been well maintained emits much less smoke and other pollutants than older engines. This section looks at some of the approaches taken to reduce diesel engine emissions.

The design of the combustion system is the most important factor in determining emissions. Fuel plays a secondary, but still significant, role. Many advances in combustion system design in recent years have led to a reduction in the formation of emissions including:

- Higher Injection Pressures. This leads to better atomization and smaller fuel droplets, which vaporize more readily than larger droplets.
- Careful Injection Targeting. The position and angle of the injecttor in the cylinder head and the design of the nozzle are optimized to minimize emissions.
- Charge Shaping. The rate of fuel (charge) injection can be controlled deliberately (shaped) during injection to achieve desired effects. For example, a small amount of fuel can be injected early and allowed to ignite before the rest of the charge is injected. Early injection acts like a pilot light for the main injection. Other strategies are also used and they are optimized for each engine design.
- More Air Motion. The cylinder head, air intake valve, and piston head are designed to provide optimal air motion for better fuel-air mixing.
- Charge Cooling (Forced Air Induction Engines). Most diesel engines employ supercharging or turbocharging in order to increase the maximum power. In these designs, an engine-driven or an exhaust-driven pump is used to force more air into the cylinders by compressing it. Compressing or pressurizing the intake air also heats it. Since NOx formation is very sensitive to temperature, this also tends to increase

NOx emissions. However, this effect can be mitigated by cooling the intake air by passing it through a heat exchanger after it has been compressed by the supercharger or turbocharger, before it enters the engine cylinder.

- Lower Oil Consumption. Diesel engines partially burn some of the crankcase lubricating oil that seeps past the piston rings into the combustion chamber. New designs minimize oil seepage.
- Exhaust Gas Recirculation (EGR). The formation of NO_x is strongly affected by the temperature in the combustion chamber. This temperature can be reduced somewhat by diluting the reaction mixture with an inert gas. The maximum temperature of the combustion gas is reduced because some of the heat generated by combustion must be used to heat this inert gas. Since engine exhaust is essentially inert, it can be used for this purpose. EGR circulates a portion of the exhaust gas back to the air intake manifold. The reduction in NO_x is accompanied by a small loss of power.

In addition to these changes to minimize the production of pollutants, there are also exhaust after treatment systems designed to remove pollutants from the exhaust gas.

To provide reliable and efficient operation of technology diesel fuels have to meet the following technical requirements:

- a sufficient raw material resource for production;
- providing timely ignition and normal combustion in a combustion chamber;
- low tendency to deposit formation;
- satisfactory compatibility with constructional materials;
- sufficient pumpability and uninterrupted supply of fuel to combustion chamber at low temperature conditions;
- satisfactory physical and chemical stability:
- good ecological properties.

Questions for self-control

1. How are fuels for diesel engines are classified?
2. Characterize main stages of diesel fuel production.
3. Describe hydrocarbon composition of diesel fuel.
4. Name operation properties of diesel fuel.
5. Describe the principle of diesel engine operation

6. What does diesel fuel cetane number mean?
7. Name main types of diesel fuel additives.
8. Describe diesel fuel environmental effects.
9. What are the technical requirements to diesel fuels?
10. What are the methods to reduce emissions from diesel engines?

Chapter 6.
CHEMMOTOLOGY OF OILS

Lubricants play a vital role in every industry including electronic, automotive, aerospace, forestry, naval, and numerous others. Lubrication failure may result in millions of hryvnas of production losses including downtime and equipment failure. Therefore, the general area of lubrication is one of the most important in industrialized societies.

6.1. Functions of oils

Regardless of application all oils perform the following basic functions:

- reduce friction between the contacting details, reduce their wear and prevent tearing;
- take away heat from heated details of machines and mechanisms;
- perform protective functions, preventing corrosive influence of external environment on friction surfaces.

The engine includes number of parts through which the engine oil flows (Fig. 6.29).

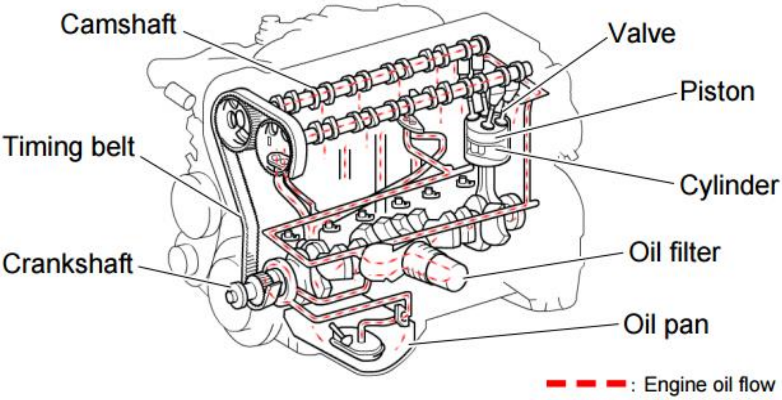


Fig. 6.29. The principle scheme of engines which motor oils flows

The five functions of engine oil are:

1. To lubricate – it requires maintenance of a slippery surface between moving parts. It is often referred to as «oiliness». This oil film must adhere very tenaciously to metal surfaces. Unfortunately, there is no laboratory procedure to fully measure these properties. Actual use in the engine is the only way to evaluate the oil's ability to lubricate.

2. To seal – immediately following the burning of fuel in the combustion chamber of the engine, the gases formed are under high pressure. It is the pressure of these gases on the piston-head which is transmitted to working horsepower. It is necessary to keep these gases from leaking through the pistons and valves (Fig. 6.30). The oil acts as a sealant. If the oil thins out too much, the gases blow by. The oil must resist excessive thinning.

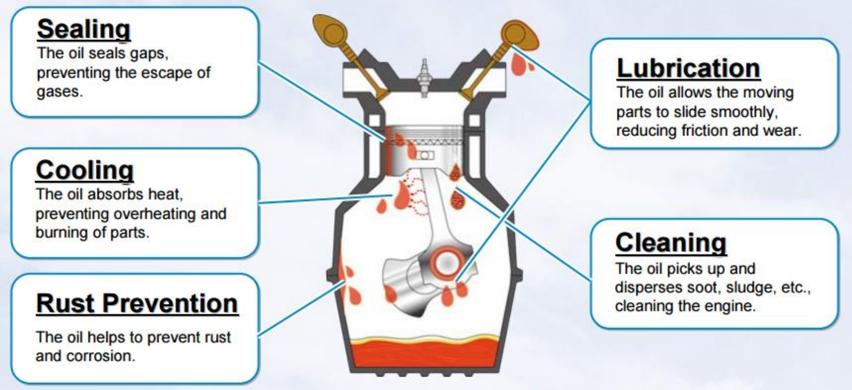


Fig. 6.30. Functions of Engine Oil

3. To cool – although the cooling system removes much of the heat from an engine, the oil must also remove a large quantity of heat. The oil can reach higher temperature than the cooling system fluid.

4. To clean – a variety of waste products are formed as fuel is burned in an engine. The type of fuel and the conditions of combustion influence the nature and quantity of these waste materials. Some of the most troublesome waste materials include water, soot, carbon, lead salts and acids. Many of these materials tend to remain in the engine and contaminate the oil. Unless these contaminants are held in a state of dispersion – so they may be removed when the oil is drained – they will

contribute to the formation of harmful and power-robbing deposits. Helping to keep an engine clean is a very important function of oil.

5. To prevent rust – protection of metal constructions from corrosion (protective properties).

6.2. Types and composition of oils

All lubricating oils are classified according to two main characteristics:

a) *origin* (or method of production) – oils are subdivided into mineral (petroleum origin), synthetic and mixed (compounded) oils;

b) *application* **–** lubricating oils are subdivided into motor (for piston internal combustion engines), gas turbine, transmission, energetic, industrial oils, and oils of other purpose (compressor, cylinder, refrigerating, turbine, oils for hydromechanical transfers, axial, electric insulation, watchmakers', transformer oils etc).

The **mineral-based oils** are more widely used than the synthetic oils and may be used in automotive engines, railroad and truck diesel engines, marine equipment, jet and other aircraft engines, and smallest 2- and 4-stroke engines. The mineral-based oils contain hundreds to thousands of hydrocarbon compounds, including a considerable fraction of nitrogen- and sulfur-containing compounds.

The hydrocarbons are mainly mixtures of straight and branched chain hydrocarbons (alkanes), cycloalkanes, and aromatic hydrocarbons. Polynuclear aromatic hydrocarbons (and the alkyl derivatives) and metal-containing constituents are components of motor oils and crankcase oils, with the used oils typically having higher concentrations than the new unused oils. Typical carbon number chain lengths range from C_{15} to C_{50}.

A synthetic lubricant is a product that is made from a chemical reaction (synthesis) of two or more simpler chemical compounds and also containing the necessary operation additives. The base stocks that form a synthetic lubricant are tailored through molecular restructuring in order to meet specific physical and chemical characteristics.

Synthetic oil is a lubricant consisting of chemical compounds, which are artificially made (synthesized) from compounds other than crude oil (petroleum). Synthetic oil is used as a substitute for lubricant refined from petroleum when operating in extremes of temperature, because it generally provides superior mechanical and chemical properties than those found in conventional mineral oils. Aircraft turbines, for example, require the use of synthetic oils, whereas aircraft piston engines don't.

Some of the most common synthetic lubricants are listed below:

- Polyglycol fluids – polyalkylene glycol, polyglycol ethers, polyalkalylene glycol ethers;
- Silicones;
- Esters: diesters (dibasic acid esters);
- Esters: polyolesters (neopentyl polyesters);
- Polymerized alpha olefin: polyalphaolefin, olefin polymers, olefin oligomers;
- Alkylated aromatics – dialkylbenzenes;
- Phosphate esters.

There are many other types of synthetic lubricants and chemical variations of these synthetic lubricants. There is also no specific synthetic lubricant that is superior in all respects, although a particular synthetic lubricant may possess certain specific advantages for a specific application.

Semi-synthetic oils (also called “synthetic blends”) are blends of mineral oil with up to 30 % synthetic oil. They are formulated to have many of the benefits of synthetic oil without matching the cost of pure synthetic oil.

The international standard ISO 6743.0 defines 18 groups of lubricants.

Commercial grade oil is oily basis (base oil), which is supplemented with additives or additions of different functional purposes. Raw material for the production of oils is fuel oil, petroleum tar, petroleum semitar, which are remaining fractions of crude oil processing (Fig. 6.31).

Base oils are divided into:

- **mineral** – they are produced as a result of crude oil processing;
- **synthetic** – they are produced as a result of chemical reactions, which results in formation of the same molecules of organic substances with necessary properties;
- **semi-synthetic** – they are produced as a result of mixing mineral and synthetic base oils.

Share of synthetic components in oil can make up to 25–50 %.

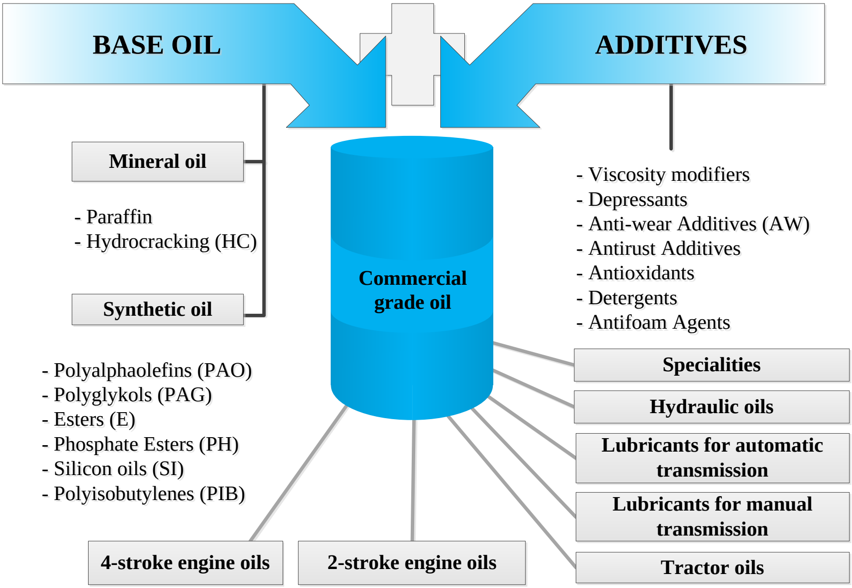


Fig. 6.31. The principle scheme of the production of motor oils

6.3. Classification of motor oils

There are following modern classifications of motor oils:

- SAE (Society of Automotive Engineers);
- API (American Petroleum Institute);
- ACEA (Association des Constracteuis Europeen des Automobiles (European Automobile Manufacturers Association), which have substituted since 1996 CCMC (European Cars Common Market Committee);
- ILSAC (International Lubricant Standardization and Approval Committee) – common American-Japanese classification);
- MIL-L (specifications of the USA Military department);

The basic indices, used in the International classification of motor oils, are:

1. the level of operating properties according to the API standards (American Petroleum Institute);
2. the class of viscosity according to the SAE system (Society of Automobile Engineers), which subdivides oils into **summer** (for

example SAE 30), **winter** (for example SAE 5W) and **multigrade** (for example SAE 15W/30).

6.3.1. API classification

Today the API system (ASTM D 4485, SAE J 183 APR 96) has established three categories of operational purpose and quality of motor oils:

- category «S» (Service) – oils for 4-cycle gasoline engines (Fig. 6.32, Table 6.20);
- category «C» (Commercial) – oils, intended for diesels motor transport, road-building technique and agricultural machines (Fig. 6.33, Table 6.21);
- category «EC» (Energy Conserving) is energy saving engine oils. New range of high-quality engine oils, which consists of low viscous, which diminish the expense of fuel.

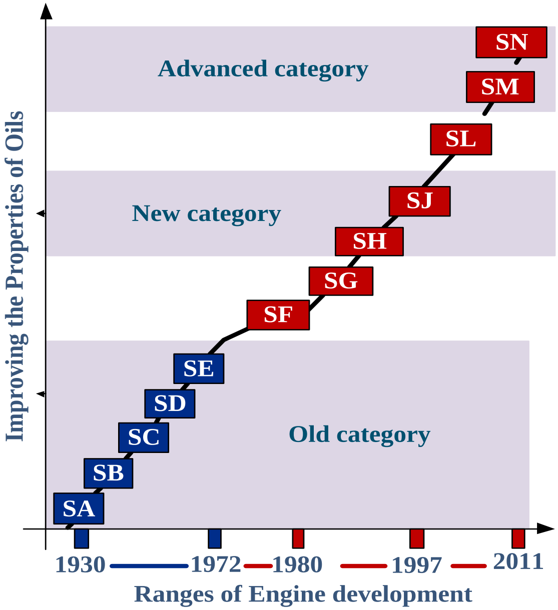


Fig. 6.32. API Classification. Category S (gasoline engines)

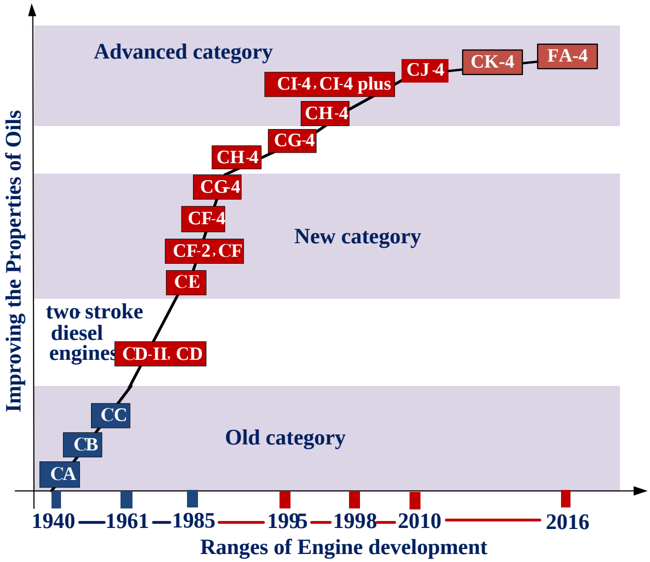


Fig. 6.33. API Classification. Category C (diesel engines)

Table 6.20

API Classification

Group of operating properties – S (for spark ignition (gasoline) engines)		
1	*2*	*3*
Category	Status	Application purpose
SN	Current	Introduced in October 2010, designed to provide improved high temperature despite protection for pistons, more stringent sludge control, and seal compatibility. API SN with resource Conserving matches ILSAC GF-5 by combining API SN performance with improved fuel economy, turbocharger protection, emission control system compatibility, and protection of engine operating on ethanol fuels up to E85.

1	*2*	*3*
SM	Current	For all automotive engines currently in use. Introduced in 2004, SM oils are designed to provide improved oxidation resistance, improved deposit protection, better wear protection, and better low-temperature operation over the life of the oil. Some SM oils may also meet the latest ILSAC specification and/or qualify as Energy Conserving For 2010 and older automotive engines.
SL	Current	For 2004 and older automotive engines.
SJ	Current	For 2001 and older automotive engines.
SH	Obsolete	For 1996 and older engines (which meet the high requirements in relation to diminishing losses from evaporation, filtration, foaming, flash temperature).
SG	Obsolete	For 1993 and older engines.
SF	Obsolete	For 1988 and older engines (free of Pb).
SE	Obsolete	Not suitable for use in gasoline-powered automotive engines built after 1979.
SD	Obsolete	Not suitable for use in gasoline-powered automotive engines built after 1971. Use in more modern engines may cause unsatisfactory operation or equipment harm.
SB	Obsolete	Not suitable for use in gasoline-powered automotive engines built after 1951. Use in more modern engines may cause unsatisfactory operation or equipment harm
SA	Obsolete	Contains no additives. Not suitable for use in gasoline-powered automotive engines built after 1930. Use in more modern engines may cause unsatisfactory operation or equipment harm.

Table 6.21

API Classification

Group of operating properties – C (for compression ignition (diesel) engines)		
1	*2*	*3*
Category	Status	Application purpose
FA-4	Advanced	Introduced on December 1, 2016. For use in select high-speed four-stroke cycle diesel engines designed to meet 2017 model year on-highway GHG emission standards. These oils are formulated for use in on-highway applications with diesel fuel sulfur content up to 15 ppm (0,0015 %). API FA-4 oils are blended to a HTHS viscosity range of 2,9 cP–3,2 cP to assist in reducing GHG emissions. These oils are especially effective at sustaining emission control system durability where particulate filters and other advanced aftertreatment systems are used. API FA-4 oils are designed to provide enhanced protection against oil oxidation, viscosity loss due to shear, and oil aeration as well as protection against catalyst poisoning, particulate filter blocking, engine wear, piston deposits, degradation of low- and high-temperature properties, and soot' related viscosity increase. API FA-4 oils are neither interchangeable nor backward compatible with API CK-4, CJ-4, CI-4 with CI-4 PLUS, CI-4, and CH-4 oils. API FA-4 oils are not recommended for use with fuels having greater than 15 ppm sulfur.
CK-4	Advanced	Introduced on December 1, 2016. For use in high-speed four-stroke cycle diesel engines designed to meet 2017 model year on-highway and Tier 4 non-road exhaust emission standards as well as for previous model year diesel engines. These oils are formulated for use in all applications with diesel fuels ranging in sulfur content up to 500 ppm (0,05 % by weight). However, the use of these oils with greater than 15 ppm (0,0015 % by weight) sulfur fuel

1	*2*	*3*
		may impact exhaust aftertreatment system durability and/or oil drain interval. API CK-4 oils exceed the operation criteria of API CJ-4, CI-4 with CI-4 PLUS, CI-4, and CH-4 and can effectively lubricate engines calling for those API Service Categories.
CJ-4	Current	Introduced in 2006. For high-speed, four-stroke engines designed to meet 2007 model year on-highway exhaust emission standards. CJ-4 oils are compounded for use in all applications with diesel fuels ranging in sulfur content up to 500 ppm (0,05 % by weight). However, use of these oils with greater than 15 ppm (0,0015% by weight) sulfur fuel may impact exhaust after treatment system durability and/or oil drain interval. CJ-4 oils are effective at sustaining emission control system durability where particulate filters and other advanced after treatment systems are used. Optimum protection is provided for control of catalyst poisoning, particulate filter blocking, engine wear, piston deposits, low and high-temperature stability, soot handling properties, oxidative thickening, foaming, and viscosity loss due to shear. API CJ-4 oils exceed the performance criteria of API CI-4 with CI-4 PLUS, CI-4, CH-4, CG-4 and CF-4 and can effectively lubricate engines calling for those API Service Categories.
CI-4 PLUS	Current	New operating class of engine oils. Comparing to API CI-4 they meet the enhanced requirements to specific content of soot, and also evaporated and high temperature stability (models after 2007).
CI-4	Current	Introduced in 2002. For high-speed, four-stroke engines designed to meet 2004 exhaust emission standards implemented in 2002. CI-4 oils are formulated to sustain engine durability where exhaust gas recirculation (EGR) is used and are intended for use with diesel fuels ranging in sulfur content up to 0,5 % weight. Can be used in place of CD, CE, CF-4, CG-4, and CH-4 oils. Some CI-4 oils may also qualify for the CI-4 PLUS designation.

1	*2*	*3*
CH-4	Current	Introduced in 1998. For high-speed, four-stroke engines designed to meet 1998 exhaust emission standards. CH-4 oils are specifically compounded for use with diesel fuels ranging in sulfur content up to 0,5% weight. Can be used in place of CD, CE, CF-4, and CG-4 oils.
CG-4	Obsolete	Introduced in 1995. For severe duty, high-speed, four-stroke engines using fuel with less than 0,5 % weight sulfur (content of sulfur in the fuel is 0,05–0,5 %). CG-4 oils are required for engines meeting 1994 emission standards. Can be used in place of CD, CE, and CF-4 oils.
CF-4	Obsolete	Introduced in 1990 (models of 1994 and later). For high-speed, four-stroke, naturally aspirated and turbocharged engines. Can be used in place of CD and CE oils.
CF	Obsolete	Introduced in 1994. For off-road, indirect-injected and other diesel engines including those using fuel with over 0,5 % weight sulfur. Can be used in place of CD oils.
CE	Obsolete	Introduced in 1985 (models of 1983 and later). For high-speed, four-stroke, naturally aspirated and turbocharged engines. Can be used in place of CC and CD oils.
CD-II	Obsolete	Introduced in 1985. For two-stroke cycle engines with high supercharge, which work in hard operating conditions on high-sulfured fuel.
CD	Obsolete	Introduced in 1955. For certain naturally aspirated and turbocharged engines which work in hard operating conditions on high-sulfured fuel.
CC	Obsolete	For use in diesel-powered engines built after 1990 (models of 1961 and later).
CB	Obsolete	For use in diesel-powered engines built after 1961 (models of 1949 and later, which work under enhanced loadings on sulfured fuel).
CA	Obsolete	Not suitable for use in diesel-powered engines built after 1959 (which work at moderate loadings on low-sulfur fuel).

Energy Conserving in conjunction with API Service Category SJ and more modern. API Service Category SJ oils, categorized as Energy Conserving, are formulated to improve fuel economy of passenger cars, sports utility vehicles, vans and light-duty trucks, powered by gasoline engines.

API Engine Service Classification System has developed since 1969 as a result of joint work of API, ASTM and SAE. The system is included into the standards of ASTM D 4485 «Standard Performance Specification for Performance of Engine Oils» and SAE J183 APR96 «Engine Oil Performance and Engine Service Classifications (Other than «Energy Conserving»).

A new high-quality step in the development of quality and classification of engine oils was done in 1983–1992, when under the guidance of the API and participation of representatives of automobile (AAMA), engines (EMMA) manufacturers and technical unions (ASTM and SAE), the new «system of licensing and certification of engine oils of EOLCS» (Engine Oil Licensing and of Certification System, API Publication № 1509) was created and developed. This system is being constantly perfected. At the moment certification of engine oils is conducted in obedience to the requirements of EOLCS and «Set of Rules of SMA» (SMA Code of Practice).

All the current gasoline categories (including the obsolete SH), have placed limitations on the phosphorus content for certain SAE viscosity grades (the xW-20, xW-30) due to the chemical poisoning effect that phosphorus has on catalytic converters. Phosphorus is a key anti-wear component in motor oil and is usually found in motor oil in the form of zinc dithiophosphate (ZDDP). Each new API category placed successively lower phosphorus and zinc limits, and thus created a controversial issue of obsolescent oils needed for older engines, especially engines with sliding tappets. Because of this, there are oils out in the market place with higher than API allowed phosphorus levels.

Most engines built before 1985 have the flat/cleave bearing style systems of construction, which is sensitive to reducing zinc and phosphorus. For example, in API SG rated oils, this was at the 1200–1300 ppm level for zinc and phosphorus, where the current SM is under 600 ppm. This reduction of anti-wear chemicals in oil has caused premature failures of camshafts and other high pressure bearings in many older automobiles and has been blamed for pre-mature failure of the oil pump drive/cam position sensor gear that is meshed with camshaft gear in some modern engines.

6.3.2. SAE Classification

The most widely used system for engine oil viscosity classification is that established by the SAE in the USA. In this system two series of viscosity grades are defined – those containing the letter «W» and those without the letter «W». Grades with the letter «W» are intended for use at lower temperatures and are based on a maximum low temperature viscosity and a maximum borderline pumping temperature, as well as a minimum viscosity at 100 °C (Fig. 6.34).

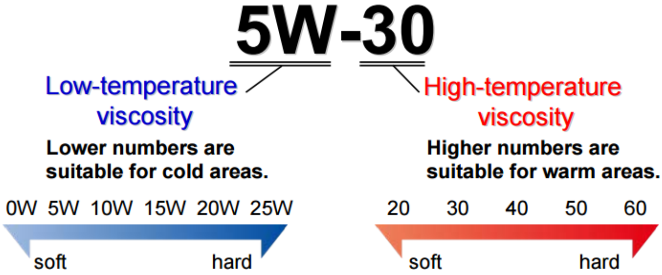


Fig. 6.34. SAE viscosity notation

The low temperature viscosity is measured by means of a multi-temperature version of ASTM D 2602 «Method of Test for Apparent Viscosity of Motor Oils at Low Temperature Using the Cold Cranking Simulator». Viscosities measured by this method have been found to correlate with engine speeds developed during low temperature cranking.

Borderline pumping temperature is measured according to ASTM D 3829 «Standard Method for Predicting the Borderline Pumping Temperature of Engine Oil». This provides a measure of an oils' ability to flow to the engine oil pump inlet and provide adequate engine oil pressure during the initial stages of operation.

Oils without the letter «W», intended for use at higher temperatures, are based on the viscosity at 100 °C only. These are measured by ASTM D 445 «Method of Test for Kinematic Viscosity of Temperature and Opaque Liquids».

«Multi-grade» oil is one whose low temperature viscosity and borderline temperature satisfy the requirements of one of the «W» grades and whose viscosity at 100 °C is within the stipulated range of one-W-grades.

The most complete description of oil viscous-temperature properties correspondence to the requirements of engines is presented in the SAE J 300 classification which is widely accepted at international level. It describes 6 winter engine oils (0W, 5W, 10W, 15W, 20W, 25W) and five summer classes of viscosity (20, 30, 40, 50 and 60).

Winter classes have the letter «W» in denotation, as the first letter of the word «winter». The higher the number, which is included in denotation of class, the higher the viscosity of oils, which belong to this class. A multigrade oil is marked with the double number, the first of which specifies the minimum values of oil dynamic viscosity at negative temperatures and guarantees starting properties, and the second determines the proper class of viscosity of summer oil at 100 °C and dynamic viscosity at 150 °C.

In 1996 the European Automobile Manufacturers Association created new more differentiated and wide classification of the ACEA in place of obsolete CCMC classification. (Fig. 6.35). In particular, it includes special oils with high level energy saving properties. The main differences between these classifications are in the requirements to physical and chemical indexes, determined with laboratory methods. CCMC Classification set only certain SAE classes of viscosity for oils of each class.

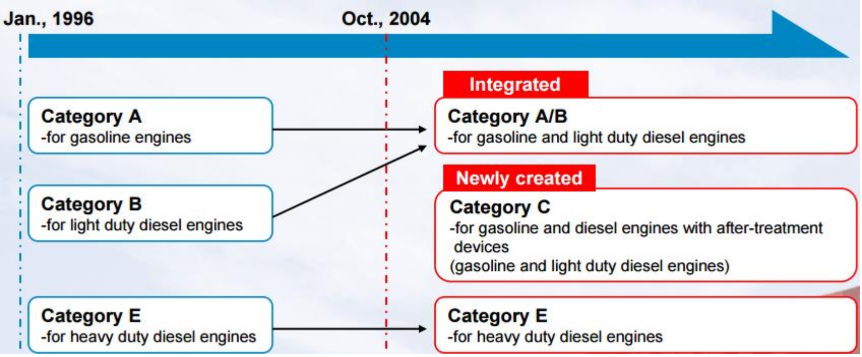
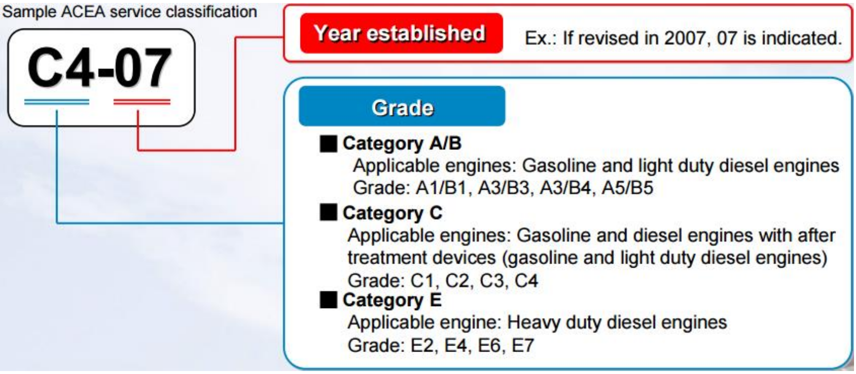


Fig. 6.35. Progression of ACEA service classifications

The ACEA classification authorizes production and use of oils of any viscosity classes by the SAE, if their resistance to mechanical destruction, dynamic viscosity at 150 °C and gradient of shear rate 10^6 sec^{-1} (10 to the sixth power of an inverse second) meet the requirements.

This classification system is the European equivalent of the API classification system, but is stricter and has more severe requirements. Hence oil that meets both API and ACEA specifications uses a better additive package than one that is designed to meet only API specifications. Unlike the API, ACEA has three main groups – «A/B» for gasoline and light duty (passenger car, 4WD etc.) diesel engines, «C» for light duty three way catalyst (TWC) and diesel particulate filter (DPF) compatible oils and «E» for heavy duty diesel engines (Fig. 6.36, Table 6.22).



Ex.: If revised in 2007, 07 is indicated.

■ **Category A/B**
Applicable engines: Gasoline and light duty diesel engines
Grade: A1/B1, A3/B3, A3/B4, A5/B5

■ **Category C**
Applicable engines: Gasoline and diesel engines with after treatment devices (gasoline and light duty diesel engines)
Grade: C1, C2, C3, C4

■ **Category E**
Applicable engine: Heavy duty diesel engines
Grade: E2, E4, E6, E7

Fig. 6.36. ACEA classification for gasoline and diesel engine oils

The classification of «ACEA European Oil Sequences for Service Fill Oils 2008» ACEA 2008 European Oil Sequences for Service-fill Oils comprise 3 sets (classes) of sequences: one for Gasoline and Light-Duty Diesel engines; one specifically for Gasoline and Light-Duty Diesel engines with after treatment devices and one for Heavy-Duty Diesel engines. Within each of these sets there are categories which reflect different operation requirements – four (A1/B1, A3/B3, A3/B4 & A5/B5) for gasoline and light-duty diesel engines; four (C1, C2, C3, C4) specifically for engines with after treatment devices, and four (E4, E6, E7, E9) for heavy-duty diesel engines.

Table 6.22

ACEA Classification

«ACEA 2008 European Oil Sequences for Service-Fill Oils»	
A/B: gasoline and diesel engine oils	
1	*2*
A1/B1	Stable, stay-in-grade oil intended for use at extended drain intervals in gasoline engines and car & light van diesel engines specifically designed to be capable of using low friction low viscosity oils with a high temperature / high shear rate viscosity of 2,6 mPa·s for xW/20 and 2,9 to 3,5 mPa·s for all other viscosity grades.
A3/B3	Stable, stay-in-grade oil intended for use in high performance gasoline engines and car & light van diesel engines and/or for extended drain intervals where specified by the engine manufacturer, and/or for year-round use of low viscosity oils, and/or for severe operating conditions as defined by engine manufacturer.
A3/B4	Stable, stay-in-grade oil intended for use in high performance gasoline and directinjection diesel engines, but also suitable for applications described under A3/B3.
A5/B5	Stable, stay-in-grade oil intended for use at extended drain intervals in high performance gasoline engines and car & light van diesel engines designed to be capable of using low friction low viscosity oils with a High Temperature High Shear (HTHS) viscosity of 2,9 to 3,5 mPa·s.
C: Catalyst compatibility oils	
C1	Stable, stay-in-grade oil intended for use as catalyst compatible oil in vehicles with Diesel Particulate Filter (DPF) and Three-Way Catalyst (TWC) in high performance car and light van diesel and gasoline engines requiring low friction, low viscosity, low SAPS oils with a minimum HTHS viscosity of 2,9 mPa·s. These oils will increase the DPF and TWC life and maintain the vehicles fuel economy.

1	*2*
C2	Stable, stay-in-grade oil intended for use as catalyst compatible oil in vehicles with DPF and TWC in high performance car and light van diesel and gasoline engines designed to be capable of using low friction, low viscosity oils with minimum HTHS viscosity of 2,9 mPa·s. They increase the DPF and TWC life and the vehicles fuel economy.
C3	Stable, stay-in-grade oil intended for use as catalyst compatible oil in vehicles with DPF and TWC in high performance car and light van diesel and gasoline engines, with a minimum HTHS viscosity of 3,5 mPa·s. These oils will increase the DPF and TWC life.
C4	Stable, stay-in-grade oil intended for use as catalyst compatible oil in vehicles with DPF and TWC in high performance car and light van diesel and gasoline engines requiring low Stands for Sulfated Ash, Phosphorus and Sulfur (SAPS) oil with a minimum HTHS viscosity of 3,5 mPa·s. These oils will increase the DPF and TWC life.
E: Heavy Duty-Diesel engine oils	
E4	Stable, stay-in-grade oil providing excellent control of piston cleanliness, wear, soot handling and lubricant stability. It is recommended for highly rated diesel engines meeting Euro I, Euro II, Euro III, Euro IV and Euro V emission requirements and running under very severe conditions, e.g. significantly extended oil drain intervals according to the manufacturer’s recommendations. It is suitable for engines without particulate filters, and for some Exhaust Gas Recirculation (EGR) engines and some engines fitted with Selective Catalytic Reduction (SCR) NO_x reduction systems.
E6	Stable, stay-in-grade oil providing excellent control of piston cleanliness, wear, soot handling and lubricant stability. It is recommended for highly rated diesel engines meeting Euro I, Euro II, Euro III, Euro IV and Euro V emission requirements and running under very severe conditions, e.g. significantly extended oil drain intervals according to the manufacturer’s recommendations. It is suitable for EGR engines, with or without particulate filters, and for engines fitted with SCR NO_x reduction systems. E6 quality is strongly recommended for engines fitted

1	*2*
	with particulate filters and is designed for use in combination with low sulphur diesel fuel.
E7	Stable, stay-in-grade oil providing effective control with respect to piston cleanliness and bore polishing. It further provides excellent wear control, soot handling and lubricant stability. It is recommended for highly rated diesel engines meeting Euro I, Euro II, Euro III, Euro IV and Euro V emission requirements and running under severe conditions, e.g. Extended oil drain intervals according to the manufacturer’s recommendations. It is suitable for engines without particulate filters, and for most EGR engines and most engines fitted with SCR NO_x reduction systems.
E9	Stable, stay-in-grade oil providing effective control with respect to piston cleanliness and bore polishing. It further provides excellent wear control, soot handling and lubricant stability. It is recommended for highly rated diesel engines meeting Euro I, Euro II, Euro III, Euro IV and Euro V emission requirements and running under severe conditions, e.g. extended oil drain intervals according to the manufacturer’s recommendations. It is suitable for engines with or without particulate filters, and for most EGR engines and for most engines fitted with SCR NO_x reduction systems. E9 is strongly recommended for engines fitted with particulate filters and is designed for use in combination with low sulphur diesel fuel.

The following companies are included in the ACEA association: BMW, Volkswagen, Daimler-Crysler, MAN, Porshe, Volvo, Renault, SAAB-Scania, Rolls-Royce, Fiat, RVI, Ford-Europe, Rover, Iveco, DAF, GM-Europe.

6.3.3. ILSAC Classification

Classification of **ILSAC** (International Lubricant Standardization and of Approval Committee) spreads only on oils for petrol engines. The American Automobile Manufacturers Association (AAMA) and Japan Automobile Manufacturers Association (JAMA) jointly created International Lubricant Standardization and Approval Committee – ILSAC.

This classification contains an obligatory requirement of presence of energy saving properties (Fig. 6.37). These are light multigrade oils with winter properties SAE 0W, 5W or 10W. The levels of operating properties of the ILSAC classes are identical to the API classes: GF-1 – SH, GF-2 – SJ, GF-3 – SL, GF-4 – SM, GF-5 – SN.

The oils of GF-4 category have requirement of reduce content of sulphur and phosphorus to provide their compatibility with catalytic neutralizers of exhaust gases. Contents of sulphur in oils of viscous classes 0WX and 5WX must not exceed 0,5 %, and 0,7 % for classes 10WX. Content of phosphorus is limited to 0,06–0,08 %. Oils of this category are less inclined to formation of high temperature deposits.

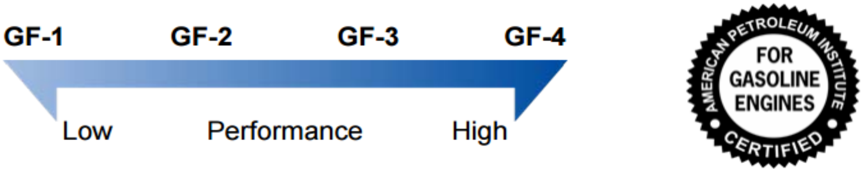


Fig. 6.37. ILSAC classifications for gasoline engine oils

Advantage of ILSAC GF-5 over GF-4 is in possibility to work with biofuel, improved protection from wearing and corrosion, higher fuel efficiency, improved compatibility with sealing materials and increased protection from sludge formation.

ILSAC grades only apply to viscosities XW-20 and XW-30. GF-4 has introduced a phosphorus limit of 0,08 % maximum and a sulphur limit of 0,2 % maximum, GF-5 is similar, but it introduced new requirements relating to phosphorus volatility and compatibility with ethanol fuels.

The ILSAC GF-6 specification is currently in development and will probably be divided into two sub-specifications. ILSAC GF-6A will be fully backward compatible with ILSAC GF-5, but would offer better fuel economy, better engine protection and improved operation while maintaining durability. ILSAC GF-6B would deliver similar performance as ILSAC GF-5A, but will allow lower viscosity oils like xW-16, taking advantage of the fuel economy benefits offered by the new SAE 16 viscosity grade.

Basic differences of oils after the ILSAC:

- dynamic viscosity is at high temperature and high shear rate (HTHS) from 2,6 to 2,9 mPa;
- small volatility (by NOACK or ASTM);
- good filtration properties at low temperatures (General Motors test);
- low tendency to foam formation (ASTM D892/D6082 sequence I-IV test);
- obligatory fuel conservation (ASTM test, Sequence VIA);
- low content of phosphorus (for prevention of catalyst contamination).

The index MIL is used for specification of the USA military departments:

- MIL-L – intended for oils;
- MIL-G – for plastic lubricants;
- MIL-H – for hydraulic liquids.

ILSAC, API and ACEA specifications require a large range of engine tests and laboratory tests on the oil. Parameters such as high and low temperature wear, oxidation, soot control, oil thickening, deposit control, volatility, stay in grade performance, fuel economy, chemical composition and many others are tested against limits and rated.

To provide reliable and continuous work of engines and other mechanisms, which are lubricated, oils must meet the following technical requirements:

- satisfactory lubricating ability;
- optimum viscosity, sufficient for creation of reliable liquid layer in knots with hydrodynamic lubrication at maximal temperature;
- smooth viscous-temperature characteristics (VTC);
- necessary anti-tearing properties at high temperatures;
- high thermal oxidation stability;
- low corrosive activity;
- low chilling point;
- high flash point;
- narrow factional composition;
- physical homogeneity, that is the absence of mechanical impurities and water;
- low tendency to foam formation.

6.3.4. Permits of automobile firms

Every member of ACEA in addition to united requirements to oils classification may establish its own specific claims through increase of requirements or introduction of additional tests in the engines of own construction. Such additional requirements are laid out in brand name specifications on engine oils.

Permits, which determine possibility of application of motor oil in the engines of the brands BMW, VW, Porsche, is the ground for application of these oils in passenger cars of other producers. Permits of MAN, Volvo, Scania define the best oils for application in the truck engines. And if oil is approved by Mercedes-Benz, which classification includes more than 10 classes – «sheets», it means, that this oil is suitable for application practically in any European engine of this class.

6.4. Aviation oils

The oil system for an aero engine is a full recirculatory system and its main function is to supply oil to the engine's internal drives, gears, and bearings, where the main rotating assemblies are. The oil is used to lubricate these locations and remove all unwanted heat throughout all operating conditions and power settings. The system is designed to ensure that the oil supplied to these drives, gears, and bearings is in the correct condition with regards to cleanliness, pressure, temperature, and quantity. The complete oil system for an aircraft gas turbine can be divided into three main subsystems:

- oil feed, lubrication, and cooling (pressure side);
- return oil (scavenge side);
- breather system (vent).

The architecture of the oil system is designed such that bearing chambers and gear boxes will be at different pressures relative to each other and, therefore, the flow from the pressure system will have to be controlled to ensure each area of the engine receives the correct oil flow. The pressure pump delivers the total oil flow for the whole engine at one pressure and this is distributed around the engine by a network of pipes. Restrictors are placed in oil supply lines upstream of the oil jets. The size of the restrictor is controlled so that the pressure drop across the oil jets is correctly maintained and within a specific range; this ensures adequate targeting and oil velocity.

Finally, before the oil enters the oil jet, it can be passed through a "last chance" filter to ensure that no debris generated downstream of any other filtration system can block the oil jet. This type of filter (or strainer) is usually a screw thread filter and will be built into the engine upstream of the oil jet.

Generally, the circulation of oil is far in excess of the capacity within the system. For example, in a large turbofan engine of approximately 32000 kg of thrust, the nominal oil quantity contained in the oil tank is approximately 23 l, of which approximately 18 l is usable. The complete oil system, including pipes, bearing chambers, and gearboxes, will have a capacity of approximately 36 l in total. To supply the various parts of the engine that need lubricating, the approximate flows required are as follows:

- The oil supply to all the bearing chambers (including any internal gearboxes) is approximately 2800 l/h.
- The oil supply to an external gearbox is approximately 210 l/h.

Therefore, the entire contents of the oil tank circulate around the oil system approximately every 29 s.

Because the design of the engine has different parts of the oil system operating at different oil pressures, all the areas that are supplied with oil will also have their own dedicated oil scavenge pump to recover the oil back to the tank. Generally, the oil scavenge system will be constructed so that there is only one pipe between the sump and each scavenge pump; this prevents recirculation and preferential scavenging.

Generally, the oil that is required for an aero gas turbine will be one of the following: 3,5, or 7,5 CentiStokes (cSt). Each has an application for which it is better suited. The 7,5 cSt oil was developed for the use in turboprop engines as the increase in viscosity gave the oil better load bearing properties, and this allowed it to be used within the reduction gearbox and torque control for the propeller.

Any oil that is to be used in an aero engine normally has to be approved for that engine type before it can be used in service, and one of the relevant manuals for the engine type will contain a list of the approved oils. As well as getting approval from the engine manufacturer, the oil will have to meet internationally recognized specifications, as follows:

- 3 cSt oil will be equivalent to SAE-5;
- 5 cSt oil will be equivalent to SAE 5W10;
- 7,5 cSt oil will equivalent to SAE 5W20.

The most common oil used in service on today's gas turbine engines is the 5 cSt oil since the properties of this oil allow it to cope with the demands of the engine's operation. Normally aero engines will be certified to operate from ambient temperatures of -40 to above 40 ^{o}C and, as part of this, the engine will be required to start at these ambient temperatures, even if the engine and all the systems including the oil have been soaked to the same temperature. Obviously, at very cold temperatures the lubricating oil will be very viscous, anywhere from 8000 to 11000 cSt; therefore, the engine must be able to cope with this kind of viscosity level and start as normal when required.

Pressure pumps can have pressure relief valves fitted to them so that the cold, viscous oil can be recirculated around the pump to speed up heating and prevent excessive oil pressure occurring in other parts of the engine. Normally in these circumstances, the person running the engine from the flight deck will be required to ensure that the oil temperature is above zero (usually 5 ^{o}C) before the engine is accelerated above the idle power level.

The oil for the gas turbine engine will also need to have other properties to suit the environment it is running in, some of which are dependent on its additives. The oil needs to have low volatility; carbon is likely to form only at higher temperatures than for normal running and only if the oil becomes stressed. The flash point, flame point, and auto-ignition point should also be at a high temperature that can cope with the extremes of normal running and above, and still have sufficient margin available to aid aircraft safety.

Gas turbine engines are constructed from many different materials and it is therefore important that the oil used, should not cause any safety issues due to possible reactions, corrosion or failure of components within the oil system. In particular, it must have good elastomer compatibility to prevent damage to any rubber seals which it comes into contact with. Today's high bypass gas turbine engines will be expected to remain installed on an aircraft for at least 20,000+ hours or approximately 5 years, during which time the oil system will be serviced, mainly by replenishment. Good practice in servicing an aero engine is for an airline to operate their fleet on the same brand of oil;

however, this may not always be the case. If an airline's gas turbines need the oil system to be replenished at an airport away from their main base, their usually brand of oil may not be available. In this case, most gas turbine manufacturers will allow the mixing of oil brands provided that the alternative used is on the engine manufacturer's approved list. When mixing of approved oil brands does occur, then the combined fluid must not affect the operation of the oil system, neither should the oil brands react with each other.

6.5. Operation properties

Viscosity. In selecting the best oil viscosity for any application, it is the viscosity at the usual operating temperature, which is most important. However, if the equipment will need to make a cold start, it is also important that the viscosity at starting temperature is low enough for the machine to be started easily. It follows that it is important to know how much the viscosity will change with temperature, which is shown by oil's viscosity index (VI).

The normal range of VI is from 0 to 100, but the measurement range is often extended till much higher values. If oil has a viscosity index of 0, its viscosity changes rapidly with change in temperature. If it has a viscosity index of 100, its viscosity changes less with change in temperature.

Among the mineral oils, the highest natural viscosity index is obtained with paraffinic oils and the lowest with naphthenic oils. Oils having a natural VI above about 80 are called HVI (high viscosity index) oils, and would be classified as Group II. Those with a natural VI below about 30 are LVI (low viscosity index) oils while the intermediate oils are MVI (medium viscosity index) oils, and both would probably be called Group I. Highly refined mineral oils may have a VI as high as 130, and are called VHVI (very high viscosity index) oils. Severely refined oils may have a VI as high as 150 and are called UHVI (ultra-high viscosity index) oils. Both of these would be called Group III oils.

The actual viscosity grade of a lubricant is determined by the Society of Automotive Engineers (Table 6.23), for example SAE-15W40 for a multigrade oil and SAE-40 for a monograde oil.

Table 6.23

Automotive Lubricant Viscosity Grades

SAE	Low Temperature Viscosities		High-Temperature Viscosities		
Viscosity Grade	Cranking (mPa.s) max at temp °C	Pumping (mPa.s) max at temp °C	Kinematic (mm^2/s) at 100 °C		High Shear Rate (mPa.s) at 150°C, 10/s
			min	max	min
0W	6200 at –35	60 000 at –40	3,8	—	—
5W	6600 at –30	60 000 at –35	3,8	—	—
10W	7000 at –25	60 000 at –30	4,1	—	—
15W	7000 at –20	60 000 at –25	5,6	—	—
20W	9500 at –15	60 000 at –20	5,6	—	—
25W	13 000 at –10	60 000 at –15	9,3	—	—
20	—	—	5,6	<9,3	2,6
30	—	—	9,3	<12,5	2,9
40	—	—	12,5	<16,3	2,9
40	—	—	12,5	<16,3	3,7
50	—	—	16,3	<21,9	3,7
60	—	—	21,9	<26,1	3,7

Viscosity is important as it enables us to rank oils and fluids in terms of their relative “thickness” and to define the appropriate “level of thickness” necessary to ensure the presence of an adequate lubricating film in the pump, bearings, or gears throughout the operating temperature range of the equipment, including low temperature start-up capability. It was noted earlier, for example, that military requirements necessitate the use of a low viscosity lubricant for engine start-up in very cold climates. At the other extreme, when using mineral oils in turbines operating in high temperature environments, it may be necessary to use higher viscosity products to achieve adequate lubrication. However, if a lubricant has too high a viscosity, cavitation will occur while too low a viscosity can result in pump slippage and internal leakage.

Pour Point / Low Temperature Storage Stability. In addition to avoiding thickening at low temperatures, either in use or in storage, it is also important to ensure that the fluid in service does not solidify or precipitate. Such behaviour could lead to pumping problems or operational failure. Conventional solvent-refined mineral oils tend to precipitate wax at low temperatures; the hydrocracked products much less so and not at all with PAOs. In comparison, the synthetic esters may, if wet, become turbid at low temperatures and also more viscous in storage. Phosphates normally solidify without precipitation but may also become turbid in the presence of water.

Additive incompatibility at low temperatures can also adversely influence the low temperature behaviour of the oil or fluid and it is mainly for this reason that aviation gas turbine lubricants are tested for extended storage stability.

Acid number. The acidity present in the new oil or fluid arises from two sources:

1. Residual acidity from manufacture (in the case of the ester-based products);
2. From the presence of additives – usually acidic rust inhibitors and/or metal passivators, but also some antioxidants.

A high level of acid in an unused, inhibited, fluid is therefore not necessarily indicative of a poorly processed product or one that has aged significantly in storage. On the other hand, the presence of a high level of acidity can be disadvantageous to surface-active properties, for example foaming and air release. It may cause corrosion and promote oxidation. The level of acid in new, uninhibited, phosphate esters is tightly controlled because this may contain strong acid, with a pH of <4, which can catalyze the hydrolytic degradation process. A low initial acidity in ester-based products therefore ensures good storage stability, a satisfactory condition on filling into the system and a longer operating life. Monitoring this parameter is therefore essential to ensure the trouble-free operation of the system.

Water content. Water is a problem contaminant for all types of fluid. It can be present in either dissolved or dispersed form and, in the case of major contamination, may form a completely separate layer. When the main reservoir contains mineral oil, free water normally falls to the bottom of the tank owing to the different density and requires removal by means of the valve on the tank base or via a sediment drain to the tank side. If the fluid has a density greater than that of water, as in the case of phosphate ester, the free water layer will be on top of the fluid in the tank and should be skimmed or siphoned off. Other methods used for free water removal include centrifugal separation and water absorbing filters. To remove dissolved water, vacuum dehydration is recommended.

Foaming and Air Release. Air is a “contaminant” of every turbine oil and fluid. Whether or not it causes problems it depends largely on whether it is soluble in the oil, or present as dispersed bubbles. System design, circulation rates, fluid cleanliness, etc., are also factors to be considered. Dissolved air is not normally a concern but if it comes out of solution when pressure is reduced locally it may cause pump cavitation. Dispersed air tends to be a problem if it is not readily released from the bulk of the fluid in the tank and compression of the bubbles by the pump does not cause their dissolution. Under such conditions dispersed air can cause a loss of control due to a change in the compressibility of the fluid, result in increased oxidation, and may have an adverse effect on lubrication. Foam is the accumulation of air bubbles surrounded by a thin film of oil and occurs at the surface of the liquid. Air release measurements, by contrast, are made in the bulk of the liquid where a relatively thick film of oil separates the air bubbles.

The ***lubrication performance*** of an oil or fluid can be regarded as its ability to reduce wear on metal surfaces sliding relative to one another under load. It is a combination of the operation of the fluid base stock and the additive package. All the finished fluids discussed so far are acknowledged to have good lubrication performance and for most steam and gas turbine applications there are no additional lubrication operation requirements.

Cleanness. The importance of clean oil, to ensure that small orifices in valves remain clear, that bearing surfaces are undamaged, and that pumps and motors run smoothly, is now well accepted. Dirt can also play a part in catalyzing oil and fluid degradation by stabilizing foam and increasing oxidation. It may also promote emulsification in the presence of water and increase the conductivity of the fluid. Limits on cleanliness have therefore become steadily tighter over the years. At the same time the variety and efficiency of filters has improved.

6.6. Environmental effects

Motor oil breaks down to give a wide variety of oxygenated and aromatic hydrocarbons. Other organic compounds found in waste oil include toluene, benzene, xylenes, and ethylbenzene. Also present are organic and inorganic compounds of chlorine, sulphur, phosphorus, bromine, nitrogen, and metals such as zinc, magnesium, barium, and lead resulting from oil additives and contamination during use or disposal.

Used engine oil is a contaminant of concern, with large volumes entering aquatic ecosystems through water runoff. The major source of petroleum contamination in urbanized estuaries comes from waste crankcase oil. Polyaromatic hydrocarbons (PAHs), heavy metals, additives, antioxidants, and trace levels of chlorinated solvents have been detected in used engine oil. Naphthalene, benz(a)pyrene, fluorene, and phenanthrene are common PAH components of used motor oil.

One of the sources of waste crankcase oils (WCOs) entering the aquatic environment is through improper disposal of used motor oil. Many people change their own car motor oil instead of having it done professionally. Shops that perform oil changes have special receptacles for used motor oil. Many private citizens do not dispose of their used oil properly.

Waste crankcase oils spilled on soil migrate downward by gravity through soil and possibly to groundwater, and spread laterally due to capillary forces and soil heterogeneity. The more water-soluble, lower molecular weight fractions tend to migrate faster than the less soluble, higher molecular weight fractions. The concentrations of constituents of waste crankcase oils decline in soil and groundwater with distance from the spill source because of adsorption by soil, biodegradation, and dilution.

Questions for self-control

1. Name functions of motor oils.
2. How are all lubricating oils classified according to origin?
3. How are all lubricating oils classified according to application?
4. Name most common types of synthetic lubricants.
5. Describe classification of motor oils according to SAE?

6. Describe classification of motor oils according to API?
7. Describe classification of motor oils according to ACE?
8. What are the main purposes of aviation oils?
9. What are the main operation properties of oils?
10. Describe the environmental effects of oils use.

Chapter 7
CHEMMOTOLOGY OF GREASES

Greases are typically used in situations where sufficient lube oil cannot be effectively maintained on machinery surfaces, or when a simplistic lubricating system is desired or required. They also act as sealants to prevent ingress of water and incompressible materials. Grease-lubricated bearings have greater frictional characteristics due to their high viscosity.

Lubricating greases are not simply very viscous lubricating oils. They are lubricating oils, in which thickeners have been dispersed to produce a stable colloidal structure or gel, similar in some respects to an emulsion.

The characteristic feature of greases is that they possess a high initial viscosity, which upon the application of shear, drops to give the effect of an oil-lubricated bearing of approximately the same viscosity as the base oil used in the grease. This change in viscosity is called **thixotropy**. After a shear load is removed, a flow of the grease stops, and structured matrix is quickly renewed, so that grease acquires solid body properties again.

Grease is sometimes used to describe lubricating materials that are simply soft solids or high viscosity liquids, but these materials do not exhibit the shear-thinning (thixotropic) properties characteristic of the classical grease. For example, petroleum jellies such as Vaseline (white oil) are not generally classified as greases.

Lubricating greases have a number of advantages over lubricating fluids. Some of these are:

- Dripping and spattering are nearly eliminated;
- Less frequent applications are required;
- Greases are easier to handle;
- Less expensive seals can be used;
- Greases can form a seal in many cases and keep out contaminants;
- They adhere better to surfaces;
- They reduce noise and vibration;
- Some grease remains even when relubrication is neglected.

Thickener forms a three-dimensional matrix which retains oil. Due to this structure lubricating greases bear both solid and liquid body properties. Thus, greases have an ability to maintain their physical shape for years while being applied with a thick layer on vertical surfaces.

Thus, the thickener determines operational properties of greases. A dispersion medium (oil) has a less significant influence. Additives dissolve in the oil and take an active part in the processes of formation of a grease structure.

A process of grease manufacturing is complex and contains the following stages: raw materials preparation, thickener preparation, thermo-mechanical dispersing of a thickener (grease compounding), product cooling, and other associated processes.

An amount of greases manufactured is relatively small and is about 5 % of all finished lubricants.

Areas of grease application include:

1) open and unsealed friction units;
2) inaccessible friction units;
3) friction units with no frequent lubricant change possible;
4) forced contacts of friction units or protected surface from water or aggressive mediums;
5) sealing of flexible packing, staffing boxes and threaded connection;
6) long-term conservation of machines, equipment, devices and metal items.

Classification system of greases is determined by **ISO 6743.9** standards.

The basis for generalized grease classification is made of three indications:

1. Consistency;
2. Composition (thickener nature);
3. Application.

Based on consistency greases are subdivided to **semisolid, plastic and solid**.

Based on composition greases are subdivided into four groups:

- greases with thickeners being salts of higher carboxylic acids (lithium, sodium, potassium, calcium, barium, aluminum, zinc and lead soaps);
- greases with inorganic thickeners (silica gel, graphite);
- greases with organic thickeners (polymer, pigment, polyurea, soot);
- greases with refractory hydrocarbon thickeners (ceresine, natural and synthetic waxes).

Based on application there are: **anti-friction, anti-wear, conservation, protective, sealing, cable** greases, etc.

A modern classification of greases based on viscosity grade (VG), which has become internationally accepted, has been developed by the National Lubricating Grease Institute (NLGI, USA). According to the NLGI classification, consistency of greases is measured by a special laboratory technique called «work penetration». Thus, 9 categories have been set, which class range from 000 to 6 (Table 7.24).

The nine grades are defined by a range of worked penetration test results. The NLGI grade of each grease is determined using two test apparatus. The first apparatus consists of a closed container and a piston-like plunger. The face of the plunger is perforated to allow grease to flow from one side of the plunger to another as the plunger is worked up and down. The test grease is inserted into the container and the plunger is stroked 60 times while the test apparatus and grease are maintained at a temperature of 25 °C. Once worked, the grease is placed in a penetration test apparatus. This apparatus consists of a container, a specially-configured cone and a dial indicator. The container is filled with the grease and the top surface of the grease is smoothed over. The cone is placed so that its tip just touches the grease surface and a dial indicator is set to zero at this position. When the test starts the weight of the cone will cause it to penetrate into the grease. After a specific time interval the depth of penetration is measured.

000-00 grade NLGI categories belong to very soft lubricating greases with penetration ranging from 400 to 430. They are the best materials for substitution of industrial oils. Soft grease class from 0 to 1 has penetration ranging between 310 and 385. These greases are used for industrial equipment and heavy-duty trucks.

Table 7.24

Definition of NLGI grades

Grade	Penetration range at 25 °C, 0,1 mm (after 60 Strokes)	Visual consistency appearance
000	445–475	Very soft, very viscous oil analogue (fluid)
00	400–430	Very soft, very viscous oil analogue (semi-fluid)
0	335–338	Very soft
1	310–340	Soft
2	265–295	Paste-like («normal» grease)
3	220–250	Almost solid (film)
4	175–205	Solid (very film)
5	130–160	Solid (hard)
6	85–115	Very solid (very hard)

Groups of greases for vehicles servicing and specific requirements for their quality are reviewed in the following standards and recommendations:

- ASTM D 4950-89 «Standard Classification and Specifications for Automotive Service Greases»;
- SAE J310 «Automotive Lubricating Greases»;
- NLGI «Recommendations for service lubrication of passenger car wheel bearings»;
- NLGI «Recommendations for service lubrication of heavy-duty truck wheel ball joints»;
- NLGI «Recommendations for service lubrication of heavy-duty truck wheel bearings».

ASTM D 4950-89, developed by ASTM, NLGI and SAE classification of automotive greases, suggest two service Category Groups: chassis lubricants (letter designation L) and wheel bearing lubricants (letter designation G). These groups are subdivided into automotive greases quality categories based on quality parameters guaranteed and are designated with the corresponding letter (Table 7.25).

NLGI LA category greases are for typical service of chassis components and universal joints in passenger cars, trucks, and other vehicles under mild duty only. These greases should satisfactory lubricate chassis components and universal joints where frequent relubrication is practiced. The greases should resist oxidation and consistency degradation and protect the chassis components and universal joints from corrosion and wear. NLGI 2 consistency greases are commonly recommended.

Table 7.25

Mandatory tests for NLGI category determination

ASTM	Test	LA	LB	GA	GB	GC
D 217	Consistency, worked penetration	+	+	+	+	+
D 566	Dropping point	+	+	+	+	+
D 1264	Water resistance	-	-	-	+	+
D 1742	Oil separation	-	+	-	+	+
D 1743	Rust protection	-	+	-	+	+
D 2266	Wear protection	+	+	-	+	+
D 2596	EP operation	-	+	-	-	+
D 3527	High temperature life	-	-	-	+	+
D 4170	Fretting protection	-	+	-	+	+
D 4289	Elastomer compatibility	+	+	-	+	+
D 4290	Leakage tendencies	-	-	-	+	+
D 4693	Low temperature operation, torque	-	+	+	+	+

7.1. Operation properties

The most important quality parameters of greases include: viscosity; mechanical stability (characterized by shear strength and penetration); thixotropic properties i.e. properties describing structural mechanical (rheological) grease properties; grease stability (thermal, colloidal, chemical, against radiation, against evaporation); resistance to other external factors (table 7.26).

Table 7.26

The main quality parameters of greases

Water resistance	A number of parameters describing solubility, lubricity, hygroscopicity, and water permeability of grease.
Penetration	A parameter that shows a distance of immersing of a standard cone into grease at standard conditions. Unit of measurement is tenth of mm.
Colloidal stability	A parameter that describes an ability of grease to resist separation of oil out of it. Unit of measurement is %.
Ultimate strength	A parameter that indicates critical load (shear stress), which, if increased, causes a rapid transfer of grease to flow as a liquid. Unit of measurement is Pa.
Dropping point	A parameter that indicates grease melting point i.e. the lowest temperature at which a drop of grease falls if heated in Ubbelohde thermometer. Unit of measurement is ^{o}C.
Tribological characteristics	A number of parameters describing anti-wear, antiscuffing and antifrictional properties of grease. These are measured using special friction test machine.

Consistency can be defined as the degree to which a plastic material, such as a lubricating grease, resists deformation under an applied force. It is a measure of the firmness or rigidity of the thickener structure of the grease. The standard method for measuring grease consistency is the penetration test.

The consistency of a grease may change with its history. Some greases may harden with age; others may change due to wide fluctuations in temperature. Evaluation of these changes needs to be on an individual basis. That is, the test grease needs to be subjected to controlled aging or temperature fluctuations, with penetration measurements taken periodically.

The consistency of greases may also change in service due to changes in the size and dispersion of thickener particles resulting from mechanical shearing. The ability of a grease to resist changes in consistency during mechanical working is referred to as consistency stability, shear stability, work stability, or mechanical stability.

Flow Properties. The consistency of a grease is a critical parameter which helps define the ability of a grease to perform under given operating conditions. Consistency, as measured by penetration, is affected by temperature. But the penetration test is not suitable for determining the minor, yet sometimes significant, changes in consistency as the grease approaches temperatures at which phase changes in the thickener occur.

Penetration is basically a flow measurement; in addition, there are other flow-measurement tests that can be utilized to evaluate this property in other conditions.

Grease is by nature a non-Newtonian material. It is characterized by the fact that flow is not initiated until stress is applied. Increases in shear stress or pressure produce disproportionate increases in flow. The term apparent viscosity is used to describe the observed viscosity of greases.

Greases designed for low-temperature applications must not stiffen or offer excessive resistance to rotation. However, greases harden and become more viscous as the temperature is lowered. Sometimes the grease can become so rigid in the bearing that excessive torque is required for rotation. In extreme cases, the grease can solidify to the point of bearing lock-up.

Heat resistance. Heat affects greases in several ways. As the temperature increases, greases soften and flow more readily; oxidation rate increases; oil evaporation increases; the thickener melts or loses its ability to retain oil. Sometimes these phenomena are all involved simultaneously.

The dropping point of a grease is the temperature at which it passes from a semi-solid to a liquid. Although a thickener can have a definite melting point, the resulting grease does not.

Rather, the thickener loses its ability to function as a grease thickener as the temperature is increased. As the temperature is raised, the grease softens to the extent that it loses its self-supporting characteristic, the structure collapses, and the grease flows under its own weight. When this phenomenon takes place in a standard cup under standard conditions, it is called the dropping point.

Greases normally do not perform satisfactorily at temperatures near or above the dropping point; other factors are involved. High-temperature operation can depend on the application method and frequency, whether a softened grease is retained at the point of application by proper seals, and whether the high temperature is continuous or intermittent. High temperature stability and evaporation properties of the grease also can affect operation.

Dropping point is most useful as a quality-control tool. Unless correlation has been established, dropping point has no direct bearing on service performance. Performance at high temperature would be better evaluated with one of the performance-type tests or by actual experience.

Exposure of a grease to high temperatures can cause evaporation of some of the liquid lubricant, thus causing the remaining grease to become drier and stiffer or leading to other undesirable changes in the grease structure. Greases containing low-viscosity oils for good low-temperature operation may be susceptible to evaporation losses at high temperatures. Evaporation also can cause problems when vapors may be hazardous or combustible, or interfere with operations. In most applications, even high-temperature applications, evaporation is not a serious problem because of effective sealing.

Nearly all greases will separate some oil during storage, but they differ markedly in the amounts that are liberated. If a grease separates too much oil, the grease could harden to the extent that lubrication will be affected. Opinions differ on whether or not lubrication depends on oil bleeding; greases that do not separate some oil during operation can be noisy in service. However, excessive liberation of free oil during storage is to be avoided. Oil can be released from a grease at varying rates depending on the gel structure, the nature and viscosity of the lubricating fluid, and the applied pressure and temperature.

Extreme Pressure and Wear. A lubricant’s functions by separating bearing surfaces. If the separation was always complete, parts would never wear. However, the integrity of the lubricant film cannot be maintained under all conditions, and contact occurs to varying degrees. Such contact depends on operating conditions (such as load and speed), lubricant properties (such as fluid viscosity and grease consistency), and lubricant chemistry (such as the presence of wear inhibitors and extreme pressure additives).

Effect of Water. Contamination with water can affect greases and grease operation in several ways. Corrosion or rust protection is one. Other effects include change in consistency, texture, or adhesiveness. An emulsion can be formed, which will probably be an inferior lubricant, or it could be washed away.

Compatibility. Mixing of two different grease types often occurs when a mechanism is service lubricated with a type of grease different from that already in the bearing. If the two greases are incompatible, the likelihood is that lubrication will be inadequate and/or the lubrication life will be greatly shortened.

7.2. Environmental effects

The total percentage of lubricant that is “successfully disposed”, meaning it is either recycled or burned, equals 32 %. The major proportions of lubricant enter the environment in one way or another, mainly due to lubricant use, i.e. ‘consumption'. As far as automotive engine oils are concerned, the results of this consumption can be seen on motor ways, roads and car parks as a black deposit of oil.

Some lubricants are intended for use such that they are “lost to the environment”, examples being two-stroke engine oils, greases and oils used on railways, chainsaw bar lubricants, rubber oils used in tyres, many white oils and so on. Conversely, provided efficient management systems are in place, many industrial oils should be largely contained and thus should not escape into the environment. Accidents, however, inevitably occur and cause the environmental release of almost any and all types of lubricants. A gearbox seal that fails, high-pressure hydraulic lines that fracture and metal parts coated in residual oils all contribute to the 'consumption' of lubricants and add to the environmental burden. In Western Europe alone, the total amount of lubricant that enters the environment can be said to be roughly the equivalent of 12 oil tankers or one "Exxon Valdez" per month.

Three major environmental aspects of lubricants can be addressed:

1. Control, via engineering to minimize losses;
2. Minimizing the impact of these losses;
3. Efficient collection and treatment of waste materials.

In terms of the lubricant, the first is largely a matter for the equipment designer and builder. The specialist lubricant company is affected by the third and can affect the second.

Questions for self-control

1. What does lubricating grease mean?
2. What is the difference between grease and lubricating oil?
3. Name grease advantages over other lubricating oils.
4. Give classification of greases according to ISO 6743.9.
5. What are the main components of greases? What are its’ functions?
6. Name main groups of grease according to composition.
7. Describe definition of NLGI grades of grease.
8. What normative documents do determine requirements to greases?
9. Describe operation properties of grease.
10. Describe environmental effects of greases use.

Chapter 8
CHEMMOTOLOGY OF TECHNICAL LIQUIDS

8.1 Coolants

Part of the heat released during the combustion process in the engine is spent for heating the engine parts. At the same time due to the very high temperature of the combustion chamber walls, engine power is lost because the filling of cylinders is deteriorating. In addition, when the lubrication conditions deteriorate, such processes as detonation, surface ignition, enhanced carbonation and lacking, increased friction and details wearing, etc. occur. To prevent the overheating of details, they should be cooled. Engine cooling system depends on its rapidity and power and consumes 15–35 % of the heat produced by fuel combustion. The quantity of heat produced by gasoline and gas engines is higher than in diesel. Current systems may use liquid or air cooling. The most popular in automobile engines are liquid cooling systems.

In the internal combustion engines, a part of the cooling system filled by fluid is located in block and the cylinder head between the double walls. The main **purpose** of coolant is to remove waste heat from the walls and gives it to the air flowing through the heat exchanger (or radiator).

Coolant is circulating in a closed space of cooling system, being heated by the block and the cylinder head and being cooled in the heat exchanger. To ensure the normal operation of the engine, the coolant must meet certain **requirements**.

The main ones are the following:

- minimal freezing temperature;
- maximal boiling point;
- minimal volumetric expansion coefficients;
- minimal viscosity;
- lack of flammability;
- no foaming;
- physical and chemical stability;
- it should not affect the properties of structural materials;
- high heat capacity and thermal conductivity.

There are no liquids that satisfy all these conditions. The most widely used are water and antifreezes.

Water. The advantages of water:

- availability;
- safety (fire and explosive);
- harmlessness (absence of toxicity);
- high specific heat capacity of 419 kJ/(kg·K).

Disadvantages of water:

- high freezing temperature (≈0 °C);
- 10 % increase in volume of formed ice in comparison with the volume of freezing fluid;
- low boiling point (100 °C);
- sedimentation ability.

Due to the second disadvantage the pressure on the walls may be increased up to 250 MP at low ambient air temperature. This leads to the destruction of the cooling system components.

The third disadvantage can be partially eliminated by pressurizing of the cooling system due to installing of two valves on the radiator tube: air valve and steam valve. In this case, the boiling temperature of water in the cooling system insignificantly increases (≈119 °C). Moreover, this makes it possible to increase the temperature difference in the cooling system and thereby to increase the efficiency of heat exchange processes. As a result, the amount of cooling fluid is reduced, the required surface of the radiator is decreased and the heat losses in coolant are reduced.

The term «scale» is used to describe a dense crystalline deposit formed on the heated walls of the cooling system. It consists of calcium and magnesium salts precipitated from water, suspended corrosion products and mechanical impurities. Slime is considered as the sludge particles and elements of scale destruction of mineral or organic origin that is accumulated in stagnant cavities of the cooling jacket and in lower radiator tank.

Deposits formation in the cooling system reduces the heat transfer from walls of cooling system jacket by 40 %, as the scale has low thermal conductivity. It reduces the cross section of the radiator tubes and all flow sections. As a result, the engine is overheated; this leads to an increase in fuel consumption. The deposits in the cooling system are formed as scale and slime.

Antifreezes. Antifreezes should be poured into the engine cooling system at ambient temperatures below 0 °C, as water freezes at lower temperatures and significantly increases in volume. The mixtures of water with alcohols, water, glycerol, hydrocarbons mixtures are used as antifreezes. The most widely used mixtures are on the diol alcohol base – ethylene glycol (CH_2OH-CH_2OH). Ethylene glycol is a clear, colorless, viscous liquid without smell.

Ethylene glycol boils at 197 °C, hardens – at minus 11.5 °C. However, mixtures of ethylene glycol and water freeze at lower temperatures. By varying the ratio of water and ethylene glycol, a mixture with a freezing point from 0 to minus 70 °C can be obtained. Lowering the freezing temperature of water and ethylene glycol solution with increasing water amount is explained by the appearance of hydrate glycol having a low pour point. Minimal freezing point of the solution is minus 73 °C at 33 % of water content. Further increase in the amount of water leads to an increase in freezing point.

Since water and ethylene glycol have different density and it is additively changed by mixing, it is possible to predict the setting point of the antifreeze by density. Due to the fact that the ethylene glycol has corrosive effect on metals, antifreeze composition is completed with anticorrosion additives: 1 g/l of dextrin (for protection of aluminum, copper, lead and stanum solder), 2,5–3,5 g/l disodium hydrogen phosphate (to protect steel, cast iron, brass, copper). Antifoam agents are added to prevent foaming of the coolant.

During the evaporation process of aqueous solutions of ethylene glycol, vapor contains considerably more water than ethylene glycol, therefore only water is lost in operational conditions by evaporation. Because of the large coefficient of volumetric expansion upon heating to operating temperature, the volume of ethylene glycol increases on 6–8 %. When setting, volume of viscous mass increases very slightly and defrosting of the cooling system does not occur.

Characteristic features of ethylene glycol antifreezes:

1. 6–8 % increase in volume at the operating temperature.

2. The thermal conductivity, heat capacity and density of the antifreezes at the same temperature are lower at about 15 % than these properties for water. Hence, the temperature mode of the engine cooled

by antifreeze is higher than in case of water cooling. For example, the piston temperature rises up to 10–15 °C. This may cause some reduction of power, efficiency and detonation at high ambient air temperatures.

3. Because of the high boiling point and a low saturated vapors pressure of ethylene glycol compared with water, water boils primarily during engine operation. Therefore, when the liquid content reduces in the cooling system due to evaporation, the water should be added.

4. Antifreeze in comparison with water has higher mobility and permeability. Therefore, the cooling system with antifreeze has higher demands on tightness.

5. When freezing, antifreezes form a rough mass with a slight increase in volume. Therefore, when antifreeze is freezing, mechanical damages of cooling systems are excluded.

6. Antifreeze destroys parts made from certain types of rubber.

Over time, the additives in antifreeze disintegrate resulting in antifreeze quality worsening. Therefore, the operation life of the antifreeze is 2 years or 60 thousand kilometers in conditions of intensive operation.

Ethylene glycol and its solutions are toxic substances. When released into the gastrointestinal tract they cause poisoning of central nervous system and the circulatory system damage.

High-boiling cooling fluids.

To cool the high performance engines, liquids with above 100 °C boiling point are applied. Such liquids consist of a mixture of high molecular alcohols, glycols and ethers with boiling temperature of 110–120 °C. Their use allows to reduce heat loss of the cooling system and to intensify heat transfer, which leads to reduction radiator surface and the power required to drive the coolant pump. Basic properties of these liquids are shown in table 8.27.

There are no conventional classifications of coolants, such as for motor or gear oils.

The cooling fluids can be classified into three main groups:

- Basic;
- Nitrite-free. Besides, they may contain amines and/or phosphates.
- Silicates-free. Besides, they may contain amines and/or phosphates and/or nitrites.

Table 8.27

The properties of coolants

Liquid property	Setting point	
	Not higher than minus 40 °C	Not higher than minus 60 °C
Density at 20 °C, kg m^{-3}	1100	1050
Initial boiling point, °C	130–145	130–140
Final boiling point, °C		195–210
Mechanical impurities content, %		
not greater than	0.005	0.005
Viscosity, mm^2/s: - at minus 35 °C - at minus 30 °C	 – 500	 410 320
Appearance	Transparent colorless or yellowish lightly turbid liquid	

Technical requirements for coolant concentrates for passenger cars and light trucks are defined in the ASTM D 3306 standard, for trucks and heavy machinery – in ASTM D 4985 and they require an initial introduction of Supplemental Coolant Additive (SCA).

Considering anticorrosion additives composition, antifreezes are classified into carboxylate, hybrid and traditional types. Traditional antifreezes include inorganic substances as corrosion inhibitors – silicates, phosphates, borates, nitrites, amines, nitrates and their combinations. They are termed as «Conventional coolants».

Traditional antifreezes are considered as morally obsolete and they are not applied at the first fueling of cars. This is due to the fact that inorganic inhibitors have short (less than 2 years) operation life and they cannot withstand high (above 105 °C) temperatures. During operation silicates cover the entire inner surface of the cooling system with the silicate layer that impairs heat transfer and reduces the cooling efficiency of the engine. At high temperatures the silicates can turn into gel-like sediments, which clog the narrow channels of the cooling system.

Hybrid antifreezes contain both organic and inorganic inhibitors (typically silicates or phosphates). Such antifreezes are termed as «Hybrid coolants».

Carboxylate antifreezes contain corrosion inhibitors based on organic (carbonic) acids. In the literature they are designated as «OAT coolants» (Organic Acid Technology). Carboxylate inhibitors do not form a protective layer over the entire surface of the system; it is adsorbed only in corrosion places where protective layer has thickness of not more than 0.1 micron. Carboxylate antifreeze has a long operation life (5 years in contrast to 3 years for hybrid and 2 years silicate ones) and it better protects the metal from corrosion and cavitation. This ensures optimum cooling of the engine.

Nowadays there is a new type of antifreeze «Lobrid coolants» or «SOAT coolants».

Regulatory documents often prohibit the addition of corrosion inhibitors containing nitrites, nitrates, amines, phosphates into antifreezes, as well as they determine the maximum allowable concentration of silicates, borax and chlorides. Nitrite and nitrates, when interact with amines, form toxic compounds, some of them are carcinogenic. Limitation of phosphates, silicates, borates reduces scale deposits in the cooling system, increases the service life of the pump compactions (less insoluble precipitates), and improves protection against cavitation corrosion.

8.2. Brake liquids

The brake liquids are used in the brake systems, hydraulic and pneumatic drives. They must have good viscosity, temperature and lubricating properties, physical and chemical stability, as well as to be inert to metals, rubber parts of hydraulic drive.

The liquid drive system typically has a temperature of ambient air. However, in the wheel brake cylinders, due to heat generated by friction in the brake mechanisms, liquid is heated. Liquid boiling is not allowed, as in these conditions the main condition of the drive operation, liquid incompressibility, is violated. Liquid vapors decrease in the volume even at low pressure, and therefore transmitted through the hydraulic system force does not income to operating wheel cylinders. The same occurs when the air passes into the hydraulic drive. Part of the system instead of incompressible fluid, is easily filled with compressed air, and the brake pedal sinks.

The main purpose of brake liquids it to transmit power to the actuators in hydraulic brake system of the vehicle.

When braking, the kinetic energy is converted by friction into heat. Large amount of heat is released, which depends on the mass and velocity of the vehicle. In case of emergency car braking temperature of pads can reach 600 °C, and the brake fluid may be heated up to 150 °C and above.

High temperatures in the brakes and hygroscopic liquids lead to flooding and early aging. Under these conditions, the fluid can adversely affect the rubber lip seals of brake cylinders, cause corrosion of metal parts. However, the greatest danger for the operation of brakes is the possibility of gas and vapor bubbles formation in the liquid at high boiling temperature, as well as if water is present. When one presses the brake pedal, gas bubbles are compressed and as the volume of the main break cylinder is small (5–15 ml), even strong pressing the pedal may not lead to an increase in the required brake pressure, i.e., brake is not working because of vapor locks in the system.

The brake liquids have to meet the following basic requirements.

Boiling point is the most significant index determining the maximum permissible operating temperature of hydraulic drive of brake. For the most of modern brake fluids, boiling temperature during operation is reduced because of their high hygroscopicity. It occurs because of water intake, mainly due to condensation from the air.

From operational experience it is known that the temperature of the liquid in hydraulic brakes of the truck usually does not exceed 100 °C. In conditions of rapid deceleration, for example on mountain roads, the temperature may rise up to 120 °C and above. In motor cars with disc brakes the temperature of the liquid when traffic on main roads, achieves 60–70 °C, in urban conditions – up to 80– 100 °C, on mountain roads – 100–120 °C, and at high speeds, air temperature and intensive braking – up to 150 °C. In addition, the beginning of the vapor phase formation of brake fluids is really going at temperature below 20–25 °C of the boiling point.

Viscosity and temperature properties. Braking process usually last a few seconds and in emergency conditions – hundredth parts of a second. Therefore, the force applied by the driver to the brake pedal, via the working fluid, should be quickly transmitted to the wheel brake. This condition is possible at necessary fluidity and it is determined by the maximum allowable viscosity at -40 °C: not more than 1500 sSt for general purpose liquids and not more than 1800 sSt for high temperature fluids. Liquids for north should have a viscosity that does not exceed 1500 sSt at 55 °C.

Anti-corrosion properties. To prevent corrosion, liquids should contain inhibitors to protect steel, iron, tin plate, aluminum, brass, copper from corrosion. Efficiency of inhibitors is assessed by change in the mass and the surface state of the metal plates after keeping in the brake fluid containing 3,5 % water for 120 hours at 100 °C.

Compatibility with rubber seals. To provide the tightness in the hydraulic system, rubber seal cuffs are installed at pistons and cylinders. Required sealing is achieved, when under the influence of brake fluid, cuff severally swell and sealing lips fit snugly to the wall of cylinder cams. In these conditions too severe swelling of the cuff is unacceptable, because pistons may be destroyed when muted, as well as cuffs shrinkage – to prevent liquid loss from the system. Rubber swelling test is carried out on exposing cuffs or rubber samples in a liquid at 70 and 120 °C. Then, the change in volume, hardness and diameter of cuffs is defined.

Lubricating properties. Effects of liquid on wearing of working surfaces of brake pistons, cylinders, cuff seals, is determined by its lubricating properties, which are checked under bench tests that simulate hydraulic brake drives in heavy conditions.

Stability at high temperatures. Brake fluids, in the range of operating temperatures from -50 to 150°C, must save initial indexes, e.g. to resist oxidation and delamination during storage and use, deposits and precipitates formation on the details of hydraulic drives of brakes.

Brake fluids are produced on the base of vegetable oil (mostly castor) or glycols (diatomic alcohols). Castor oil has high lubricity and does not cause swelling or softening of rubber and sealing details made of it. However, the high viscosity and relatively high pour point (-16 °C) preclude the use of castor oil in its pure form. Therefore, brake fluid is prepared by mixing of castor oil with alcohols: isopentanol, butanol and ethanol. Castor brake fluids at temperatures below -20 °C are not recommended.

Glycol-based and ethylcarbitol fluids have much better properties than alcohol and castor mixtures. They have good low temperature properties (do not freeze at -60 °C), low volatility and high flash point.

All these mixtures are neutral with respect to rubber non-oil resist details, so they may be applied in the braking system of cars with conventional rubber seals. Use of the glycol-based and ethylcarbitol fluids provides the work of hydraulic drive at the ambient temperatures of 50 – -50 °C. All these liquids are toxic.

Two basic standards are applied for the bake fluids: the first one is SAE J1703 and the second one (US) – DOT (Department of Transportation) norm. Currently, manufacturers of brake fluid in advertisements, documents and packages, indicate, as a rule, compliance with DOT fluid standards.

For passenger cars, depending on the design, technical specifications and year of release, fluids conforming to DOT-3, DOT-4 and DOT-5 requirements, are applied. The most advanced fluids designed for high-speed and sport cars, meet DOT-5 norms.

The main disadvantage of currently used brake liquids is hygroscopicity. It is found that during a year in the brake system fluid accumulate 2–3 % water, leading to reduction of the boiling temperature by 30–50 °C. Therefore, automobile companies recommend changing the brake liquid 1 time every 2 years regardless of mileage.

8.3. Damping liquids

Damping fluids are applied as the liquid medium in telescopic and lever-cam shock absorbers of motor vehicles and other machines. The work of the shock absorber is based on the absorption of kinetic energy of the sprung mass vibrations during percolation under pressurized fluid through the narrow hole from one cavity to another. These liquids should have slope viscosity and temperature characteristics, low pour point, the required viscosity.

The temperature of the shock absorber fluid may vary due to ambient temperature, for example from -50 °C, in the northern regions, to 120–140 °C during operation. The fluid pressure in the shock absorbers reaches 8–12 MPa. The main requirement for dumping liquids is optimal viscosity with minimal changes in the whole operating temperature range.

As a substitute of shock absorber fluids, mixture of turbine and transformer oils, in a ratio of about 1:1, is applied. However, the mixture does not fully meet the requirements, as it has not enough viscosity and temperature characteristics and high pour point (-30 °C).

8.4. Hydraulic liquids

In some car support mechanisms hydraulic oils may be used. They must have good lubricating properties, chemical stability, they should not be decomposed and not delaminate, not corrode ferrous and non-ferrous metals, rubber and leather.

ISO 6443.4 standard establishes a classification of H group – hydraulic system, which belongs to the L class – L – lubricants, industrial oils and related products. Each category of H products signified by a symbol consisting of a number of letters, for example ISO – L – HV or abbreviated L – HV. The symbol may be supplemented by a number corresponding to viscosity according to ISO 3448.

Primary **purpose** of a hydraulic liquid is to transfer power. The concept of liquid power is based on the principle articulated by Blaise Pascal, which is usually given as follows: “Pressure applied to an enclosed fluid is transmitted undiminished to every portion of that fluid and the walls of the containing vessel”. Within the context of liquid power, pressure is related to the force acting on a confined liquid. This principle has given rise to modern hydraulics, which entails highly engineered systems for efficiently controlling liquid flow to transfer energy and accomplish work.

The heart of any hydraulic system is the pump, which pulls in liquid from a reservoir by creating a vacuum at its inlet and then forces the fluid through its outlet, usually against pressure created by flow controllers and/or actuators downstream of the pump. Pumps, actuators, and other system components have surfaces that move relative to each other, often at high speeds, pressures, and temperatures. These components require cooling and lubrication for efficient operation and durability. Consequently, hydraulic liquids not only must transmit power, they serve critical functions as lubricant and heat transfer medium.

To transfer power efficiently, a hydraulic liquid must exhibit minimal compressibility. Low compressibility allows all of the pressure applied to the liquid to be available for direct and effective transmission to system components such as motors, cylinders, or other actuators. The compressibility of a fluid is generally discussed in terms of its “bulk modulus,” which describes the change in fluid volume as a result of applied pressure.

Heat is generated as a by-product of normal operation of a hydraulic circuit. Friction between the moving parts of a pump or hydraulic motor, as well as friction between the liquid and surfaces of valves, pipes, and other circuit devices generates heat. In addition, heat is generated in a hydraulic system as a result of the dissipation of the potential energy of pressurized fluid. As a hydraulic fluid is circulated through a system, heat is transferred from high temperature areas to coolers, reservoirs, and other regions of the circuit where it is dissipated. Typical specific heat and thermal conductivity values for hydraulic oils are a fraction of that of water. These factors are an important consideration in sizing hydraulic system coolers because the inherent cooling efficiency of petroleum based hydraulic fluid is less than that of water.

The durability of hydraulic equipment depends to a large extent upon the lubricating properties of the fluid. As a lubricant, the key function of the hydraulic fluid is to reduce friction between contact surfaces. A reduction in friction lowers contact temperatures and wear. This is accomplished through a combination of hydrodynamic and boundary lubrication mechanisms. The hydrodynamic lubricating properties of a fluid are governed by its physical properties while boundary lubrication is a function of fluid chemistry.

Oxidation and thermal stability. An important characteristic of a hydraulic fluid is its ability to withstand high temperatures. This is because horsepower losses in hydraulic systems directly result in transfer of heat to the fluid. Resulting high temperatures can cause hydraulic fluids to react with oxygen. The rate of this reaction accelerates exponentially with increasing temperatures and is further catalyzed by metals like copper and iron, especially at temperatures above 125 °C. Rate constants for the oxidation of saturated hydrocarbons at 125 °C are as much as 40 times higher than rate constants at 60 °C. Thus, fluid oxidation is highly dependent upon hydraulic system operating temperatures. Lubricants expected to operate in high temperature environments are typically fortified with additives known as antioxidants. Oxidative stabilization of the fluid translates directly into extended oil service life. Failure to resist oxidation can result in thickening of the oil (viscosity increase), formation of acidic by-products, and subsequent deposit formation.

Not only can cause heat oxidation, fluids may thermally degrade upon exposure to high temperatures with little or no oxygen present. The thermal stability of a hydraulic fluid is dependent mainly on the intrinsic ability of the base fluid or its components to resist decomposition at high temperatures.

Unlike oxidation, controlled thermal degradation of certain types of additives is desirable, because it is the very mechanism by which they react with the metal surfaces they are designed to protect. Similar to oxidation, however, the negative effects of thermal degradation may include increased acidity, thickening of the oil, and deposit formation. Therefore, good control of thermal degradation results in the retention of desired fluid properties.

Wear protection. Reduction of friction and prevention of wear is the fundamental purpose of a lubricant. Lubricants reduce friction in machine components by producing a physical or chemical barrier between surfaces that slide or roll past each other. Depending on equipment design and function, lubricants function within three commonly recognized regimes: hydrodynamic, mixed-film, and boundary lubrication.

Hydrodynamic lubrication is often the dominant lubrication regime under conditions of moderate temperatures and loads. Hydrodynamic lubrication is a system of lubrication in which the shape and relative motion of the sliding surfaces causes the formation of a fluid film that has sufficient pressure to separate the surfaces. In this regime, viscosity is the most important fluid characteristic because it, in combination with sliding speed, contact geometry and load, determines the thickness of the lubricating film, and determines whether or not the surfaces will contact each other.

Fluid viscosity plays an important role in hydraulic applications. A hydraulic fluid that is too low in viscosity will cause low volumetric efficiency, fluid overheating, and increased pump wear. A hydraulic fluid that is too high in viscosity will cause poor mechanical efficiency, difficulty in starting, and wear due to insufficient fluid flow. Since viscosity is a function of fluid temperature, the temperature operating window (TOW) for a particular viscosity grade of hydraulic fluid is a function of temperature.

The majority of hydraulic fluids are formulated with anti-wear additives because surface loads associated with high-pressure pump operation necessitate the use of fluids with enhanced wear protection.

Water content and hydrolytic stability. In many hydraulic systems, the lubricant is susceptible to contamination with water. Contamination with water can lead to a host of problems including loss of lubricity, corrosion, additive degradation, and filter plugging. Consequently, machine builders and equipment users often attempt to limit the amount of water that enters their hydraulic systems. At the same time, fluid formulators endeavor to manufacture hydraulic fluids that resist chemical degradation or hydrolysis in the presence of water and heat.

Deemulsibility. Deemulsibilty is the term used to describe a fluid's ability to separate from water. Water contamination of the hydraulic oil may lead to various problems that adversely affect both fluid and equipment durability. Thus, it is desirable for hydraulic oil and water to separate as quickly as possible. In many industrial applications, water is drained from the hydraulic oil reservoirs as it separates and settles on the bottom. For fluids with poor deemulsibility, the separation is either very slow or unlikely to occur to any significant degree.

Aeration and foam. Under normal conditions there is always air present in a hydraulic fluid. By volume, it is present at about 7–9 % at room temperature and atmospheric pressure. In this state, it is not visible to the human eye and thus referred to as dissolved air. Higher temperatures and/or lower pressures (such as vacuum conditions) lead to lower dissolved air levels.

Fluid circulation through hydraulic systems and reservoirs may cause mechanical introduction of air into hydraulic fluids, particularly if reservoir size or design does not allow sufficient residence time for air separation to occur. At elevated levels, entrained air is visible to the human eye as larger bubbles and can cause the oil to become cloudy.

Uncontrolled air contamination results in a number of undesirable consequences. Entrained air increases the compressibility of the fluid and can adversely affect its response to hydraulic control mechanisms or devices, especially in high-pressure systems. Dissolved or entrained air expands into larger bubbles as its solubility in the fluid decreases as a result of exposure to vacuum conditions at the pump inlet. This leads to noise and cavitation, which is the dynamic process of gas cavity growth and collapse in a liquid. Several studies of this phenomenon have suggested theoretical mechanisms and documented experimental evidence of wear and increased oxidation due to cavitation.

Foaming is very much rooted in the fundamental problem of air contamination and consequently, results in many of the same negative effects of air entrainment. It is characterized by the formation of a mass of relatively large bubbles on the surface of the fluid and is usually brought about by turbulent return of oil to the reservoir or migration of entrained air to the surface. It is desirable to have fluids with a low tendency to form foam in the first place and have the foam collapse quickly once formed. For effective foam control, the rate of foam collapse must be faster than the rate at which entrained air migrates to the surface to form the foam. Otherwise, the foam layer will continue to increase and air may eventually be re-dispersed in the bulk fluid. In severe cases, oil that produces a significant amount of foam may bubble out of hydraulic reservoir breathers, creating a fluid spill.

Air entrainment has increasingly become a concern due to a trend toward smaller reservoir sizes. Shorter fluid residence times therefore dictate use of hydraulic fluids with improved air release characteristics for the reasons discussed above. Several studies have shown that fluid viscosity is a critical factor influencing air release properties. Within a given class of fluids, higher viscosity and lower oil temperatures translate into slower air release characteristics. While different classes of base fluids have demonstrated unique air release advantages, there has been little success in identifying additives that improve air release properties of a base fluid.

Corrosion protection. Chemical contaminants and corrosive by-products of fluid degradation can cause surface attack of metallic hydraulic system components. Ferrous metal corrosion in a hydraulic system is most often caused by water contamination, while copper and its alloys are susceptible to attack by the products of high temperature fluid degradation. Rusting of ferrous metal is an electrochemical reaction that occurs between the parent metal and the thin oxide layer on the metal surface formed as a result of exposure to the atmosphere. Rust, which is hydrated iron oxide, compromises the integrity of the metal surface and adversely affects other important fluid properties when it contaminates the bulk fluid. Ferrous metal corrosion protection in hydraulic systems is usually accomplished by incorporating surface-active additives such as rust inhibitors.

Seal compatibility. Very critical to the successful operation of a hydraulic system is the ability to prevent leakage and accidents that are a result of failed seals. Leaks can lead to contamination, loss of pressure, loss of lubricating fluid, and environmental damage depending on the severity of the spill. In extreme temperature and pressure operations, sudden failure of seals may have life threatening consequences, considering the potential for explosions, fires, etc. Hydraulic fluids and elastomeric seals are composed of complex chemical components that can interact as they come into contact. Depending on the chemistries involved, time, temperature, and mechanical stresses cause fluid interactions with the seal material, resulting in swelling or shrinkage of the elastomer compound. It is desirable to select seal materials that exhibit minimal change in hardness, volume, tensile strength etc. in service.

Coolant separability. Hydraulic systems used in machine tool operations are susceptible to contamination by aqueous cutting fluids, which contain components with poor oxidation resistance, high deposit forming tendency, and/or high corrosiveness. In metal-working applications, the hydraulic fluid may be considered a contaminant of the cutting fluid that alters its effectiveness in metal removal operations. Regardless of the perspective, a mix of these two categories of fluids is undesirable, especially if they have not been designed to be compatible. In this case, compatibility is defined as the ability of either fluid to complement, enhance, or at least have no impact on the operation of the other when mixed. The lubricant's ability to readily separate from coolants is highly desirable in most cases. However, the variety and complexity of coolant chemistries makes it difficult to ensure good separability of the hydraulic oil from all metal working fluids.

Shear stability. Mobile hydraulic equipment such as excavators, farm tractors, cranes, and timber harvesters frequently are required to operate under extreme high and low temperature conditions. To accommodate wide-ranging environmental conditions, hydraulic fluids with enhanced viscosity – temperature properties are often employed. These fluids typically contain viscosity index improving polymers that thicken oil at high temperatures, while having little impact upon their low temperature fluidity.

8.5. Starting liquids

Engine starting properties depend on the quality of used fuels and oils. Start engine at low temperatures is facilitated by the use of gasoline with a lot of light fractions, diesel fuel with a high cetane number and oils with low viscosity at low temperatures. However, even very good fuels cannot provide both engine starting at low temperatures, and the smooth operation of the warmed engine. In connection with it, special liquids, due to which the engine starts at low temperatures, become more popular.

An obligatory component of starting liquid is ethyl ether C_2H_5-O-C_2H_5. It has a low self-ignition temperature, high saturated vapor pressure and wide flammability limits.

When cold engine starts, heat transfer to the cylinder walls increases, and the temperature drops at the end of the compression stroke because of other reasons. In this state, ethyl ether makes it possible self-ignition of flammable mixtures at relatively low temperatures of 190–220 °C. Wherein, the most efficient is the use of pure ethyl ether. However, in this case, there is a very sharp increase in pressure in the engine cylinder, which may lead to breakage of parts. To avoid it, the content of the ethyl ether in starting fluids for diesel engines is usually adjusted to 60–75 %.

In gasoline engines, at start-up, ethyl property to ignite when mixed with air over a wide concentration range is valuable. This allows achieving the spark ignition of very poor mixtures. But the content of the ethyl ether as starting fluid for gasoline engines may be less than in liquids for diesel ones.

When start fluid used in a diesel engine, inflammation begins with an ethyl ether ignition and last of all the fuel ignites itself. To ensure a gradual and sequential ignition of the starting fluid, isopropylenitrate and the mixture of low-boiling hydrocarbons are introduced.

Isopropylenitrate inflames later than ethyl ether, but earlier than the main fuel. The mixture of low-boiling hydrocarbons after complete evaporation in the cylinder, inflames later than isopropylenitrate, but before the main fuel as well. The existence of such a consequent chain ensures good preparation of the main fuel to ignition and visible combustion, significantly reducing the rate of pressure rise. Optimal isopropylenitrate content and mixtures of low-boiling hydrocarbon liquids for diesel engines is 15 %.

In liquids for gasoline engines, the mixture of low-boiling hydrocarbons ensures formation of a flammable mixture capable to be ignited by spark. Considering the need for the combustible mixture to be prepared at fairly low temperatures, greater amount of mixture of low-boiling hydrocarbons is added into liquid gasoline engines, in comparison with diesel engines. Reliable preparation of the fuel-air mixture to the spark ignition is promoted by the introduction of a small amount of isopropylenitrate into the liquids for gasoline engines.

Reducing wearing of friction parts in the first engine start period is achieved by the introduction of the starting fluid oils containing anti-wear and extreme pressure additives. In diesel engines, when starting, higher loads on the friction pairs occur, in comparison with the gasoline engines. Research showed that in order to reduce start wearing, the diesel start fluid should contain not less than 10 % of oil. The use of such liquid in gasoline engines leads to «oiling» the spark plugs, the spark disruptions. In this regard, the starting fluid for gasoline engine should contain no more than 2 % of oil. Such amount of oil ensures lubrication of wearing details at the first start period of less tensed gasoline engine and at the same time it does not cause disruption to the spark plugs.

In addition to these basic components, into start fluids some additives are added in small concentration, which improve certain operation properties. Application of start liquids helps to reduce the minimal crankshaft rotation speed in several times when start-up.

Thus, the use starting fluids is effective to reduce motor starting terms and to increase its reliability under any below-zero temperatures.

8.6. Air conditioning liquids

Air-conditioner is required to maintain inside car comfortable for the driver and passenger climate. For this purpose, applied in air-conditioner liquid refrigerant after passing through valve exchanger (evaporator), evaporates and turns into a gas at low pressure. This process is accompanied by a sharp drop in temperature. The surface temperature of the evaporator should be close to the freezing point of water, but not lower than it; otherwise ice would be formed on the evaporator, impeding the passage of air and transfer of heat to the refrigerant. After transformed into a low-pressure gas, refrigerant passes through the heat exchanger and extracts heat from the air inside the vehicle.

Moisture in the air condenses on the outer surface of the heat exchanger and is drained outside. The air passing through the heat exchanger is returned to the interior cooler and drier.

The heat accumulated by refrigerant should be transmitted into the atmosphere, while the refrigerant with the help of compressor is directed to condenser.

Freons are applied as refrigerants. They are a fluorine-containing derivatives of saturated hydrocarbons.

These are colorless and odorless liquids or gases. There are more than forty different types of freons.

Freon R-12 was applied in cars' air conditioners as refrigerant. However, it contained chlorofluorocarbons (CFC), currently banned because of the damaging effects on the ozone layer of the planet. In addition, under the influence of the open flame, R-12 releases the deadly phosgene gas.

Refrigerant R-22 comprises hydrofluorocarbons (HFC) and destroys the ozone layer to a lesser extent than the others, but nevertheless significantly. Therefore, international programs, restricting and prohibiting the production and use of these refrigerants, are developed. Production of CFCs has been stopped, however, CFC are still used in many countries. In this connection, «green» refrigerant R-134A is used, which does not contain chlorine. Its molecule consists of only fluorine and hydrogen, and does not destroy the ozone. However, its thermal parameters are lower than that of conventional freons.

8.7. Electrolytes

Electrolytes are the substances having ionic conductivity. Since the electric current passing through them is accompanied by the transfer of substance, they are called conductors of the second kind. Electrolytes include molten salts, oxides or hydroxides, as well as solutions of salts, acids or alkalines in polar solvents such as water, which occurs more often. To bypass electric current through the electrolyte solution, two metal or carbon plates – electrodes are poured into it and they are connected to the poles of a DC source. The positive electrode is called the anode, negative one – cathode.

Current flow through the electrolyte is accompanied by chemical reactions at the electrodes. Thus, at the cathode, immersed in molten salt or an oxide or salt solution, is usually deposited metal, part of the electrolyte. At the cathode, immersed in an aqueous solution of acid or alkali salts or alkaline earth metal, hydrogen gas is produced. At the anode, made of an inert material such as platinum or carbon, in aqueous solution, gaseous oxygen is released, and in the concentrated aqueous chloride solutions or in molten chlorides – chlorine. Zinc, copper or cadmium anodes are subjected, due to electric current, to be gradually dissolved themselves; gas in this case is not formed.

As the electrolyte in vehicle lead-acid batteries, an aqueous solution of sulfuric acid is used. For the preparation of the electrolyte distilled water is used as well as a special accumulator concentrated sulfuric acid – transparent oily liquid with no odor. Acid is subjected to be mixed with water in all proportions. Electrolyte of required density may be prepared directly from concentrated sulfuric acid and distilled water. However, dissolution of concentrated sulfuric acid in water is accompanied by a large amount of heat. For this reason, to prepare the electrolyte, vessels, not only resistant to the impact of sulfuric acid, but also to high temperatures, are used.

The vessel for preparation of electrolyte is first of all filled with water, and then with sulfuric acid while continuous stirring. Water addition to the concentrated sulfuric acid is forbidden, since the infusion of water into the acid cuses rapid warming up water, it is heated, boils and is sprayed with the acid which, coming into contact with human skin, causes burns.

The electrolyte density used for starter batteries, may vary from 1,20 to 1,28 g/cm^3.

A solution of 1,40 g/cm^3 density is used as well, and it is applied as an intermediate in the preparation of the electrolyte of required density and when there is need to increase the density of the electrolyte in the battery. In the preparation of the electrolyte of required density, may be used rates of the components for the preparation of 1 liter of electrolyte.

The density of electrolyte is determined by the densimeter with a rubber bulb. Simultaneously, with the measurement of density, the temperature of the electrolyte is measured.

New accumulators are filled with electrolyte of 0,02 g/cm^3 less density than that which would be at the charge end, taking into account the climate zone of the vehicle.

Questions

1. What are coolants? What are their purposes?
2. What are the main groups of cooling liquids?
3. What are brake liquids? What are their purposes?
4. What are damping liquids? What are their purposes?
5. What are hydraulic liquids? What are their purposes?
6. Characterize main function of hydraulic liquids.
7. What are starting fluids? What are their purposes?
8. What are air-conditioning fluids? Which of them are the most widely used nowadays?
9. What are electrolytes? What are their purposes?
10. Describe the mechanisms of electrolytes action.

Chapter 9.
CHEMMOTOLOGY OF ALTERNATIVE FUELS AND LUBRICANTS

Fuel sources are those sources that can be used to produce fuels (gas, liquid, and solid), which are combustible or energy-generating molecular species that can be harnessed to create mechanical energy.

Today the main energy sources are crude oil (~40 % of the world energy consumption), natural gas (~23 %), black and brown coal (~20 %). The minor share is taken by nuclear energy (~6 %), hydroenergy (~2.5 %), biofuels (~4 %) and other alternative energy sources. At the same time the world energy demand growths constantly. According to the data of the World Oil Outlook 2010, the world demand in primary energy resources was 229,9 mln BOE[6]/day in 2010, and till 2030 it should reach 322,9 mln BOE[6]/day. As main energy resources are exhausting, its share in total energy balance will slowly decrease (Table 9.29).

Table 9.29

The world energy balance for 2010–2050, %

Kind of energy source	Years			
	2010	2020	2–30	2050
Crude oil	35–39	30	29–31	28–29
Natural gas	24–25	29	29–30	28–30
Coal	18–19	17	19–21	22–24
Others (including biofuels)	13–14	24	22–23	20

Petroleum-based fuels are well-established products that have served industry and consumers for more than one hundred years. Over the past four decades, in spite of the energy shocks of the 1970s, there has been rapid escalation in fuel demand to the point that many countries, are net importers of petroleum and petroleum products and this is projected to continue. However, the time is running out and these fuel sources, once considered inexhaustible, are now being depleted at a rapid rate. In fact, there is little doubt that the supplies of crude oil are being depleted with each year that passes. However, it is not clear just how long it will take to reach the bottom of the well.

Today there is a great variety of thoughts about future development of oil processing industry. However, the common idea is that in the nearest future the humanity will face the problem that crude oil is not enough to satisfy its energy needs. IEA forecasts that the world oil deposit will be enough for 40–45 years, natural gas for 50–70 years, and coal for 200–400 years. Some scientists believe that humanity will be provided with oil during 120 years, according to other forecasts oil and natural gas deposits will end in around 250 years.

The question of rapid increase of prices for crude-oil and other fossil fuels is connected to the deficiency of primary energy and rapidly increasing demand for them. Except that, the price for energy resources is stipulated by expenses for their extraction. So, the notion of energy efficiency was introduced in order to estimate the efficiency of extraction and use of certain resources – EROEI (energy returned on energy invested). The general EROEI formula is presented as following:

$$EROEI = \frac{energy\ delivered\ (usable\ energy)}{energy\ required\ to\ deliver\ that\ energy}$$

It means the ratio between the energy used for extraction (production) of energy and energy obtained. When EROEI = 1, it means that production of one unit of energy for the raw material required investment of the same quantity of energy. Thus, only in case when EROEI is more than 1, production process in profitable. For example, for crude-oil EROEI has decreased in 6–9 times during last 75–85 years (Table 9.30). Rising of prices for crude-oil is connected to the decrease of its EROEI.

As we can see, crude-oil that is a source for more than 90 % of all motor fuels and other fossil fuels need to be replaced. And this question becomes more and more challenging. Along with the situation in oil extracting and processing industries, the state of environment that is constantly worsening causes a special concern. First of all, the question is in global warming that is being intensified in a result of fossil fuels extraction, processing and use.

Table 9.30

EROEI values for certain energy sources

Kind of energy resource	Calculated year	EROEI value
Crude oil and gas	1930	>100
	1970	30
Crude oil extraction in the USA	1970	20
	2013	11
The world crude oil extraction	1990	35
	2000	30
	2013	17
Crude oil extraction from ultra low depth of sea beds	2013	>10
Oil production from oil-shales	2013	1,5
Oil production from oil-sands	-	2–4
Coal	1930	>100
	1970	30
Natural gas	2005	10

The search and widening of new feedstock, development of progressive technologies of alternative fuels production and their rational use in transport, is one of the priority tasks nowadays. The advantages of renewable energy are: natural origin, rapidity of renewal, absence of extra CO_2 emissions, less negative impact on environment, easy biodegradation in nature. At the same time fuels from renewable feedstock must meet the requirements connected to efficiency, reliability and durability of equipment.

Today there is a great variety of renewable feedstock or biomass for alternative fuels production. Biomass-derived fuels can provide a near-term and even a long-term solution to the transport industry with a lower environmental impact than petroleum fuels.

Potential feedstock for producing biofuels is classified as:

- *oil-based feedstocks*, such as vegetable oils, waste oils, algal oils, and pyrolysis oils,
- *solid-based feedstocks*, such as lignocellulosic biomass (including wood products, forestry waste, and agricultural residue) and municipal waste (the organic portion),
- *gas-based feedstocks*, such as biogas and syngas.

The key to the successful implementation of biofuel is the availability of feedstock at a large and sustainable scale and low price. Improved yields and reduced plantation or transportation costs would promote commercialization of biofuel conversion processes and, therefore, would allow the industry and government to assess and address the feedstock’s potential and impacts.

It is obvious that each kind of feedstock requires certain technology of its processing. Some of them are already popular and some are still developing. According to the complexity and the level of maturity these technologies are traditionally classified according to generations (Fig. 9.38). So here we talk about the four main categories under which biofuels fall: first-, second-, third- and fourth- generation biofuels.

First Generation Biofuels. We already know that many plants contain high-energy organic matter that is the lifeblood of any type of renewable biofuel. The biofuels sector began positively appropriating this knowledge by producing renewable fuel as a counterpart to the dominant fossil fuel industry. This first kind of biofuel production was termed “first-generation”.

In simple terms, first-generation biofuels are those which are made from feedstock that can also be consumed as human food. First generation of alternative fuels (biofuels), which are widely popular today, are produced from traditional agricultural plants. Whether it is sugar, starch, or vegetable oil, all of them are also human food products which makes them a first-generation fuel. The feedstock that typically top this list for first-generation fuels include food crops like corn, sugarcane, sugar beet, wheat and sorghum.

Since they are easily extracted using conventional technology, they are also known as "conventional biofuels."

Most common first-generation biofuels include:

Biodiesel – extraction of vegetable oils, with or without esterification, from the seeds of plants like soybean, rape (canola) and sunflower

Ethanol – fermentation of simple sugars from sugar crops (sugarcane) or starch crops (corn, wheat)

Biogas – anaerobic fermentation of organic waste and crop residues as energy crops

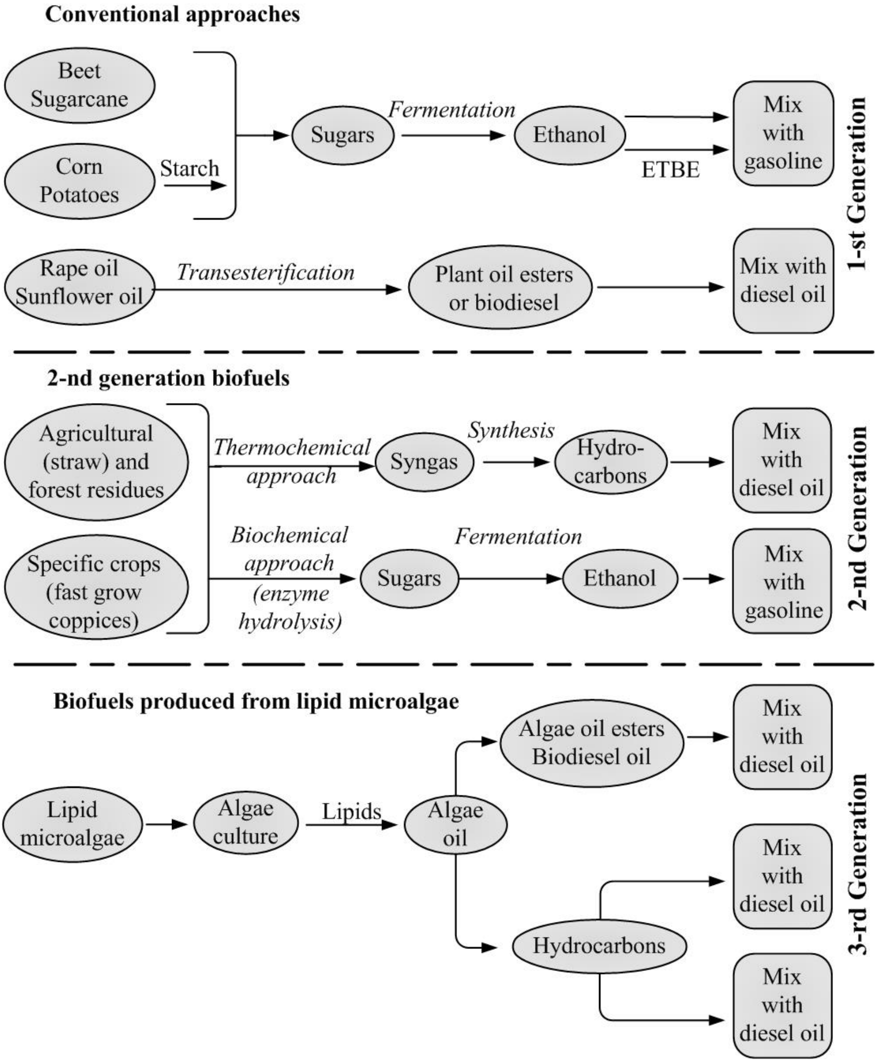


Fig. 9.38. Development of technologies for biofuels production

As with any industry, certain concerns (in this case related to cost and inefficiency) arose out of first-generation biofuel production. This evolution naturally led to second-generation biofuels.

Second Generation Biofuels. Like first-generation fuels, second-generation fuels are also produced from sustainable feedstock but, in this case, this feedstock is not normally used for human consumption. That is, no second-generation feedstock is also a food crop, though certain food crops may become second-generation fuels if and when they're no longer useful for consumption.

Second generation of biofuels is produced by processing the whole plant – particularly its lignocelluloses, the main component of plant cell walls. The resource is available in large quantities in a variety of forms: wood, straw, hay, forestry waste, plants' residues, etc. second generation processes do not compete with food uses.

Second-generation feedstock is a little more difficult to extract. For this reason, advanced conversion technologies are needed in the process, which is also why second-generation biofuels are known as "advanced biofuels." Two processes are being studied: biochemical conversion and thermochemical conversion.

The plus side of second-generation biofuels is the increased efficiency that uses the vast majority of the biomass feedstock which avoids the waste seen in first-generation bioful production.

Third generation of biofuels can be produced using either autotrophic (operating via photosynthesis) algal biomass or heterotrophic process (operating via the supply of an external carbon, such as sugar).

Algae's use in biofuel production was formerly relegated to second generation, but there exist some key differences that have warranted its own separate category. These are, mainly:

Impressive diversity: Algae can produce such fuels as biodiesel, butanol, gasoline (petrol), ethanol, and even jet fuel!

Higher yields: Algae is capable of producing much more than its other feedstock counterparts, and with lower resource inputs. By some estimates, algae can produce 10-fold what even the best conventional feedstock can generate.

Except that third generation biofuels foresee applying the already known technologies for new kinds of oil-containing feedstock, which do not compete with food industry (jatropha, camellina, etc).

The capital and operating costs of third-generation production are the highest. This sub-sector requires additional research and development to reach the point of being a sustainable method of consistent biofuel production on a commercial scale, but the potential is highly promising.

Fourth generation biofuels (Fig. 9.39) are considered only during the last 3–5 years and now still at the early stage of development. They are derived from specially engineered biomass, which has higher energy yields or are able to be grown on non-agricultural land or water bodies.

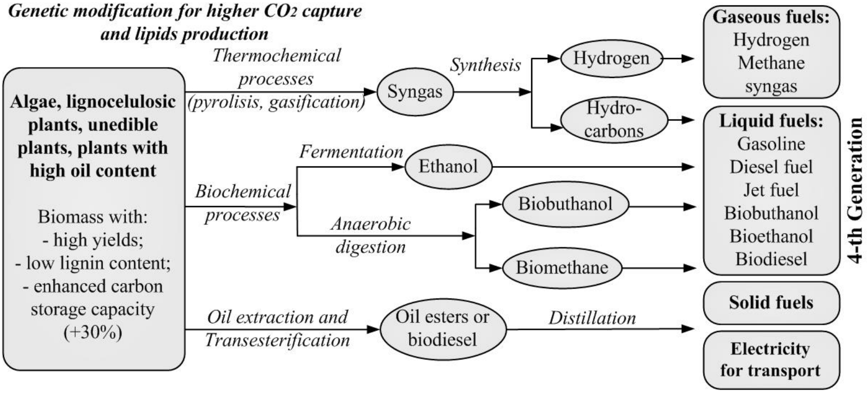


Fig. 9.39. Technologies for fourth generation alternative fuels production

Biomass crops are seen as efficient 'carbon capturing' machines that take CO_2 out of the atmosphere and ‘lock’ it in their branches, trunks and leaves. The carbon-rich biomass is converted into fuels by means of second generation techniques. The GHG is then geosequestered – stored in depleted oil and gas fields, in unmineable coal seams or in saline aquifers, where it stays locked up for hundreds of years.

9.1. Synthetic and bio-based fuels

Fuels from Coal. The production of fuels from coal in relation to fuels from other energy technologies is dependent upon the cost of fuels from other sources and, most important, the degree of self sufficiency required by various level of government. The nature of coal is a major factor (assuming an ample supply of coal reserves) and the need for desulfurization of the products as well as the various steps leading from the mining of coal to its end use. Nevertheless, the production of fuels from coal is an old concept having been employed since it was first discovered that the strange black rock would burn when ignited and produce heat.

Coal can be liquefied by either direct or indirect processes (i.e., by using the gaseous products obtained or by breaking down the chemical structure of coal) to produce liquid products. Four general methods are used for liquefaction:

- pyrolysis and hydrocarbonization (coal is heated in the absence of air or in a stream of hydrogen);
- solvent extraction (coal hydrocarbons are selectively dissolved and hydrogen is added to produce the desired liquids);
- catalytic liquefaction (hydrogenation takes place in the presence of a catalyst);
- indirect liquefaction (carbon monoxide and hydrogen are combined in the presence of a catalyst).

The carbon monoxide and hydrogen are produced by the gasification of coal in which a mixture of gases is produced. In addition to carbon monoxide and hydrogen, methane and other hydrocarbons are also produced depending on the conditions involved. Gasification may be accomplished either in situ or in processing plants. In situ gasification is accomplished by controlled, incomplete burning of a coal bed underground while adding air and steam. The gases are withdrawn and may be burned to produce heat, generate electricity, or are used as synthesis gas in indirect liquefaction or the production of chemicals.

Producing light distillate fuels from coal can be done through converting coal to syngas, a combination of carbon monoxide, hydrogen, carbon dioxide, and methane. The syngas is reacted through the Fischer-Tropsch synthesis (FT-process) to produce hydrocarbons that can be refined into liquid fuels.

At the first stage the synthetic gas (syngas), which is a mixture of hydrogen and carbon monoxide ($CO+H_2$), is obtained in a result of coal gasification. Syngas, coming from coal gasifier contains the considerable amount of CO_2 and certain percentage of gaseous substances, formed by additives present in the raw material, for example, sulphur. The next important stage is removal of harmful substances from synthetic gas flow. The next stage is the catalytic process of CO hydration with further formation of liquid hydrocarbons mixtures: alkanes, olefins, paraffins, alcohols, *etc*. It is possible to vary ratios of obtained fractions by changing the reaction conditions. After finishing the FT-process, synthesized fractions of hydrocarbons are treated in the way similar to the processes of fuel production from crude oil.

Research into the process of increasing the quantity of high-quality fuels from coal while reducing the costs could help ease the dependence on ever-increasing cost but depleting stock of petroleum.

Furthermore, by improving the catalysts used in directly converting coal into liquid hydrocarbons, without the generation of the intermediate syngas, less power could be required to produce a product suitable for upgrading in existing petroleum refineries. Such an approach could reduce energy requirements and improve yields of desired products.

While coal is an abundant natural resource, its combustion or gasification produces both toxic pollutants and GHGs. By developing adsorbents to capture the pollutants (mercury, sulfur, arsenic, and other harmful gases), researchers are striving not only to reduce the quantity of emitted gases but also to maximize the thermal efficiency of the clean-up.

Fuels from natural gas. Natural gas is widely used along with coal for fuels production by FT-process. The main component of natural gas is methane. Technological scheme of fuel production for motor transport from natural gas is similar to the scheme, where coal is used, but the exception is the absence of the first preparatory stage of coal gasification.

Natural gas refining fractions are characterized by almost zero content of sulphur heteroatom compounds. Fuels, obtained by FT-process, are composed mainly of paraffin hydrocarbons; comparing to conventional kerosene, aromatic hydrocarbons are practically absent. As a result, their tendency to soot formation is considerably lower, and they are more thermally stable. In addition, motor fuels obtained during coal processing possesses a higher heat value, so its consumption during flight is less. However, the results of experiments indicate that this fuel has worse lubricating properties and this fact requires application of additives.

Fuels from oil-shale. During last decades scientific literature pays much attention to the technology of fuels production from oil-shales. Shale oil, sometimes termed retort oil, is the liquid oil condensed from the effluent in oil shale retorting and typically contains appreciable amounts of water and solids, as well as having an irrepressible tendency to form sediments.

Oil-shales contain 20–35 % of kerogen (sometimes up to 50 %) that is made of aromatic, acyclic, and also organic oxygen-and sulphur-containing compounds.

The base part of the oil-shales refining process is dry distillation in a retort, that can be performed both right after its extraction on the surface, and directly in the places of layers' natural occurrence. The main advantage of underground oil-shales processing is absence of need for its extraction, transportation to the dry distillation plant and removal of the ash, remaining in the form of wastes.

Retorting is the process of heating oil shale in order to recover the organic material, predominantly as a liquid. To achieve economically attractive recovery of product, temperatures of 400–600 °C are required. A retort is simply a vessel in which the oil shale is heated from which the product gases and vapors can escape to a collector.

Shale-retorting processes produce oil with almost no heavy residual fraction. With upgrading, shale oil is a light boiling premium product more valuable than most crude oils. Shale oil contains a large variety of hydrocarbon compounds but also has high nitrogen content compared to a nitrogen content of 0,2 to 0,3 weight percent for typical petroleum. In addition, shale oil also has a high olefin and diolefin content. It is the presence of these olefins and diolefins, in conjunction with high nitrogen content, which gives shale oil the characteristic difficulty in refining and the tendency to form insoluble sediment. Crude shale oil also contains appreciable amounts of arsenic, iron, and nickel that interfere with refining.

The most widely used technology of oil-shale processing today is fractionation, slow coking and hydrocracking. Inside the retort oil-shales are subjected to the pyrolysis at temperature of about 480–540 °C and decomposed with formation of vapours of shale tar (10–30 %), gasoline gas (1,0–1,5 %), pyrogenetic water and flammable gases. In the following processes, shale tar, that contains 20–25 % of phenols, paraffinic, aliphatic, naphtenic and aromatic hydrocarbons can be distilled like the traditional oil.

Blending shale oil products with corresponding crude oil products, using shale oil fractions obtained from a very mildly hydrogen treated shale oil, yields kerosene and diesel fuel of satisfactory properties. Hydroprocessing shale oil products, either alone or in a blend with the corresponding crude oil fractions, is therefore necessary. The severity of the hydroprocessing has to be adjusted according to the particular property of the feed and the required level of the stability of the product.

Gasoline from shale oil usually contains a high percentage of aromatic and naphthenic compounds that are not affected by the various treatment processes. The olefin content, although reduced in most cases by refining processes, will still remain significant. It is assumed that diolefins and the higher unsaturated constituents will be removed from the gasoline product by appropriate treatment processes. The same should be true, although to a lesser extent, for nitrogen- and sulfur-containing constituents.

The sulfur content of raw shale oil gasoline may be rather high due to the high sulfur content of the shale oil itself and the frequently even distribution of the sulfur compounds in the various shale oil fractions. Not only the concentration, but also the type of the sulfur compounds is important when studying their effect on the gum-formation tendency of the gasoline containing them.

Gasoline derived from shale oil contains varying amounts of oxygen compounds. The presence of oxygen in a product, in which free radicals form easily, is a cause for concern. Free hydroxy radicals are generated and the polymerization chain reaction is quickly brought to its propagation stage. Unless effective means are provided for the termination of the polymerization process, the propagation stage may well lead to an uncontrollable generation of oxygen bearing free radicals leading to gum and other polymeric products.

Diesel fuel derived from oil shale is also subject to the degree of unsaturation, the effect of diolefins, the effect of aromatics, and to the effect of nitrogen and sulfur compounds.

Shale oil is applicable also for jet fuels production. However, it has a high density, medium sulphur, nitrogen and unsaturated hydrocarbons content. Density and freezing point of shale tar are higher than those of many oil fractions with the same viscosity. Production of jet fuels from oil-shales requires hydrotreating to reduce the content of mentioned organic compounds and to improve its quality. In general, production of jet fuels from oil-shales of appropriate quality requires deeper processing and higher expenses than production of jet fuels from crude oil.

Jet fuels obtained by processing of oil-shales possess the average content of aromatic hydrocarbons (10–25 %) and doesn't cause problems associated with lubricating properties. Moreover, it shows a high level of stability during long-term storage.

Fuels from biomass. Biomass refers to living and recently dead biologic material which can be used as fuel or for industrial production. For example, manure, garden waste, and crop residues are all sources of biomass. Biomass is a renewable energy source, unlike other resources such as petroleum, natural gas, tar sand, coal, and oil shale. But like coal and petroleum, biomass is a form of stored solar energy.

Biofuel is derived from biomass (recently living organisms or their metabolic by-products) and has the potential to produce fuels that are more environmentally benign than petroleum-based fuels. In addition, ethanol, a crop-based fuel alcohol, adds oxygen to gasoline thereby helping to improve vehicle operation and reduce air pollution. Biodiesel, an alternative or additive to petroleum diesel, is a nontoxic, renewable resource created from soybean or other oil crops.

Agricultural products specifically grown for use as biofuels include crops such as corn, soybeans, flaxseed, rapeseed, wheat, sugar beet, sugar cane, palm oil, and Jatropha. Biodegradable outputs from industry, agriculture, forestry, and households can be used as well; examples include straw, timber, manure, rice husks, sewage, biodegradable waste, and food leftovers. They are converted to biogas through anaerobic digestion. Biomass used as fuel often consists of underutilized types, like chaff and animal waste. The quality of timber or grassy biomass does not have a direct impact on its value as an energy source.

Unlike other forms of renewable energy, biofuels do not reduce the amount of GHGs in the atmosphere. The combustion of biofuels produces CO_2 and other GHGs. The carbon in biofuels is often taken to have been recently extracted from atmospheric CO_2 by plants as they have grown. The potential for biofuels to be considered carbon neutral depends upon the carbon that is emitted being reused by plants for further growth. Clearly however, cutting down trees in forests that have grown for hundreds or thousands of years for use as a biofuel, without the replacement of this biomass would not have a carbon-neutral effect.

It is generally believed that a way to reduce the amount of carbon dioxide released into the atmosphere is to use biofuels to replace nonrenewable sources of energy. Dried compressed peat is also sometimes considered a biofuel. However, it does not meet the criteria of being a renewable biofuel. Though more recent than petroleum or coal, on the time scale of human industrialization, peat is a fossil fuel and burning it does contribute to atmospheric carbon dioxide.

The production of biofuels to replace oil and natural gas is in active development, focusing on the use of cheap organic matter (usually cellulose, agricultural and sewage waste) in the efficient production of liquid and gas biofuels which yield high net energy gain. One advantage of biofuel over most other fuel types is that it is biodegradable, and so relatively harmless to the environment if spilled.

Direct biofuels are biofuels that can be used in existing unmodified petroleum engines. Because engine technology changes all the time, direct biofuel can be hard to define; a fuel that works well in one unmodified engine may not work in another. In general, newer engines are more sensitive to fuel than older engines, but new engines are also likely to be designed with some amount of biofuel in mind.

Conventional vegetable oil can be used in many older diesel engines (equipped with indirect injection systems), but only in the warmest climates. Usually it is turned into biodiesel instead. No engine manufacturer explicitly allows any use of vegetable oil in their engines.

Biodiesel can be a direct biofuel. In some countries manufacturers cover many of their diesel engines under warranty for 100 percent biodiesel use. Many people have run thousands of miles on biodiesel without problem, and many studies have been made on 100 percent biodiesel.

Butanol is often claimed as a direct replacement for gasoline. It is not in wide spread production at this time, and engine manufacturers have not made statements about its use. While on paper (and a few laboratory tests) it appears that butanol has sufficiently similar characteristics with gasoline such that it should work without problem in any gasoline engine, no widespread experience exists.

The advantages of butanol are the high octane rating (over 100) and high energy content, only about 10 percent lower than gasoline, and subsequently about 50 % more energy-dense than ethanol, 100 % more so than methanol. The major disadvantage of butanol is the high flashpoint (35 °C).

Ethanol is the most common biofuel, and over the years many engines have been designed to run on it. Many of these could not run on regular gasoline, so it is debatable whether ethanol is a replacement in them. In the late 1990s, engines started appearing that by design can use either fuel. Ethanol is a direct replacement in these engines, but it is debatable if these engines are unmodified, or factory modified for ethanol.

There is increasing interest in the use of a blend of 85 % fuel ethanol with 15 % gasoline. This fuel blend called E85 has a higher fuel octane than premium gasoline allowing in properly optimized engines to increase both power and fuel economy over gasoline.

In reality, small amounts of biofuel are often blended with conventional fuels. The biofuel portion of these fuels is a direct replacement for the fuel they offset, but the total offset is small. For biodiesel, 5 % or 20 % are commonly approved by various engine manufacturers.

Using waste biomass to produce energy can reduce the use of fossil fuels, reduce GHGs emissions, and reduce pollution and waste management problems. A recent publication by the European Union highlighted the potential for waste-derived bioenergy to contribute to the reduction of global warming. The report concluded that 140 million barrels of oil equivalent will be available from biomass by 2020, 46 % from bio-wastes: municipal solid waste (MSW), agricultural residues, farm waste, and other biodegradable waste streams.

Landfill sites generate gases as the waste buried in them undergoes anaerobic digestion. These gases are known collectively as landfill gas (LFG); this can be burned and is a source of renewable energy. Landfill gas contains approximately 50 % methane (the same gas that is found in some types of natural gas) and can be burned either directly for heat or to generate electricity for public consumption. If LFG is not harvested, it escapes into the atmosphere; this is not desirable because methane is a GHG, and is more harmful than carbon dioxide. Methane has a global warming potential of 23 relative to carbon dioxide (i.e., 1 ton of methane produces the same GHG effect as 23 tons of carbon dioxide).

Anaerobic digestion can be used as a distinct waste management strategy to reduce the amount of waste sent to landfill and generate methane, or biogas. Any form of biomass can be used in anaerobic digestion and will break down to produce methane, which can be harvested and burned to generate heat, power, or to power certain automobiles.

Cryogenic Fuels. The term cryogenic fuels refer to materials that are gases at normal ambient conditions that have been cooled to their boiling point and stored as low temperature liquids. Examples are liquid hydrogen and liquid methane. Table 9.31 lists the energy content, boiling point and density for these fuels.

Table 9.31

Characteristics of Cryogenic Fuels

Fuel	Energy content MJ/kg	Boiling point, °C	Density at boiling point, g/cm^3
Hydrogen	120	- 253	0,071
Methane	50	- 162	0,424

Both of these fuels have very high gravimetric energy content, but their low density leads to low volumetric energy content. Both fuels are fundamentally different from jet fuel and would require a new fuel infrastructure in addition to new engines and airframes. Hydrogen from renewable resources is positioned as the fuel of the future. We are starting to see hydrogen used in fuel cells both for stationary power generation and to power ground vehicles. More than ninety percent of hydrogen produced today is generated by reforming natural gas, methane, into hydrogen and carbon dioxide. While meeting today's industrial hydrogen demands, the overall efficiency of this process for the production of transportation fuels should be questioned as it basically converts one fuel into another and generates CO_2, a GHG. Before hydrogen will displace fossil fuels as a major source of energy, an efficient and economical process will be needed to generate hydrogen from water and other renewable resources such as solar or biomass.

Cryogenic fuels may be used in commercial aviation, but not for several decades.

Hydrogen energy and fuel cells. Hydrogen and fuel cells are seen by many as key solutions for the 21th century, enabling clean efficient production of power and heat from a range of primary energy sources. TheHigh Level Group for Hydrogen and Fuel Cells Technologies was initiated in October 2002 by the Vice President of the European Commission, Loyola de Palacio, Commissioner for Energy and Transport, and Mr Philippe Busquin, Commissioner for Research. The group was invited to formulate a collective vision on the contribution that hydrogen and fuel cells could make to the realisation of sustainable energy systems in future.

This final report has been produced as a follow-up to the summary report presented at the conference “The hydrogen economy – A bridge to sustainable energy” held in Brussels on 16-17 June 2003. The terms of reference for the group requested the preparation of a vision report outlining the research, deployment and non-technical actions that would be necessary to move from today’s fossil-based energy economy to a future sustainable hydrogen-oriented economy with fuel cell energy converters (Fig. 9.40).

The benefits of hydrogen and fuel cells are wide ranging, but will not be fully apparent until they are in widespread use. With the use of hydrogen in fuel-cell systems there are very low to zero carbon emissions and no emissions of harmful ambient air substances like nitrogen dioxide, sulphur dioxide or carbon monoxide. Because of their low noise and high power quality, fuel cell systems are ideal for use in hospitals or IT centres, or for mobile applications. They offer high efficiencies which are independent of size.

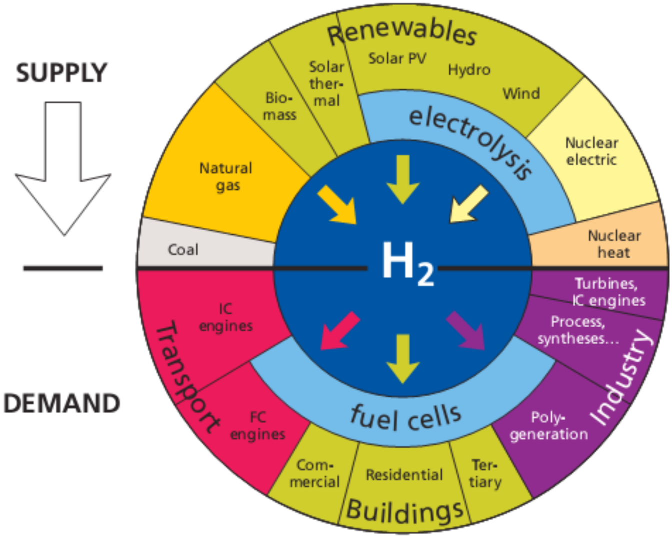


Fig. 9.40. Hydrogen: primary energy sources, energy converters and applications

Fuel-cell electric-drive trains can provide a significant reduction in energy consumption and regulated emissions. Fuel cells can also be used as Auxiliary Power Units (APU) in combination with internal combustion engines, or in stationary back-up systems when operated with reformers for on-board conversion of other fuels – saving energy and reducing air pollution, especially in congested urban traffic (Fig. 9.40).

In brief, hydrogen and electricity together represent one of the most promising ways to realise sustainable energy, whilst fuel cells provide the most efficient conversion device for converting hydrogen, and possibly other fuels, into electricity. Hydrogen and fuel cells open the way to integrated “open energy sys- ems” that simultaneously address all of the major energy and environmental challenges, and have the flexibility to adapt to he diverse and intermittent renewable energy sources that will be available in the Europe of 2030.

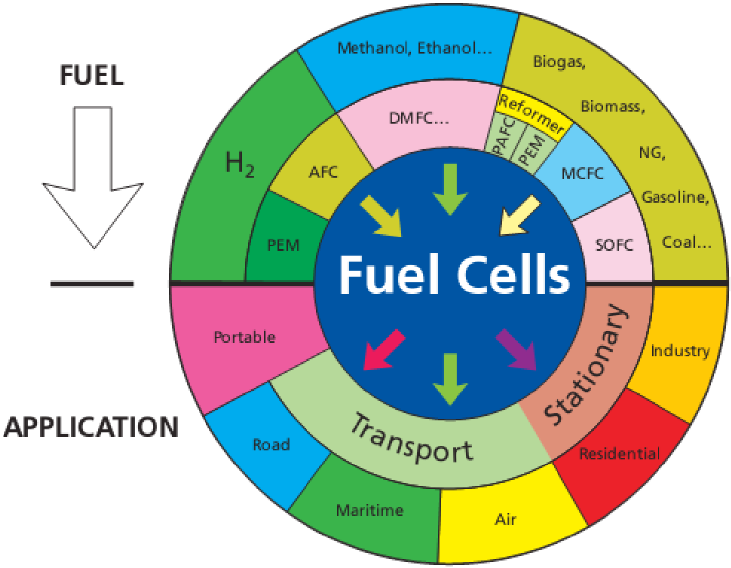


Fig. 9.41. Fuel cell technologies, possible fuels and applications.
NB: Size of "sectors" has no connection with current or expected markets;
PEM = Proton Exchange Membrane Fuel Cell; AFC = Alkaline Fuel Cells;
DMFC = Direct Methanol Fuel Cell; PAFC = Phosphoric Acid Fuel Cell;
MCFC = Molten Carbonate Fuel Cell; SOFC = Solid Oxide Fuel Cell

Europe should lead in undertaking rational analysis of alternative energy options and in demonstrating the benefits of a transition to a widespread use of hydrogen and fuel cells. They will have to provide cost-effective solutions to the following key challenges – the main drivers for Europe's future energy systems.

Today's society depends crucially on the uninterrupted availability of affordable fossil fuels which, in future, will be increasingly concentrated in a smaller number of countries – creating the potential for geopolitical and price instability. Hydrogen opens access to a broad range of primary energy sources, including fossil fuels, nuclear energy and, increasingly, renewable energy sources (e.g. wind, solar, ocean, and biomass), as they become more widely available. Thus, the availability and price of hydrogen as a carrier should be more stable than any single energy source. The introduction of hydrogen as an energy carrier, alongside electricity, would enable Europe to exploit resources that are best adapted to regional circumstances.

Hydrogen and electricity also allow flexibility in balancing centralised and decentralised power, based on managed, intelligent grids, and power for remote locations (e.g. island, and mountain sites). Decentralised power is attractive both to ensure power quality to meet specific customer needs, as well as reducing exposure to terrorist attack. The ability to store hydrogen more easily than electricity can help with load levelling and in balancing the intermittent nature of renewable energy sources. Hydrogen is also one of the few energy carriers that enables renewable energy sources to be introduced into transport systems.

Economic competitiveness. Since the first oil crisis in the 1970s, economic growth has not been directly linked with growth in energy demand in the Industrial sector, whereas in the transport sector increased mobility still leads to a proportionate increase in energy consumption. The amount of energy needed per unit growth must be reduced, while the development of energy carriers and technologies to ensure low-cost energy supply is of great importance. Development and sales of energy systems are also major components of wealth creation, from automobiles to complete power stations, creating substantial employment and export opportunities, especially to the industrialising nations. European leadership in hydrogen and fuel cells will play a key role in creating high-quality employment opportunities, from strategic R&D to production and craftsmen.

In the US and Japan, hydrogen and fuel cells are considered to be core technologies for the 21 century, important for economic prosperity. There is strong investment and industrial activity in the hydrogen and fuel cell arena in these countries, driving the transition to hydrogen – independently of Europe. If Europe wants to compete and become a leading world player, it must intensify its efforts and create a favourable business development environment.

Air quality and health improvements. Improved technology and post-combustion treatments for conventional technologies are continuously reducing pollutant emissions. Nevertheless, oxides of nitrogen and particulates remain a problem in certain areas, while the global trend towards urbanisation emphasises the need for clean energy solutions and improved public transport. Vehicles and stationary power generation fuelled by hydrogen are zero emission devices at the point of use, with consequential local air quality benefits.

GHG reduction. Hydrogen can be produced from carbon-free or carbon-neutral energy sources or from fossil fuels with CO capture and storage (sequestration). Thus, the use of hydrogen could eventually eliminate GHG emissions from the energy sector. Fuel cells provide efficient and clean electricity generation from a range of fuels. They can also be sited close to the point of end-use, allowing exploitation of the heat generated in the process. The table 9.32 illustrates how, in a mature hydrogen oriented economy, the introduction of zero carbon hydrogen fuelled vehicles could reduce the average GHG emissions from the European passenger car fleet, compared to the average level of 140g/km CO projected for 2008.

Table 9.32

The average GHG emissions, important for ecosions from the European passenger car fleet

Year	New cars (1) fuelled by zero-carbon hydrogen, %	Feet fuelled by zero-carbon hydrogen, %	Average CO_2 reduction (all cars) (2)	CO_2 avoided per year, $MtCO_2$
2030	5	2	2,8 g/km	15
2040	25	15	21,0 g/km	112
2050	35	32	44,8 g/km	240
(1) Figures based on an assumed European fleet of 175m vehicles. The fleet size will increase significantly by 2040, with correspondingly larger benefits. (2) Calculation is independent of total number of cars.				

The last column shows the corresponding amounts of CO_2 emissions that could be avoided. This may be compared to a projected total level of 750-800 $MtCO_2$ emissions for road transport in 2010. The numbers for H_2-fuelled cars are an assumption based on a survey of experts for conventional and alternative automotive drive trains, but not a prediction of future production or sales.

GHG savings of about 140 $MtCO_2$ per year (14 % of today's levels of CO_2 emissions from electricity generation) could be achieved if about 17 % of the total electricity demand, currently being supplied from centralised power stations, is replaced by more efficient decentralised power stations, incorporating stationary high-temperature fuel-cell systems fuelled by natural gas. Fuel-cell systems will be used as base load in the future decentralised energy systems.

These examples are not proposed as targets, but merely to serve as illustrations of the CO_2 savings that could be achieved with quite modest penetrations of hydrogen vehicles and fuel cell-based stationary power generation. Together, 15 % regenerative hydrogen vehicles and the above distributed fuel cell/gas turbine hybrid systems could deliver about 250 $MtCO_2$ savings per year. This is approximately 6 % of the energy-related CO_2 emissions forecast in 2030, and progress such as this would allow Europe to move beyond the Kyoto Protocol.

Hydrogen and fuel cells are firmly established as strategic technologies to meet these objectives. They can create win-win situations for public and private stakeholders alike. The benefits will only start to really flow after public incentives and private effort is applied to stimulate and develop the main markets –stationary power and transport. This should be done in a balanced way that reflects the most cost-effective use of the various alternative primary energy sources and energy carriers.

Hydrogen production. Hydrogen can be produced in many different ways, using a wide range of technologies. Some of these involve established industrial processes while others are still at the laboratory stage.

Some can be introduced immediately to help develop a hydrogen energy supply system; while others need considerable research and development.

Current hydrogen production is mostly at a large scale. Before a hydrogen energy system is fully proven and fully introduced, many regional demonstration and pilot projects will be required. Aside from large-scale industrial equipment, small-scale production technologies, including electrolysers and stationary and on-board reformers, which extract hydrogen from gaseous and liquid fuels like natural gas, gasoline and methanol, will be needed. Many organisations are developing technologies specifically for this scale of operation. Safety will be a paramount issue. The table 9.33 below compares the principal hydrogen production routes.

Table 9.33

The hydrogen production technologies

Hydrogen production technology	Benefits	Barriers
1	*2*	*3*
Electrolysis: splitting water using electricity	Commercially available with proven technology; Well-understood industrial process; modular; high purity H_2, convenient for producing H_2 from renewable electricity, compensates for intermittent nature of some renewables	Competition with direct use of renewable electricity
Reforming (stationary and vehicle applications): splitting hydrocarbon fuel with heat and steam	Well-understood at large scale; widespread; lowcost hydrogen from natural gas; opportunity to combine with large scale CO_2 sequestration ('carbon storage')	Small-scale units not commercial; H_2 contains some impurities; gas cleaning may be equired for some applications; CO_2 sequestration adds costs; CO_2 emissions; primary fuel may be used directly
Gasification: splitting heavy hydrocarbons and biomass into H_2 and gases for reforming	Well-understood for heavy hydro-carbons at large scale; can be used for solid and liquid fuels; possible synergies with synthetic fuels from bio-mass-biomass gasification being demonstrated	Small units very rare; H_2 requires extensive cleaning before use; biomass gasification still under research; biomass has land-use implications; competition with synthetic fuels from biomass
Thermochemical cycles using cheap high temperature heat from nuclear or concentrated solar energy	Potentially large scale production at low cost and without GHG emission for heavy industry or transport; International collaboration on research, development and deployment	Complex, not yet commercial, researches are needed over 10 years on the process: materials, chemistry technology; High temperature nuclear reactor deploy ment needed, or solar thermal concentrators

1	2	3
Biological production: algae and bacteria produce H_2 directly in some conditions	Potentially large resource	Slow H_2 production rates; large area needed; most appropriate organisms not yet found; still under research

Hydrogen storage. Hydrogen storage is common practice in industry, where it works safely and provides the service required. Also, hydrogen can easily be stored at large scale in vessels or in underground caverns. However, for mobile applications, to achieve a driving range comparable to modern diesel or gasoline vehicles, abreakthrough in on-board vehicle hydrogen storage technology is still required. Innovative vehicle designs could help overcome current drawbacks. Significant research and development is under way, with new systems in demonstration. Conventional storage, such as compressed gas cylinders and liquid tanks, can be made stronger, lighter and cheaper. Novel methods, including hydrogen absorption using metal hydrides, chemical hydrides and carbon systems, require further development and evaluation.

Hydrogen end-use. Hydrogen can be burned either to provide heat, or to drive turbines, or in internal combustion engines for motive and electrical power. Many of these technologies are quite mature, although improvements in materials and processes will help them work better and last longer. Fuel cells are in the early stages of commercialisation and offer a more efficient hydrogen use. Hydrogen internal combustion engines in vehicles may provide an important route to enable hydrogen introduction while other technologies, such as fuel cell electric drive trains develop.

9.2. Alternative jet fuels

Today we have to take into account that air travel currently accounts for only 2 % of anthropogenic CO_2 emissions worldwide, but its relative share of global emissions could expand as other sectors decarbonize while the aviation industry continues to expand.

The contribution of jet fuel to the total energy consumption in transport is expected to increase from 11 % to 14 % in the next 20 years. More than 99 % of airline emissions are generated by the combustion of jet fuel, and the emissions from international aviation, which account for approximately 65 % of global aviation fuel consumption, are expected to increase to 1,1 – 1,5 billion t CO_2 by 2035. Aircraft also emit other gases and particles that have climate impacts.

To facilitate carbon-neutral growth of international civil aviation GHG emissions after 2020, ICAO introduced the *Carbon Offsetting and Reduction Scheme for International Aviation (CORSIA)*. CORSIA is a global market-based measure system to offset international aviation emissions growth if in-sector measures – technological improvements, operational efficiency measures, and alternative aviation fuels – are insufficient to keep emissions at 2020 levels. The remaining reductions would be met with offsets, such as emissions-reduction credits from the UNFCCC's Clean Development Mechanism.

Technology improvements**:** This is the range of estimated emission reductions due to aircraft technology improvements. Such improvements are driven by international standards developed by ICAO, in addition to competition and fuel prices. For example, in February 2016, ICAO finalized a proposed performance standard for new aircraft that will impose binding improvements in fuel efficiency and reductions in CO_2 emissions. The standards will require, on average, a 4 % reduction in the cruise fuel consumption of new aircraft starting in 2028 compared to 2015 deliveries, with the actual reductions ranging from 0 to 11 %, depending on the maximum takeoff mass of the aircraft. This compares to research suggesting that the average fuel burn of new aircraft can be reduced by approximately 25 % in 2024 and 40 % in 2034 using emerging technologies.

Operations improvements: This is the range of estimated emission reductions due to operational improvements, such as new communications, navigation, surveillance, and air traffic management systems. These measures permit more direct routings and the use of more efficient flight conditions, such as optimum altitude and speed. Other operational techniques to minimize fuel consumption are to maximize the aircraft's load factor or to minimize the empty mass of the aircraft.

Alternative jet fuels: This comprises emission reductions due to the substitution of petroleum-based JFs with alternative JFs.

Market-based measures: This includes a variety of strategies to reduce emissions through various flexible approaches, including levies on carbon, emissions trading, and offsetting. Under CORSIA, this mostly comprises emission reductions achieved through offsetting. Offsets represent a way for the emitters to invest in emission reductions elsewhere, and to count the achieved emission reductions, represented as offset certificates, as part of their contribution to emission reductions.

Technological and operational improvements alone cannot reduce aviation emissions enough to meet ICAO's target of carbon-neutral growth. ICAO's findings indicate that before factoring in the contribution of carbon offsets, the bulk of the emissions reductions needed for international aviation would have to come from a transition to alternative jet fuels. Alternative jet fuels do not necessarily generate lower carbon emissions than conventional petroleum-based fuels.

However, the contribution of alternative jet fuels to GHG mitigation rests on a variety of assumptions and is limited by two main considerations: the carbon intensity of alternative jet fuels and the availability of the feedstock that would be required to produce them in a sustainable manner.

At present days the basic principles of European policy in sphere of alternative fuels use in aviation are identified in the following documents:

- Directive 2009/28/ EC of the European Parliament and the Council "On the promotion of the use of energy from renewable sources" (The Renewable Energy Directive – RED),
- The agreement of the European Commission "EU Biofuel Strategy" that determines seven strategic directions for development and production of biofuels by the member countries and developing countries,
- Directive 2009/30/EC of the European Parliament and the Council, "On the technical requirements to gasoline, diesel and gas fuels, and introduction of a mechanism for monitoring and reduction of greenhouse gases emissions" (Directive on fuel quality).

Nevertheless, the large scale deployment of SAFs in air transport has been slow down by inadequate policies and regulations. The RED Directive sets up the objective of 10 % of renewable energy consumption in transport in 2020, promoting the use of biofuels (through the double counting mechanism), but in rail and road sector only. The strong efforts towards the production of sustainable biofuels endorse the terrestrial transport sector, following a limited access for air transport to renewable sources. However, there are some important recent developments in the regulatory field:

- From January 2013 it is mandatory that also alternative JFs meet the RED sustainable requirements in order to be eligible for exemption from EU ETS,
- The potential introduction of the Indirect Land Use Change as new parameter (ILUC factors) to evaluate the sustainability of a biofuel, together with the usual direct emissions, creates new challenges to the whole biofuel sector.

The European Parliament, in response to the EC proposal for amendment of the RED Directive, on 11 September 2013 proposed a cap to first generation biofuels with potential negative impact on ILUC: this class should account for no more than 6 % of the 10 % target (in energy) for renewable energy use in transport by 2020 under the EU RED. The proposal also would ensure that advanced biofuels with low ILUC effects account for 2,5 %, counted fourfold when derived from algae, bacteria and carbon captures.

Currently aviation is still exempt from quotas of renewable fuels that have been imposed on other transport sectors. However, the ongoing discussion on the policy framework should drive the sector – even if no mandatory targets are set – to focus on highly GHG-efficient fuels deriving by feedstock that do not harm current land use patterns, such as lignocellulosic fuels, or algae and waste fuels. In other terms, not only GHG emission reduction is important, but also the direct and indirect land use becomes a major element in sustainability assessment of a biofuel supply chain. Finally, depending on the outcome of the RED revision, different impacts on feedstock costs will occur: aviation biofuel users will have to carefully take into consideration to achieve economic balance.

Today the concept of sustainable growth requires the aviation sector to meet today’s needs without depleting the resources available to future generations. The industry is conscious of aviation’s environmental impacts and its contribution to climate change.

In 2009 the aviation industry collectively agreed to the world's first set of sector-specific climate change targets (Fig. 9.42). These targets are:

- 1,5 % fuel efficiency improvement from 2009 until 2020;
- carbon neutral growth from 2020;
- 50 % reduction in carbon emissions by 2050 relative to a 2005 baseline.

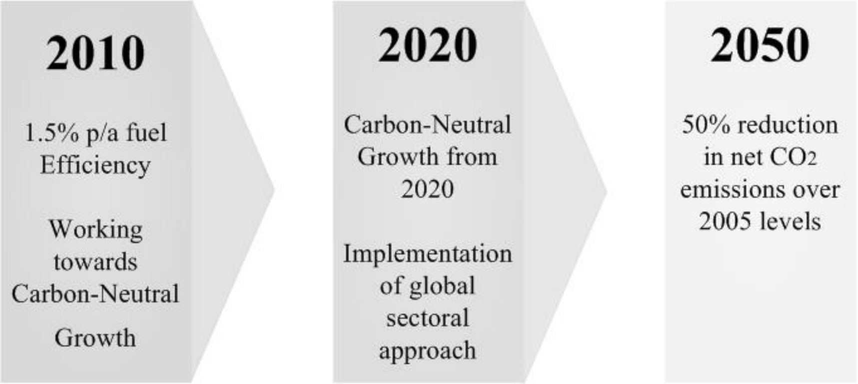


Fig. 9.42. Climate change targets for aviation industry

In 2009, the ICAO organized the Conference on Aviation and Alternative Fuels, during which ICAO Member States endorsed the use of sustainable alternative fuels for aviation as an important means of reducing aviation emissions. This turning point, where consideration of alternative fuels became global, further led to the inclusion of recommendations in the Resolution on Aviation and Climate Change, Resolution A37-19, adopted by the 37th ICAO. In particular, ICAO maintains and develops the GFAAF, a web platform through which a unique database on aviation alternative fuels developments is made available to the aviation community. ICAO was also tasked by the 38th Assembly to provide a global view on the future use of alternative fuels and on the associated changes in life cycle emissions, in order to assess the progress towards achieving ICAO's Member States' goal to stabilize aviation emissions at their 2020 level. Assessing fuel life cycle emissions is a topic for which increased harmonization amongst aviation stakeholders is important in order to acquire a shared understanding of the potential benefit of alternative fuels. The *Alternative Fuels Task Force (AFTF)* was created within the ICAO technical body on environment, the *CAEP*. The AFTF is tasked to develop a methodology to assess fuels life cycle emissions and apply it to quantify the emissions associated to a projection of alternative jet fuels production to 2050. The results were delivered to the 39th Session of the ICAO Assembly in 2016, and included in ICAO's environmental trends assessment for international civil aviation. The President of the ICAO Council delivered a joint action statement by ICAO and ATAG on the partnership between governments and the aviation industry on actions to reduce CO_2 emissions, including supporting the development of sustainable alternative fuels for aviation.

9.2.1. Technologies for alternative jet fuels production

Many biojet fuel conversion technologies, whether in the research and development, demonstration, or commercial stages, are described in

types, based on the feedstocks and conversion processes (Table 9.34):

1. *alcohol-to-jet (ATJ),*
2. *oil-to-jet (OtJ),*
3 *gas-to-jet (GtJ),*
4. *sugar-to-jet (StJ*).

Table 9.34

Summary of JF Production Pathways

No	Category	Production Pathways
1.	Alcohol-to-Jet (AtJ)	Ethanol-to-Jet
		Butanol-to-Jet
2.	Oil-to-Jet (OtJ)	Hydroprocessed Renewable Jet (HRJ)
		Catalytic Hydrothermolysis (CH)
		Hydrotreated Depolymerized Cellulosic Jet (Pyrolysis or HDCJ)
3.	Gas to Jet (GtJ)	FT Synthesis
		Gas Fermentation
4.	Sugar to Jet (StJ)	Catalytic Upgrading of Sugar to Jet
		Direct Sugar Biological to Hydrocarbons

Some of the technologies that convert bio-based feedstocks to JF have been widely reviewed in the literature in areas including feedstock availability, upgrading technology, process economics, lifecycle GHG analysis, and commercial progress. Most of the studies have focused on approved technologies such as Fischer-Tropsch synthesis and hydroprocessed renewable jet (HRJ) processes; few studies are available for either ATJ or STJ processes because they are still in the development stage.

Many process technologies that convert biomass-based materials into jet fuel substitutes are available. Some are available at commercial or pre-commercial scale, and others are still in the research and development stage. These technologies are varied and depend strongly on the type of feedstock.

Oil-based feedstocks are converted into biojet fuels through hydroprocessing technologies, including hydrotreating, deoxygenation, and isomerization and hydrocracking. Processes such as catalytic hydrothermolysis (CH) have also been developed to treat triglyceride-based oils. Solid-based feedstocks are converted into biomass-derived intermediate through gasification, into alcohols through biochemical or thermochemical processes, into sugars through biochemical processes, and into bio-oils through pyrolysis processes. Syngas, alcohols, sugars, and bio-oils can be further upgraded to biojet fuel via a variety of synthesis, either fermentative or catalytic processes. Hydroprocessing technologies using vegetable and waste oils represent the only conversion pathways that are ready for large-scale deployment. Industries are currently working on developing optimal processes that utilize sustainable feedstocks and can be produced economically.

The conversion of biomass into hydrocarbon alternative jet fuel can be carried out according to various different pathways: a summary of the most interesting routes – currently under investigation and demonstration by companies and research institutions worldwide – is given in the following Fig. 9.43. The most perspective and promising technologies for biomass processing into alternative jet fuels will be considered in details.

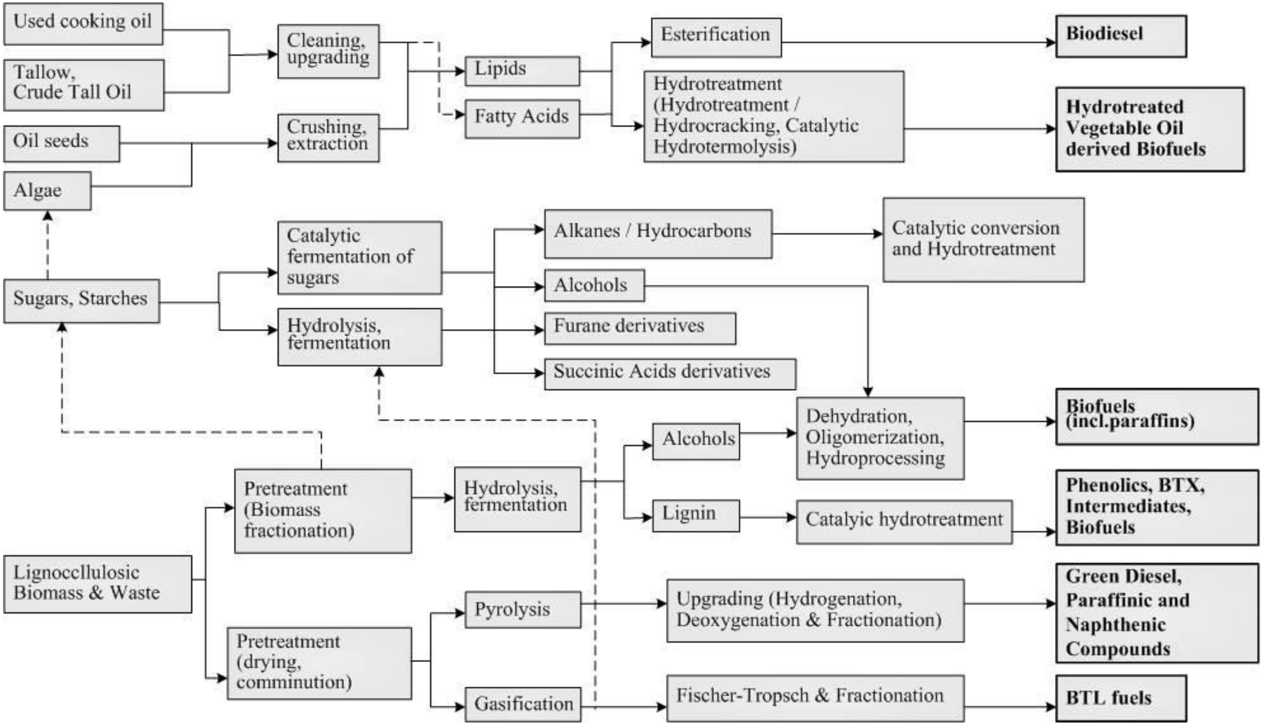


Fig. 9.43. Technologies for biomass processing into alternative jet fuels

Technology of biokerosene production. One of the first, who started studying and development of alternative jet fuels, was the group of scientist from Brazil leaded by Dr. E. Parente. In 1980’s he proposed using biokerosene as an alternative to conventional jet fuel. The technology of biokerosene production includes transesterification of various plant oils or animal fats at the presence of methanol or ethanol and some basic catalyst with further extraction of certain fraction.

There is data about the positive impact of new fuel on exploitation characteristics of jet engines. Except that, it was emphasized on the improvement of ecological properties comparing to conventional fuels.

Since times of the early alternative jet fuel developments numerous experimental studies have been done. A number of technologies, which allows production of high quality jet fuel of biological origin, have been proposed.

Today the more and more scientists agree that the most perspective technologies among the existing nowadays are the following:

- biomass to liquid (BtL),
- hydroprocessed esters and fatty acids (HEFA).

Today the mentioned above technologies are approved not only by scientific community but also by producers and operators of aircrafts. They are the only technologies, which are approved by the ASTM as technologies for production of jet fuel additives from non-conventional feedstock. These additives meet requirements of specification ASTM D7566. According to this specification, components may be blended with conventional jet fuel up 50 % (v/v). Today fuels obtained by these technologies are related to second generation alternative fuels.

Jet fuel production by hydrotreatment of fat-containing feedstock. Bio-additives production by *HEFA* technology is quit complicated multi-stage process. At the first stage the feedstock (microalgae, various plant oils, animal fats) are pressed for fats extraction. Then fats undergo processes of hydrogenation, deoxygenation of mono-, di- and triglycerides, free fatty acids and fatty acids esters. After that the processes typical for crude-oil processing are applied. Among them are: hydrotreatment, hydrocracking, hydroizomerization, polymerization, isomerization and fractionation. The result is hydrogenated synthetic paraffinic kerosene *(SPK or Bio-SPK)*. The new product is used as a component of conventional jet fuel in quantity up to 50 %. Since 2008 this kind of biofuel is studied by aircraft producers: Boeing, General

Electric, CFM, Pratt & Whitney and Rolls-Royce, Honeywell/UOP in cooperation with companies Air New Zealand, Continental Airlines, Japan Airlines.

This component is a synthetic kerosene fraction and doesn’t contain sulfur and aromatic hydrocarbons. Its low-temperature properties may be regulated according to the local climates by increasing hardness of hydrotreatment regime or additional catalytic processing. In general, these fuels are of high quality and possess properties similar to conventional jet fuels. Another advantage of the technology is possibility to use waste and by-products. Solid residues at the stage of primary feedstock processing (meal, flakes, vegetable stalk) may be used for production of solid organic fuel, various organic fertilizers or animal feed.

However, the abovementioned fuel component has some disadvantages. Its chemical composition is a mixture of synthetic paraffinic hydrocarbons. Thus, when they get into natural environment, its life-cycle is analogous to conventional JFs and makes harm to objects of ecosystems.

Jet fuel production by biomass processing. *BtL* technology is another commonly approved technology of jet fuel biocomponents production. Principally this technology is similar to the process of JF production via FT-synthesis from coal or natural gas. Various kinds of biomass may be used as a feedstock: wood residues, straw, plant residues, etc. At first the feedstock is decomposed under high temperatures – pyrolysis. After that obtained liquid biomass is used for production of synthesis-gas for the following FT-process. It is known that jet fuel produced by this technology is completely synthetic and its properties are similar to jet fuel made of coal.

The main advantage of this technology is its independence on the feedstock. Almost all plant biomass may be used for fuel production. Due to the natural origin at the end of new fuel life-cycle, the total amount of emitted CO_2 will decrease.

The comparatively new technology that is being developed now is *Alcohol-to-jet (AtJ)* – jet fuel made of alcohols. One of the aapproaches is convertion of agricultural waste by bacteria or yeasts into jet fuel directly or through the number of reactions of alcohol conversion. The technology is potentially easily achievable and cheap comparing to abovementioned. The feedstock is widespread and not expensive and the production process doesn't require high energy expenses.

Another sugar-based approach uses microorganisms converting the sugars into terpenes (and then kerosene, diesel-like fuels, and chemicals), another is based on catalyst chemistry to produce alkanes and a range of hydrocarbons and chemicals. The direct conversion of sugars to hydrocarbon fuels ferments the sugars to farnesene, which is then converted in a range of products as emollients, surfactants, industrial lubricants and biofuels, including aviation ones.

One more possible way is to grow lipids-accumulating microorganisms on sugars, and then to extract and process the lipids as previously described. The technology based on proprietary heterotrophic microalgae modified to accumulate more than 80 % oil, is a good example of industrial development in this direction. Alcohols, especially higher alcohols, can also be feedstock to jet fuels production through dehydration, oligomerization and hydroprocessing.

As regards lignocellulosic biomass, two possible process routes can be implemented: the biochemical pathway and the thermochemical one. The biochemical path starts with biomass pretreatment, which aims at opening the biomass structure to allow the enzyme to penetrate the feedstock and hydrolyse the sugar polymers cellulose and hemicellulose. The severity of the pretreatment step (in terms of temperature and pressure) however can generate fermentation inhibitors: therefore, being the cellulose and hemicellulose two very different polymers in terms of degradation behavior, several companies developed a two step pretreatment approach, which first separates and liquefies the hemicellulose (C_5) sugars and then process the cellulose (C_6) at higher severity. When monomeric sugars are available, fermentation occur by dedicated yeasts into ethanol and other products, and then lignin is separated from the stream. Being lignin a phenolic and aromatic rich feedstock, it can be the base for further processing into a range of products, either chemicals or fuels, including aviation kerosene.

The thermochemical pathway is instead based on high temperature oxygen gasification followed by the well known Fischer Tropsch process that was described previously.

Another new technology is pyrolysis of biomass (industrial, household or municipal waste). It is based on biomass heating to high temperatures and obtaining fat-containing feedstock. Later it is converted in JF. The advantage of this technology except biofuel production is solving the problem of waste disposal, which are the source of extra CO_2 emissions in case of conventional decomposition.

Pyrolysis of biomass is another option to derive a liquid intermediate energy carrier from a solid lignocellulosic feedstock. This highly oxygenated acidic fuel is not suitable for transport application and needs extensive upgrading before being processed into a transport fuel, for instance through emulsification. Pyrolysis of vegetable oil followed by further stabilization and upgrading through catalytic hydrotreating is instead a feasible alternative to produce bioderived jet fuels: even more interesting, the high-density upgraded pyrolysis-derived biojet fuel is rich in aromatics and cycloparaffins, and shows excellent cold flow properties, thus a perfect blending component with FT synthetic paraffinic kerosene and hydroprocessed esters and fatty acid. Hydrothermal liquefaction of biomass, which is still a thermochemical process but carried out under pressure and in near-critical water environment, could instead offer better perspectives but still need significant researches.

9.2.2. World experience in alternative jet fuels use

American Standard *ASTM D7566* was firstly enacted in 2009. It covers the production of jet fuels, which consist of a mixture of conventional and synthetic components. It determines certain types of jet fuels for civil aviation that contain synthetic hydrocarbons, and that are satisfactory for use in aircrafts. It determines quality of jet fuels and its synthetic components at all life cycle stages: from production to fueling of aircrafts. This standard provides two grades of jet fuels: Jet A and Jet A-1 –distillate fuels of kerosene type, with a relatively high flash point. According to the standard JFs should consist of traditional fuel grades Jet A or Jet A-1, which are in compliance with D1655, and up to 50 % of the synthetic component, defined by this standard. Today standard ASTM D7566 determines only tree technologies, according to which synthetic components are produced:

Hydrogenated synthetic kerosene produced entirely from synthetic gas by the Fischer-Tropsch synthesis with further application of such traditional processes as hydrotreatment, hydrocracking, hydroisomerization, and also polymerization, isomerization and fractionation.

Hydrogenated synthetic paraffinic kerosene derived entirely from esters of fatty acids and free fatty acids by their hydrogenation and deoxygenation, followed by processing with the above mentioned processes.

Renewable Synthesized Iso-Paraffinic (SIP) kerosene – produced from hydro processed fermented sugars. The process converts sugar molecules to the hydrocarbon farnesane which can be blended to a maximum of 10 % with fossil kerosene. In 2014 the ASTM committee has included the use of renewable farnesane as a blending component in jet fuels for commercial aviation. The allowable blending percentage is 10 % with the balance of 90 % fossil kerosene.

Enlargement of feedstock for jet fuels production was reflected in the normative base by amending standards Def Stan 91-91 and ASTM D1655, as well as introduction of a new standard ASTM D7566, which regulates JFs production from alternative feedstock.

Technical certification of alternativejet fuels took place, primarily led by ASTM International with strong support from the United States *Commercial Aviation Alternative Fuels Initiative (CAAFI)* and the US Air Force. In 2009, ASTM approved fuels produced by the Fischer-Tropsch process as the first SAF suitable for use in commercial flights, up to a blend percentage of 50 %. However, insufficient amounts of Fischer-Tropsch fuels were available for actually performing commercial flights.

This was followed in 2011 by the ASTM approval of HEFA fuels in July 2011, which allowed, as a result of the improved availability of HEFA fuels, numerous SAF-powered commercial flights. In June 2014, the third production pathway for SAF was approved by ASTM, namely *Synthetic Iso-paraffin from Fermented Hydroprocessed Sugar (SIP)*, (also known as *Direct Sugar to Hydrocarbon (DSHC)* fuel). All SAF certifications occur under the ASTM D7566 specification. Fuels that comply with D7566 are automatically recognized as meeting the ASTM D1655 specification for conventional jet fuel.

Further pathways (Fig. 9.44) are currently undergoing the ASTM certification process, with specific task forces for each of them. For the following ones research reports are currently under review:

- *Alcohol-to-Jet (AtJ),* which by the end of 2014 has finished its test phase and was expected to receive certification in 2015;
- *FT synthetic paraffinic kerosene with aromatics (SKA);*
- *Hydroprocessed depolymerized cellulosic jet.*

Testing procedures are currently being compiled for the following:

- *Alcohol to jet SKA;*
- *Catalytic hydrothermolysis;*
- *SKA by catalytic conversion of sugar;*
- *SPK by catalytic conversion of sugars.*

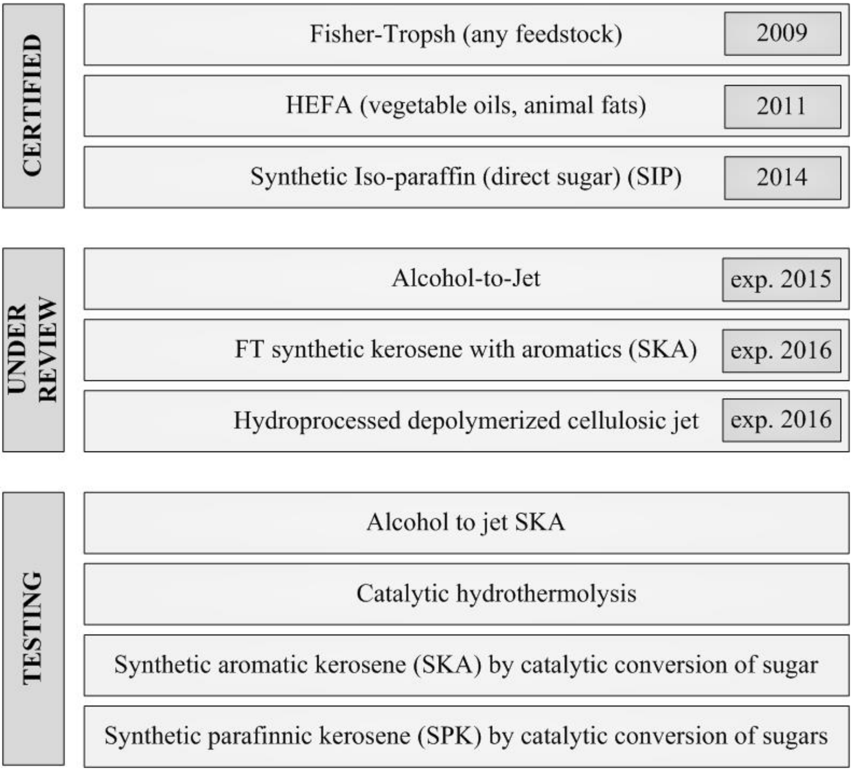


Fig. 9.44. ASTM certification and approval stages for diiferent SAF pathways

Following a proposal by Boeing, green diesel (also known as renewable diesel) at a low blending ratio (around 10 %) is also being considered to produce aviation drop-in fuel. A test flight with a 15 %

green diesel blend was completed on 3 December 2014. The possibility to use a fuel produced for the much larger automotive market would offer cost competitive SAF option without the need for large investments in production plants. A significant ramp-up of green diesel blend uptake could be achieved within this decade.

It should be noted that the duration of the fuel certification process, which for the Fischer-Tropsch process took several years, is becoming progressively shorter, and is no longer viewed as an impediment to introducing additional fuel production pathways. This in turn encourages research and development of new and potentially more economically viable feed stocks and production processes.

9.2.3. Feedstock for alternative jet fuels production

This diversity of technologies provides the ability for jet fuels 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.

Camelina is a genus within the flowering plant family of Brassicaceae and it includes *Camelina sativa & Subularia aquatic* (Fig. 9.45 There are also known about eight species growing in the Mediterranean region, Central Asia and Central Europe.

Camelina relates to energy crops with high oil content. Camelina grows to the height of one to three feet, with branching stems, which become woody at maturity. It is a short season crop, reaching maturity in 85–100 days, and it has attracted attention for being able to withstand water shortages in early stages of development. Its abundant, four-petaled flowers are pale yellow in colour. The leaves are pointed with smooth edges and grow approximately three inches long. Camelina is cultivated as an oilseed and, as such, has seeds with high oil content (40 %). Seeds, which mature in seed pods, have a characteristic orange colour and are very small in size. Camelina is harvested and seeded with conventional farming equipment, which makes adding it to the crop rotation relatively easy for farmers who do not grow it yet.

Fig. 9.45. Camelina Sativa culture

Camelina is widely distributed in Ukraine, the Crimea, Belarus and the European part of Russia (all areas, except the Volga-Donsky, Zavolzhsky, Nizhnedonskiy and Nizhnevolgsky), in Western and Eastern Siberia (all regions), in the Caucasus, Moldova, Central Asia.

The main consumers are the producers of biofuels. Camelina cultivation is currently implemented at sufficiently large scale so to achieve a considerable production of crude vegetable oil, that will then be converted into paraffinic biofuels (HEFA). 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. 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. Camelina is a very promising crop that is expected to offers a high level of sustainability, that can be grown in EU and elsewhere in marginal land where conventional agriculture is not sufficiently productive to be carried out by farmers. Nowadays this culture is widespread in the US, Canada and some European countries.

Rapeseed is considered to be one of the main crops for biofuels during the last 10–15 years. During 2000–2010 years leading producers of rapeseed oil were Canada, the US and European countries such as Germany, France, Czech Republic, Poland, UK (Fig. 9.46).

Fig. 9.46. Brassica napus (rapeseed) culture

The chemical composition and basic characteristics of rapeseed oil are well suited for alternative fuels. But then the question arose about the necessity of rapeseed cultivation as the main biofuels feedstock. Rape culture is highly depending on growing conditions, needs constant fertilizing and other care while significantly depletes the soil in areas that are traditionally used for agriculture. Analyzing these data, scientists have concluded that rape is competitive in needs of the food industry, and thus the process of production and usage of biofuels will not be sustainable. Numerous researches on selection rapeseed crops with improved physicochemical and agronomic characteristics were held. Thus, the oil content in the seed yield was increased as well as average oil output to 1200–1300 l/ha. The so-called low-erucic breeds with the corresponding fatty acid composition of the rapeseed oil were selected that is the best for biofuels. The scientists were able to increase crop resistance to pests, climatic conditions or other adverse growing conditions, and thus reduce the cost of oil production and fuel respectively. We can conclude that the denial of rapeseed as a feedstock for biofuels is not fully justified.

Jatropha is grown to obtain inedible oil that can be used to produce biofuels. Oil content in the seeds is about 30–40 %. It is known that due to the physical-chemical properties jatropha oil is well suited for the production of alternative jet fuels. This culture is not a depending on soil quality and can give good yields in dry uncultivated areas, leaving fertile soils for agriculture. Genus Jatropha includes about 175 species of plants growing in tropics and subtropics of the Old and New Worlds (Fig. 9.47).

Fig. 9.47. Jatropha culture

These are grasses, bushes and trees of the family Euphorbiaceae. Some of them are grown as ornamental plants in the tropical gardens and as indoor decoration. Most species of Jatropha are poisonous.

Jatropha fruits and oil are not used for food production. Jatropha grows in dry and marginal lands and requires watering only the first 2 years. Jatropha oil is used for protective coverage. However, the factor that limits the widespread use of jatropha, is the possibility of growing only in warm climates.

The first test flight of the aircraft, filled with a mixture of 50 % standard jet fuel and biofuel from jatropha was performed by the Air New Zealand on January 31, 2008. A two-hour flight was successful, and the company called the test a real milestone in the development of new types of aviation fuel, called on to reduce emissions and at the same time reduce the cost of operations.

Algae are recognized as the most promising raw materials for the production of large amounts of aviation biofuels. These microscopic plants can be grown in salt or fresh water, polluted water bodies, bodies of water in deserts and other uninhabited areas. During the lifecicle algae consume CO_2, which makes them extremely effective tool for the absorption of carbon from the atmosphere produced from burning of fossil fuels. Microalgae are capable for producing up to 15 times more oil on 1 km^2 than other energy crops. The can grow in low-boundary land not used for farming (desert areas).

It might be feasible to convert algae oil directly into green diesel or aviation fuel. Catalytic conversion of second generation oil with hydrogen into paraffins has already been investigated for application in industry. Production of algae-based aviation fuel has attracted a considerable interest from the aviation industry, especially after trials on commercial and military aeroplanes using algae biofuel blend.

The most common liquid fuel from algae is FAME that is typically produced by a reaction (transesterification) between triglycerides and alcohol (most commonly methanol) at 60–70 ^{o}C and in the presence of an alkaline or acidic homogeneous catalyst at atmospheric pressure. In addition to triglycerides in the lipid fraction, algae oil also contains a substantial quantity of free fatty acids and some moisture. Their occurrence is undesirable for transesterification because in alkaline catalysed reaction, they produce soap and reduce biodiesel yield. In this instance, an acid catalyst is better suited for the purpose as it is able to process low grade feed. Current processes used for manufacturing biodiesel are not entirely suitable for algae oil. A feasible option is to carry out the reaction at high temperature and pressure. The supercritical transesterification of first and second generation oil by various research groups showed almost complete conversion in reasonable reaction time. At supercritical conditions, the reaction can process moisturerich feed with free fatty acids and subsequently eliminate pre-treatment process units. Application of catalyst-free supercritical alcohol esterification is desirable due to feed stock flexibility and the relatively small reactor volume needed to achieve high production rates.

One of the main advantages of using algae is their massive biodiversity, which makes it possible to select strains for a particular geographical location or a specific purpose. Different algal strains have adapted to grow in UK soil, on the surface of the ocean, underneath desert sand, next to hydrothermal vents, and in freezing Siberian rivers. There is an optimal algal strain for every location. One potential algal application is to capture the CO_2 emitted by fossil fuel combustion in power stations. To achieve this, it is necessary to select an extremophile with high temperature and low pH tolerance, as well as a very active Calvin Cycle.

However, at this stage of development the issue of the best technologies development for algae cultivation is not yet fully resolved. Scientists project this process requires at least 8–10 years.

Halophytes are herbaceous plants that are combined in a separate group due to the possibility of their growth on saline soils (salt marshes and other areas with access to sea water) (Fig. 9.48).

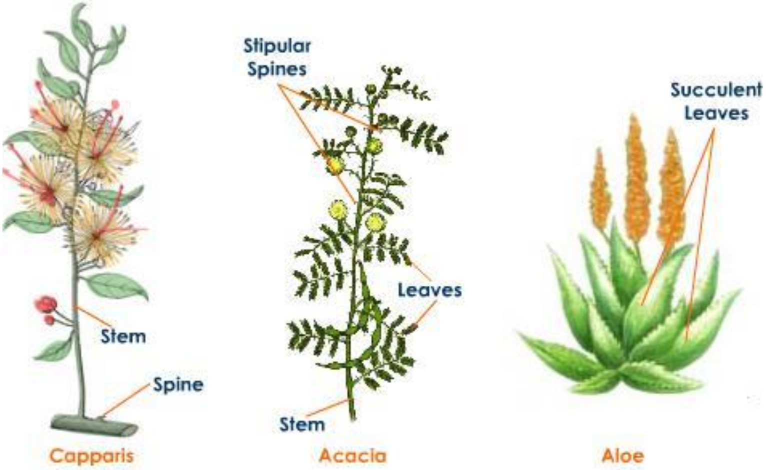


Fig. 9.48. Examples of halophytes plants

The using of this type of material is very promising in terms of the idea of sustainability of alternative JF. Today about 20–25% of the Earth is not used for agriculture through increased soil salinity levels. Typical examples of halophytes are rich in unsaturated fatty acids containing 90 % of carbon chains in triglycerides. Overall cultivation of halophytes is an important component of the system designed to reduce the amount of greenhouse gases. The use of these plants as a feedstock for the production of aviation biofuels is still at the research stage, but could be widely implemented in 2–4 years.

MSW and industrial waste in recent years are also considered a promising raw material for production of aviation biofuels. Currently factories are actively building, where as a result of complex processes such as waste wood, paper, wood residues, agricultural residues, by-products of livestock, some industrial waste, food waste, municipal sewage and others are processing into fuels. One of the advantages of the use of waste is the ability to ensure the production of biofuels from waste plant material. In addition, recycling of waste into alternative fuels is one of the solutions to the problem of waste recycling that accumulates on numerous landfills.

Used cooking oil (UCO) is another feedstock that is being investigated. Compared to other more traditional oily feedstock, UCO shows a high variability in quality and composition depending on the collection area, the collection method, and the period of the year (when different vegetable oils are consumed). Contaminations in the oil represent a serious technical challenge to be dealt with before catalytic hydrotreatment process.

The upgrade of crude UCO to a suitable feedstock is an activity that still requires R&D work, and new approaches can be considered. This variability could be reduced by proper pre-treatments. Once collected, UCO is usually filtered and de-watered: water in UCO can create problems in the downstream processes, and is source of damages to plant equipment, enhancing the corrosion.

The water content of UCO is normally reduced by means of paper filters, a cost-effective solution with high removal efficiency. The use a paper filtration contextually reduces the amount of suspended solids. The total contamination has to be significantly reduced, since solids in aviation engines are cause of injector and blade corrosion and erosion, increasing the maintenance engines costs and risks. The final biojet fuels have therefore to meet strict specifications.

Due to vegetable oil cooking processes, and contamination from the food, UCOs usually show high free acidity (1–5 %). A common possible mean to improve the UCO quality, reducing acidity without losses in its energy content, is the esterification process. This process, widely used in the biodiesel sector, rebuilds the triglycerides by using glycerine in a dedicated reactor, sometimes in presence of catalysts. However, the interest in this technique depends on the type of downstream processes: this process is normally adopted in the biodiesel sector, where in most of the cases transesterification to biodiesel does not tolerate high level of fatty acids, and could also be of interest for HEFA production.

Other possible means for UCO upgrading could be represented by thermochemical processing. An ad-hoc thermo-chemical treatment system is developed aimed at upgrading and improving the oil characteristics in a significant way, in view of further hydrotreatment. This work is still at the initial stage, and a small scale catalytic pilot reactor is being built: it will be used to test process conditions and different catalysts.

Today most of scientists claim about such property of alternative jet fuels as its sustainability. Sustainable aviation fuels (SAF) can be considered as sustainable only if they have a substantially better GHG balance than their fossil alternative, do not harm the environment, or involve any negative socio-economic impacts. Not all biomass feedstock is fit to produce SAF. The type and origin of the biomass feedstock largely determines the overall sustainability of the SAF, including the lifecycle of its GHG mainly through production and transport energy needs, use of fertilizers and land-use change (LUC) effects. Some types of biomass feedstock may actually cause more GHG emissions than conventional fossil jet fuel especially when considering indirect land use change impacts.

Table 9.35 presents a summary of the GHGs reduction for a number of feedstock. SAF derived from wastes (such as animal fat and used cooking oil), or based on wood and agricultural residues (such as straw), have significantly lower emissions than those based on conventional oil crops. SAF from algae can potentially be carbon neutral or even produce a reduction on GHG thanks to the absorption of CO_2 in co-products other than fuel. While these numbers are a useful guide, actual GHG reductions are ultimately dependent on the design of each specific project.

Table 9.35

Greenhouse gas emissions of SAF

Technology pathway	Feedstock	Emissions (gCO_2/MJ fuel)	Savings CO_2 vs jet fuel (baseline)
	Jet fuel (average value)	87,5	
FT	Wood residues/straw	4,8	95 %
HEFA	Conventional oil crops (palm oil, soy, rapeseed)	40–70	20–54 %
	Jatropha	30	66 %
	Camelina	13<5	85 %
	Animal fat	10	89 %
	Algae (from open ponds)	- 21 (best case) 1,5 (realistic case)	124 % (best case) 98 % (realistic case)

The estimation of the current biojet production cost still present a considerable degree of uncertainty. Currently, aviation biofuels are not yet produced on a commercial scale: thus, available figures are largely derived from modeling exercises or pilot experiences, rather than real market transaction.

It is clearly understood that feedstock is generally the largest cost item of alternative JFs production. Its share in the total alternative JFs cost may range from 45 % to 90 %. As a rule of thumb, the feedstock cost share is highest for *HEFA* technology, lowest for *FT* synthesis (waste residues) and somewhere in the middle for *AtJ* and *synthetic iso-paraffin (SIP)*.

Evidence on biojet fuel costs remains scarce, but recent studies, modeling processes and input for the HEFA chain, indicate that it should be possible to produce bio-kerosene at less than US $ 1.50 per liter. The economic evidence on the cost structure show relevant differences between FT-BTL and HRJ production, the main two classes of alternative jet fuel technologies already approved for use by ASTM.

The first type of biojet fuel requires large scale oxygen-blown biomass gasification technology, so the capital costs represent the major component of the cost structure, with high level of fixed costs: the total cost should range from $ 0,60 to $ 4,1 per liter. As regards HRJ, feedstock cost represents a very important component, accounting for almost 60 % of the gate price, as well as the size of the facility, for a total cost ranging from $ 1 to 1,16$ per liter. If jet cuts have to be maximized in the production chain versus other hydrocarbon (diesel, gasoline, naphtha), then costs would become even slightly higher ($ 0,06 per liter) due to additional hydrogen requirements and reduced revenues.

In many cases the cost competitiveness of biojet fuels therefore depends on the price of feedstock. The cost of feedstock includes the price of raw material and its eventual pre-treatments. Transport costs from the feedstock supplier to the alternative JF plant must be added too. Table 9.36 shows a selection of the wide range of variables influencing feedstock, logistics and pre-processing costs.

Table 9.36

Variables influencing feedstock, logistics and pre-processing costs

Feedstock costs	Logistics and pre-processing costs
- Geographic origin - Feedstock type - Seasonality (droughts) and availability - Level of mechanization and inputs - Scale	- Distance - Accessibility - Mode of transportation - Technology level - Scale

Projects and strategies to increase feedstock yields and to optimize logistics in terms of availability and infrastructure are required to ensure the provision of feedstock at competitive prices.

9.3. Synthetic and bio-based lubricants

Natural oils as lubricants. The benefits of vegetable oils being both renewable and biodegradable have provided an incentive to find application for these fluids as chain-saw bar lubricants, outboard engine lubricants, drilling muds, and in partial loss applications such as hydraulic fluids and greases.

Vegetable oils cost approximately twice that of mineral oils, are biodegradable, and renewable. They are also able to provide biodegradable features, generally achievable by synthetic esters, but at substantial cost savings. Vegetable oils in general are deficient relative to mineral oils, chemically modified mineral oils (CMMOs), and most synthetic lubricants in terms of their thermal and oxidative stability. There are also, in some cases, serious limitations to the use of vegetable oils when used in applications requiring operation at low temperatures.

Vegetable oils can be considered environmentally friendly because these materials are renewable, possess high levels of biodegradability, low aquatic toxicity, and do not accumulate in the environment.

Most vegetable oils are triglycerides, which are composed of a glycerol molecule esterified with various fatty acids.

The viscosity of lubricating oils is one of their most important properties when specifying an oil for a particular application. The chemical structure of the vegetable oil affects the flow properties of the oil. For example, if a fluid oil that contains a significant quantity of oleic, linoleic, or linolenic acids or other unsaturated components is hydrogenated to produce a saturated version, the new material would have the properties of grease. The effect of this hydrogenation is to convert molecular structures that are bent at the double bond to molecular structures that are essentially linear in nature.

The key to the use of vegetable oil-based lubricants is that they cannot be used in every application. There is simply not enough vegetable oil produced globally on an annual basis. The entire production of vegetable oil does not go into lubricant application. Therefore, it is useful to consider the application of vegetable oils in lubricant applications where the properties and performance are best matched. For vegetable oils, this is in applications where the maximum operating temperatures are of less than 120 ^{o}C. At the other end of the spectrum are the low-temperature properties of the vegetable oils relative to synthetic lubricants, mineral oils, and chemically modified mineral oils (CMMOs). Many of these lubricants have excellent low-temperature properties and can be used under aretic conditions for extended periods of time. The limitations exist on how vegetable oils should be employed in applications where the ambient temperatures remain above -40 °C.

Oxidative stability is dependent on the predominant fatty acids present in the vegetable oil. Oils containing mostly saturated fatty acids will have good oxidative stability compared to a vegetable oil containing oleic acid or other monounsaturated fatty acids. The vegetable oils that contain mostly polyunsaturated fatty acids exhibit poor oxidative stability.

Chemically functionalized vegetable oils. Synthetic lubricant base oils offer improved stability and performance characteristics over refined petroleum oils, but at a price. Most of the biodegradable synthetic oils are chemical esters that offer superior thermal and oxidative stability. Prices for these niche products are higher than vegetable oils (VOs) and significantly higher than petroleum-based lubricants. Synthetic oils are partly derived from petroleum products and therefore are dependent on petroleum crude oils. VO based lubricants cannot replace all synthetic and petroleum based lubricants, but play an important role among the alternate energy sources and contribute to the goal of energy independence and security. Although the cost of VO based lubricants is higher than conventional mineral oil based lubricants, still environmental advantages in short, medium, and long range can balance the difference in cost. Moreover, choice of biobased lubricant contributes to the public image of the company, and with it opens up the possibility of conquering new markets. Two possible avenues are available for the improved biobased base oil:

– genetically modified oils: Oleic acids are more thermally stable than polyunsaturated fats, and therefore are highly desired components in VOs. Some other specialty canola oil products include high stearate oil for food applications, high myristate for soap and detergent manufacturing, and medium-chain fatty acids (FAs) for lubricants, nutritional, and high energy food products.

– chemical modification: Modification of the oil through chemical processing to improve oxidation stability and low temperature fluidity is still a subject under active investigation.

Without sacrificing favorable viscosity–temperature characteristics and lubricity, unsaturated VOs can be converted into thermo-oxidatively stable products by saturation of the carbon–carbon double bonds using alkylation, arylation, cyclization, hydrogenation, epoxidation, and other reactions. Chemical modifications of the carboxyl group of VOs include transesterification, hydrolysis, etc.

In general, VOs show better lubricity than mineral oils. The ester linkage delivers inherent lubricity and helps sticking to metal surfaces. Lubricity of chemically modified vegetable oils (CMVO) can be increased by increasing their viscosity (high molecular weight), improving the flow of lubricant to the wear surface, by reducing degree of branching (more linear), and by using antiwear/EP additives. In hydrodynamic lubrication, viscosity, which is related to film thickness, has a noticeable effect on friction and wear. The viscosity of the lubricant, in turn, depends on the viscosity of base fluid at 40˚C, temperature (viscosity index (VI)), pressure (pressure viscosity coefficient), and the effect of shear rate on viscosity. Viscosity and VI of CMVO depends on various factors as described above. Pressure viscosity coefficient (PVC) can be increased by increasing the length of the branched chains, with a greater degree of branching and more aromaticity. As the distance between contact surfaces decreases, (i.e., toward elastohyrodynamic from hydrodynamic lubrication), the material of construction, PVC (because of pressure increase between contact surfaces) and polarity of CMVO become very important.

The polar CMVO sticks to the surface and stays in the contact area, while the nonpolar material is squeezed out. In boundary lubrication, the physical properties of lubricants play a minor role. Surface phenomena, such as films formed by tribochemical reactions and physically and chemically absorbed layers of lubricants determine boundary lubrication. CMVOs have a high degree of polarity because of ester linkages in the molecules and it helps them to form physical bonds with metal surface using lone pairs of electrons on the oxygen atom of ester linkage, and are more efficient lubricants than nonpolar mineral oils. At higher loads, CMVOs tend to produce chemisorbed films due to the formation of metal soaps. The soaps usually get desorbed, once their melting temperature is reached (120 to 200 ^{o}C) whereby their boundary lubrication properties are lost. The incorporation of EP agents such as sulfur react at 100 ^{o}C to form a sulfide (which are stable over 1000 ^{o}C) film on the rubbing metal surface, and thus provides high temperature boundary lubrication. The free oxygen in the lubricant or from the atmosphere also acts as EP lubricant by forming oxide layers.

The energy efficiency of a system can be increased by decreasing viscosity and lower PVC. Low viscosity is desired for high energy efficiency to reduce energy lost to viscous drag. CMVOs have low PVC compared to isoviscous mineral oils.

The anticorrosion properties of VOs are better than those of mineral oils, and they have a higher affinity to metal surfaces. Certain properties such as corrosion, foaming, and demulsibility are mostly additive dependent. VOs have superior solubilizing power for contaminants and additive molecules than mineral base fluids. Most of the CMVOs are fully compatible with mineral oils and other functional fluids, thus most additives that were designed for mineral oils can be used for CMVOs as well. Better solvency and additive acceptability of CMVO permits application of even those additives, which are not soluble in mineral oils. Blending of CMVO with functional fluids such as PAOs, TMP esters, and others improve their low temperature performance and can also overcome solubility problem of additives in PAOs. Some of the disadvantages with CMVO can be overcome using specially formulated additive packages. VOs have very low volatility due to the high molecular weight of the triacylglycerol structure and the narrow range of viscosity change with temperature. Volatility decreases with increasing molecular weight, increasing polarity, increasing oxidation stability, and decreasing degree of branching.

Mineral oils are superior to VOs and their chemical derivatives if hydrolytic stability is considered. The presence of ester functionalities makes CMVOs susceptible to hydrolysis when exposed to a humid atmosphere, or when in contact with water. In practice, hydrolysis has proven to be a less serious problem than expected. The resistance to hydrolysis is dependent on the type of alcohol in the ester (if it is transesterified product), the extent of acyl branching in the FA chains, molecular geometry, additives used, and operating conditions.

Questions for self-control

1. What is the difference between the synthetic and bio based fuels?
2. Characterize fuels which are produced from oil shales.
3. Characterize fuels which are produced from biomass.
4. Name main types of biofuels.
5. Describe perspectives of hydrogen use on transport.
6. Describe the main reasons for alternative jet fuels implementation.
7. What are the technologies for alternative let fuels production?
8. Name the standard that determine requirements to alternative jet fuels?
9. What kinds of feedstock for alternative jet fuels production do you know?
10. Characterize synthetic and bio-based lubricants.

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Motor Gasoline Test Methods

Property	Standard Test	Method Description
1	*2*	*3*
VaporPressure	ASTM D323 – Vapor Pressure of Petroleum Products (Reid Method)	In all six methods, a chilled, fixed volume of gasoline is placed in a test chamber and heated to 37.8°C (100°F). Then the pressure developed by gasoline vapors is measured in units of psi or kPa. The methods differ in the design of the apparatus, including the design of the test chamber. D323 yields Reid vapor pressure (RVP), and the other methods yield dry vapor pressure equivalent (DVPE). ASTM D323 cannot be used to measure the vapor pressure of gasoline containing ethanol and therefore is no longer recognized by ASTM D4814.
	ASTM D5190 –Vapor Pressure of Petroleum Products (Automatic Method)	
	ASTM D5191 – Vapor Pressure of Petroleum Products (Mini Method)	
	ASTM D4953 – Vapor Pressure of Gasoline and asoline-Oxygenate Blends (Dry Method)	
	ASTM D5482 – Vapor Pressure of Petroleum Products (Mini Method – Atmospheric)	
	ASTM D6378 – Vapor Pressure (VPX)of Petroleum Products, Hydrocarbons, and Hydrocarbon-Oxygenate Mixtures (Triple Expansion Method)	

1	*2*	*3*
Octane Number	ASTM D2699 – Research Octane Number of Spark-Ignition Engine Fuel	Both of these test methods employ a CFR single-cylinder, variablecompression, knock-test engine. The engine is operated under different test conditions of speed, mixture temperature, and spark advance for each method. During a gasoline test, the compression ratio of the test engine is adjusted to produce a knock of standard intensity. The knock intensity of the gasoline being rated is then matched to the primary reference fuel at the set compression ratio. The octane number of the reference fuel is assigned as the octane number of the test gasoline. The series of primary reference fuels are blends of normal heptane (octane number defined equal to zero) and isooctane (2,2,4-trimethylpentane, with a defined octane number equal to 100). The octane number of each primary reference fuel is equal to the volume percent of isooctane it contains.
	ASTM D2700 – Motor Octane Number of Spark-Ignition Engine Fuel	See Chapter 1, "Gasoline and Driving Performance," for information on Research octane number (RON), Motor octane number (MON), and antiknock index (AKI) and how these values are used to define the antiknock quality of gasoline.
Road Octane Number		Generally, road octane number (RdON) is determined by the CRC's Modified Uniontown Technique F-28-651. In this procedure, a test vehicle is operated on a series of primary reference fuels of increasing octane number under maximum throttle acceleration. (This test cannot be run on modern vehicles that have timing regulated by engine control modules). The. basic timing is advanced for each reference fuel until trace knock – the

1	*2*	*3*
		lowest knock level detected by the ear of the person rating the fuel – is detected. The plot of basic spark timing vs. RON rovides a primary reference curvefor the test car. Then the car is operated on the gasoline to be rated until the spark advance needed to cause trace knock under maximum throttle acceleration is found. The octane number associated with that spark timing advance in the primary reference curve is the RdON of the test gasoline. For a statistically significant determination, 10 to 15 test vehicles (usually different models) must be used because of the numerous variables involved. The RdONs of the individual vehicles are averaged to determine the final RdON of the test gasoline
Distillation Profile	ASTM D86 – Distillation of Petroleum Products at Atmospheric Pressure	In this test, a 100-milliliter fuel sample is placed in a round-bottom flask and heated to a controlled rate of evaporation. The temperature is recorded when the first drop of condensate falls from the lower end of the condenser tube into the receiving cylinder (the initial boiling point) and then at recovered volume percentages of 5 percent, 10 percent, every increment of 10 percent to 90 percent, 95 percent, and at the end of the test (end point/final boiling point). For gasoline samples, it is possible to correct for any sample loss by converting the temperatures associated with each incremental volume percentage recovered to temperatures for each incremental volume percentage evaporated.

1	*2*	*3*
Vapor-Liquid Ratio	ASTM D5188 – Vapor-Liquid Ratio Temperature Determination of Fuels (Evacuated Chamber Method)	In D5188, a calculated volume of air-saturated sample (all fuels) at 0 °C (32 °F) is introduced into an evacuated, thermostatically controlled test chamber of known volume. The sample volume is calculated to obtain the desired V/L ratio in the chamber. After injection, the chamber temperature is adjusted until a stable chamber pressure of 101.3 kPa (760 mm Hg) is achieved. ASTM D4814, Appendix X2 – Two calculation methods are specified: a computer method and a linear equation method. These methods are used to estimate vapor-liquid ratio (V/L) from vapor pressure and distillation test results and are not applicable for oxygenated gasolines. A procedure for correcting the estimated V/L values for ethanol blends is now part of D4814.
API Gravity (see page 41)	ASTM D1298 – Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method	For D1298, the sample is placed in a cylinder and the appropriate hydrometer is lowered into the sample. After temperature equilibrium has been reached, the sample temperature and hydrometer scale reading are recorded. ASTM Petroleum Measurement Tables are used to convert the recorded value to the value at a standard temperature such as 15 °C or 60 °F. For D4052, a small volume of liquid sample is introduced into an oscillating sample tube, and the change in oscillating frequency caused by the change in the mass of the tube is used in conjunction with calibration data to determine the density of the sample.
	ASTM D4052– Density and Relative Density of Liquids by Digital Density Meter	

1	*2*	*3*
Oxidation Stability (Induction Period)	ASTM D525 – Oxidation Stability of Gasoline (Induction Period Method)	Fifty milliliters of gasoline are placed in a glass sample container in a pressure vessel. Oxygen is introduced to a pressure of about 700 kPa (100 psi). The charged pressure vessel is placed in a 100 °C (212 °F) bath, and the pressure is continuously monitored. The break point of the fuel is determined to be the point just prior to a specified drop in pressure ithin a 15-minute interval. The number of minutes to the break point is reported.
Solvent-Washed Gum Content	ASTM D381 – Gum Content in Fuels by Jet Evaporation	Fifty milliliters of gasoline are evaporated under controlled air flow at about 155 °C (310 °F) for 30 minutes. The residue is weighed before and after extraction with n-heptane. The result is reported as milligrams per 100 mL.
Potential Gum	Chevron's test method for determining the gumming potential of a gasoline is based on ASTM D873 – Oxidation Stability of Aviation Fuels (Potential Residue Method), which combines ASTM D525– Oxidation Stability of Gasoline (Induction Period Method) and ASTM D381 – Gum Content in Fuels by Jet Evaporation.	One hundred milliliters of gasoline, free of deposit control additive, is oxidized for four hours at 100°C (212°F) in a bomb initially charged with 700 kPa (100 psi) of oxygen. After this treatment, the amount of insoluble gum is collected by filtration and measured. The soluble gum is isolated by ASTM D381 and measured. The total insoluble and soluble gum is eported as potential gum in units of milligrams per 100 mL.

1	*2*	*3*
Sulfur Content	ASTM D1266 –Sulfur in Petroleum Products (Lamp Method)	As the names of the sulfur test methods indicate, several technologies are used to determine the sulfur content of gasoline. Some of the methods are applicable only for samples with high sulfur concentration, others cover a broad range of sulfur concentration, and some can be used only for amples with low sulfur concentration. Specific test methods need to be reviewed for applicability before selecting one to use.
	ASTM D2622 – Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry	
	ASTM D3120 – Trace Quantities of Sulfur in Light Liquid Hydrocarbons by Oxidative Microcoulometry	
	ASTM D4045 – Sulfur in Petroleum Products by Hydrogenolysis and Rateometric Colorimetry	
	ASTM D4294 –Sulfur in Petroleum and Petroleum Products by Energy Dispersive X-ray Fluorescence Spectrometry	
	ASTM D5453 – Determination of Total Sulfur in Light Hydrocarbons, Spark Ignition Engine Fuel, Diesel Engine Fuel, and Engine Oil by Ultraviolet Fluorescence	
	ASTM D6334 – Sulfur in Gasoline by Wavelength Dispersive X-Ray Fluorescence	

1	2	3
	ASTM D6445 – Sulfur in Gasoline by Energy-Dispersive X-ray Fluorescence Spectrometry	
Copper Strip Corrosion	ASTM D7039 – Sulfur in Gasoline and Diesel Fuel by Monochromatic Wavelength Dispersive X-ray Fluorescence Spectrometry	D130 can be used to detect the presence of free sulfur or reactive sulfur compounds. In this test, a polished copper strip is immersed in 30 ml of gasoline and heated to 50 °C (122 °F) for three hours. The test strip is compared to standard strips and reported on a scale of one to four (one being best). It is becoming clear that as sulfur levels in gasolines are forced lower, many sulfur species that actually provide protection for copper surfaces are being greatly reduced or eliminated. In reformulated gasolines that have extremely low sulfur content, levels of free sulfur or reactive sulfur compounds that would not have caused a failed copper strip test in conventional gasolines may now cause a failure. This factor increases the urgency for minimizing contamination with even minor levels of free sulfur or reactive sulfur compounds in processing at the refinery.
Silver Strip Corrosion	ASTM D4814 Annex A1 – Corrosiveness of Silver From Petroleum Products by Silver Strip Test	This interim test method uses the ASTM D130 test apparatus except a silver coupon replaces the normal copper one and the test is conducted at 37,8 °C (100 °F) for three hours.
Lead Content	ASTM D3237 – Lead in Gasoline by Atomic Absorption Spectroscopy	These methods are applicable for determining the low levels of lead that may be present in unleaded gasoline.
	ASTM D5059 – Lead in Gasoline by X-Ray Spectroscopy	

1	*2*	*3*
Oxygenates Content	ASTM D4815 – Determination of MTBE, ETBE, TAME, DIPE, tertiary Amyl Alcohol, and C1to C4 Alcohols in Gasoline by Gas Chromatography ASTM D5599 – Determination of Oxygenates in Gasoline by Gas Chromatography and Oxygen Selective Flame Ionization Detection ASTM D5845 – Determination of MTBE, ETBE, TAME, DIPE, Methanol, Ethanol, and tert-Butanol Gasoline by Infrared Spectroscopy	In addition to using a gas chromatography column, D4815 uses either a flame ionization detector or a thermal conductivity detector and D5599 uses an oxygen-selective flame ionization detector. D5845uses a mid-infrared spectrometric analyzer to detect oxygenates.
Appearance	ASTM D4176 – Free Water and Particulate Contamination in Distillate Fuels (Visual Inspection Procedures)	This test can be used to visually determine appearance. The sample is placed in a clear glass jar and inspected for undissolved water, sediment, and suspended matter. For gasoline, the inspection is done at ambient temperature or 21 °C (70 °F), whichever is higher. Acceptable fuel is reported to be clear and bright and free of suspended material.

Diesel Fuel Test Methods

Property	Standard Test Method	Description
1	*2*	*3*
Flash Point	ASTM D 93 – Flash-Point by Pensky-Martens Closed Cup Tester (IP 34)	At least 75 ml are required for this test. The sample is stirred and heated at a slow, constant rate in a closed cup. The cup is opened at intervals, and an ignition source is moved over the top of the cup. The flash point is the lowest temperature at which the application of the ignition source causes the vapors above the liquid to ignite.
Water and Sediment	ASTM D 2709 – Water andSediment in Middle Distillate Fuels by Centrifuge	Water and sediment are fuel contaminants. In this test, a 100 ml sample is centrifuged under specified conditions in a cali- brated tube. The amount of sediment and water that settles to the bottom of the tube is read directly using the scale on the tube.
Distillation	ASTM D 86 – Distillation of Petroleum Products	The distillation profile is a fundamental fuel property. In this test, a 100-ml sample is placed in a round-bottom flask and heated to obtain a controlled rate of evaporation. The temperature is recorded when the first drop is collected (the initial boiling point), at recovered volume percentages of 5 %, 10 %, every subsequent 10 % to 90 %, 95 %, and at the end of the test (end point/final boiling point).

1	*2*	*3*
	ASTM D 2887 – Boiling Range Distribution of Petroleum Fractions by Gas Chromatography (IP 406)	This test can be used as an alternate to ASTM D 86 with the limits listed in Table 1 of ASTM D 975. The boiling range distribution determination by distillation is simulated by the use of gas chromatography. A non-polar packed or open tubular (capillary) gas chromatographic column is used to elute the hydrocarbon components of the sample in order of increasing boiling point. The column temperature is raised at a reproducible linear rate and the area under the chromatogram is recorded throughout the analysis. Boiling points are assigned to the time axis from a calibration curve obtained under the same chromatographic conditions by analyzing a known mixture of hydrocarbons covering the boiling range expected in the sample. From these data, the boiling range distribution can be obtained.
Viscosity	ASTM D 445 – Kinematic Viscosity of Transparent and Opaque Liquids (IP 71)	The sample is placed in a calibrated capillary glass viscometer tube and held at a closely controlled temperature. The time required for a specific volume of the sample to flow through the capillary under gravity is measured. This time is proportional to the kinematic viscosity of the sample.
Ash	ASTM D 482 – Ash from Petroleum Products (IP 4)	The sample is placed in a crucible, ignited, and allowed to burn. The carbonaceous residue is heated further in a muffle furnace to convert all the carbon to carbon dioxide and all the mineral salts to oxides (ash). The ash is then cooled and weighed.

1	*2*	*3*
Sulfur	ASTM D 5453 – Total Sulfur in Light Hydrocarbons, Spark Ignition Engine Fuel, Diesel Engine Fuel, and Engine Oil by Ultraviolet Fluorescence	This method is applicable to all grades and is the referee method for all S15 grades. Up to 20 µL of the sample (sample size is based on estimated sulfur concentration) is injected into a high-temperature combustion tube where the sulfur is oxidized to sulfur dioxide (SO_2) in an oxygen- rich atmosphere. Water produced during the sample combustion is removed and the sample combustion gases are then exposed to ultraviolet (UV) light. The SO_2 absorbs the energy from the UV light and converts it to excited sulfur dioxide (SO_2*). The fluores- cence emitted from the excited SO_2* as it returns to a stable state, SO_2, is detected by a photomultiplier tube, and the resulting signal is a measure of the sulfur contained in the sample.
	ASTM D 2622 – Sulfur in Petroleum Products by X-Ray Spectrometry	This is the referee method for all S500 grades. The sample is placed in an x-ray beam and the intensity of the sulfur x-ray fluorescence is measured This method is not recommended for determining the sulfur concentration of S15 diesel fuel because the repeatability is poor.
	ASTM D 7039 – Sulfur in Gasoline and Diesel Fuel by Monochromatic Wavelength Dispersive X-ray Fluorescence Spectrometry	NOTE: At the time of this publication, this method has been proposed for addition to D975. This test method covers the determination of total sulphur by monochromatic, wavelength-dispersive X-ray fluorescence (MWDXRF) spectrometry in single-phase gasolines, dieselfuels,and refinery process streams used to blend gasoline and diesel, at sulfur concentrations from 2 to 500 mg/kg.

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	ASTM D 129 – Sulfur in Petroleum Products (General Bomb Method) (IP61)	This is the referee method for No. 1-D and No. 2-DS5000and No.4-D. This test method covers the determination of sulfur in petroleumproducts, including lubricating oils containing additives, additive concentrates, and lubricating greases that cannot be burned completely in a wick lamp. The test method is applicable to any petroleum product sufficiently low in volatility that can be weighed accurately in an open sample boat and contains at least 0,1 % sulfur.
CopperStrip Corrosion	ASTM D 130 – Detection of CopperCorrosion from PetroleumProductsby the Copper Strip Tarnish Test(IP154)	A polished copper strip is immersed in the sample for three hours at 50 °C (122 °F) and then removed and washed. The condition of the copper surface is qualitatively rated by comparing it to standards.
Cetane Number	ASTM D 613 – Cetane Number of Diesel FuelOil(IP41)	The cetane number of a diesel fuel oil is determined by comparing its combustion characteristics in a test engine with those for blends of reference fuels of known cetane number under standard operating conditions. This is accomplished using the bracketing handwheel procedure. This procedure varies the compression ratio (handwheel reading) for the sample and each of two bracketing reference fuels to obtain a specific ignition delay permitting interpolation of cetane number in terms of handwheel reading.

1	*2*	*3*
Calculated Cetane Index	ASTM D 4737 – Calculated Cetane Index by Four VariableEquations	ASTM D 4737 provides a means for estimating the ASTM cetane number (Test Method D 613) of distillate fuels from density and distillation recovery temperature measurements. Two correlations in SI units have been established between the ASTM cetane number and the density and 10 %, 50 %, and 90 % distillation recovery temperatures of the fuel. Use Procedure A for Grades No. 1–D S500, No. 1–D S5000, No. 2–D S5000, and No. 4–D S5000. *Procedure A* $CCI = 45{,}2 + (0{,}0892)\,[T10N] + [0{,}131 + (0{,}901)\,(B)]\,[T50N] + [0{,}0523 - (0{,}420)\,(B)]\,[T90N] + [0{,}00049]\,[(T10N)\,2 - (T90N)\,2] + (107)\,(B) + (60)\,(B)2$ Where: CCI = Calculated Cetane Index by Four Variable Equation; D = Density at 15°C, g/ml determined by Test Methods D 1298 or D 4052; DN = D – 0,85; B = [(-3,5) (DN)] -1; T10 = 10 % recovery temperature, °C, determined by test method D 86 and corrected to standard barometric pressure; T10N = T10 – 215; T50 = 50 % recovery temperature, °C, determined by test method D 86 and corrected to standard barometric pressure; T50N = T50 – 260; T90 = 90 % recovery temperature, °C, determined by test method D 86 and corrected to standard barometric pressure; T90N = T90 – 310.

1	*2*	*3*
		Use Procedure B for Grade No. 2–D S500. *Procedure B* $CCI = -386{,}26\,(D) + 0{,}1740\,(T10) + 0{,}1215\,(T50) + 0{,}01850\,(T90) + 297{,}42$ Where: CCI = Calculated Cetane Index; D = Density at 15°C, g/ml determined by Test Methods D 1298 or D 4052; T10 = 10 % recovery temperature, °C, determined by test method D 86 and corrected to standard barometric pressure; T50=50 % recovery temperature, °C, determined by test method D 86 and corrected to standard barometric pressure; T90 =90 % recovery temperature, °C, determined by test method D 86 and corrected to standard barometric pressure. At the time of publication, Procedure B is commonly used to determine the Calculated Cetane Index of S15. Work is in progress at ASTM International to determine if a third procedure is required for ultra-low sulfur diesel fuels.
	ASTM D 976-80 – Calculated Cetane Index of Distillate Fuels	While this method is listed in Table 1 of ASTM D 975, its use is not recommended for low sulfur diesel fuel. ASTM D 4737 should be used for ultra-low sulfur diesel fuels in the U.S. ASTM D 976 is retained for use by the U.S. Navy and others outside the U.S. where they use high-sulfur distillates which can have higher aromatic levels and higher end points and where the Calculated Cetane Index determined by ASTM D 976 correlates better with the cetane number determined by ASTM D 613.

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Derived Cetane Number	ASTM D 6890 – Ignition Delay and Derived Cetane Number (DCN) of Diesel Fuel Oils by Combustion in a Constant Volume Chamber	A small specimen of diesel fuel oil is injected into a heated, temperature-controlled constant volume chamber, which has previously been charged with compressed air. Each injection produces a single-shot, compression ignition combustion cycle. Ignition Delay (ID) is measured using sensors that detect the start of fuel injection and the start of significant combustion for each cycle. A complete sequence comprises 15 preliminary cycles and 32 further cycles. The ID measurements for the last 32 cycles are averaged to produce the ID result. An equation converts the ID result to a DCN.
	ASTM D 7170 – Derived Cetane Number (DCN) of Diesel Fuel Oils – Fixed Range Injection Period, Constant Volume Combustion Chamber Method	A small specimen of diesel fuel oil is injected into a heated, temperature-controlled constant volume chamber, which has previously been charged with compressed air. Each injection produces a single-shot, compression ignition combustion cycle. Ignition Delay (ID) is measured using sensors that detect the start of fuel injection and the start of significant combustion for each cycle. A complete sequence comprises two preliminary cycles and 25 further cycles. The ID measurements for the last 25 cycles are averaged to produce the ID result. An equation converts the ID result to a DCN.

1	*2*	*3*
Aromaticity Tests	ASTM D 1319 – Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption (IP 156)	A small amount of sample is placed at the top of a special glass adsorption column packed with activated silica gel. The top layer of the silica gel in the column is treated with fluorescent dyes. Isopropyl alcohol is used to transport the sample and the fluorescent dyes down the column. Hydrocarbons are separated into bands of aromatics, olefins, and saturates according to their affinity for the silica gel.
	ASTM D 1319 – Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption (IP 156)	The fluorescent dyes are also selectively separated and make the boundaries of the aromatic, olefin, and saturate zones visible under ultraviolet light. The volume percentage of each hydrocarbon type is calculated from the length of each zone in the column.
	ASTM D 5186 – Determination of Aromatic Content of Diesel Fuels by Supercritical Fluid Chromatography	The sample is chromatographed on silica gel using supercritical carbon dioxide as the mobile phase to separate the aromatics from the rest of the sample and to separate the aromatics into monoaro- matics and polycyclic aromatics.
Cloud Point	ASTM D 2500 – Cloud Point of Petroleum Products (IP 219)	A clean clear sample is cooled at a specified rate and examined periodically. The temperature at which a haze is first observed is the cloud point.
Pour Point	ASTM D 97 – Pour Point of Petroleum Products (IP 15)	A clean sample is first warmed and then cooled at a specified rate and observed at intervals of 3 °C (5 °F). The lowest temperature at which sample movement is observed when the sample container is tilted is the pour point.

1	2	3
Low-Temperature Operability	ASTM D 4539 – Filterability of Diesel Fuels by Low-Temperature Flow Test (LTFT)	A sample is cooled at a rate of 1 °C/hour (1,8 °F/hour) and filtered through a 17-micron screen under 20 kPa vacuum. The minimum temperature at which 180 milliliters can be filtered in one minute is recorded.
	ASTM D 6371 – Cold Filter Plugging Point (CFPP) of Diesel and Heating Fuels (IP 309)	A sample is cooled at a rate of about 40 °C/hour. The highest temperature at which 20 milliliters of the fuel fails to pass through a 45-micron wire mesh under 2 kPa vacuum in less than 60 seconds is the CFPP.
Carbon Residue	ASTM D 524 – Ramsbottom Carbon Residue of Petroleum Products (IP 14)	The sample is first distilled (ASTM D 86) until 90 % of the sample has been recovered. The residue is weighed into a special glass bulb and heated in a furnace to 550 °C (1,022 °F). Most of the sample evaporates or decomposes under these conditions. The bulb is cooled and the residue is weighed.
Lubricity	ASTM D 6079 – Evaluating Lubricity of Diesel Fuels by the High-Frequency Reciprocating Rig (HFRR) (ISO/FDIS 12156- 1(2005)(E))	A hardened steel ball oscillates across a hardened steel plate under a fixed load for 75 minutes. The point of contact between the ball and plate is immersed in the sample. The size of the resulting wear scar on the steel ball is a measure of the sample’s lubricity.
	ASTM D 6078 – Evaluating Lubricity of Diesel Fuels by the Scuffing Load Ball-on-Cylinder Lubricity Evaluator (SLBOCLE)	This test is based on the BOCLE test, but determines the maximum load that can be applied without causing scuffing. A ball-on-cylinder apparatus immersed in the sample is run under a series of loads to closely bracket the highest non-scuffing load the sample can tolerate.

1	*2*	*3*
Oxidation Stability	ASTM D 2274 – Oxidation Stability of Distillate Fuel Oil (Accelerated Method) (IP 388)	After filtration to remove any particulate contamination, a 350 ml sample is transferred to a special glass container and held at 95 °C (203 °F) for 16 hours while oxygen is bubbled through the sample. At the end of the treatment period, the sample is allowed to cool to room temperature and filtered to collect any insoluble material that formed. The adherent insolubles are washed off the glass container with a trisolvent (mixture of equal parts methanol, toluene, and acetone); the trisolvent is evaporated to obtain the amount of adherent insolubles.
Storage stability	ASTM D 4625 – Distillate Fuel Storage Stability at 43°C (110°F) (IP 378)	After filtration to remove particulate contamination, separate 400 ml portions of the fuel are transferred to glass containers and stored at 43 °C (110 °F) for periods of 0, 4, 8, 12, 18, and 24 weeks. At the end of its treatment period, each sample is allowed to cool to room temperature and filtered to collect insoluble material that formed. Insolubles are washed off glass container with trisolvent; trisolvent is evaporated to obtain amount of adherent insolubles.
	ASTM D 5304 – Assessing Distillate Fuel Storage Stability by Oxygen Over	After filtration to remove particulate contamination, a 100 ml sample is placed in glass container, which is placed in a pressure vessel preheated to 90 °C (194 °F). The vessel is pressurized with oxygen to 100 psig and heated in an oven at 90 °C for 16 hours. At the end of the treatment period, the sample is allowed to cool to room temperature and filtered to collect insoluble material. The adherent insolubles are washed off glass container with trisolvent; trisolvent is evaporated to obtain amount of adherent insolubles.

1	*2*	*3*
Thermal stability	ASTM D 6468 – High Temperature Stability of Distillate Fuels	After filtration to remove any particulate contamination, separate 50 ml samples are placed in open tubes and aged for either 90 minutes or 180 minutes at 150 °C (302 °F) with air exposure. At the end of the treatment period, the samples are allowed to cool to room temperature and filtered. The amount of insoluble material collected on the filter pad is estimated by measuring the light reflected off of the pad.
Red dye	ASTM D 6756 – Determination of the Red Dye Concentration and Estimation of the ASTM Color of Diesel Fuel and Heating Oil Using a Portable Visible Spectrophotometer	Test method describes determination of the red dye concentration of diesel fuel and heating oil and estimation of the ASTM color of undyed and red-dyed diesel fuel and heating oil. The test method is appropriate for use with diesel fuel and heating oil of Grades 1 and 2 described in Specifications D 396, D 975, D 2880, and D 3699. Red dye concentrations are determined at levels equivalent to 0,1 to 20 mg/L of Solvent Red 26 in samples with ASTM colors ranging from 0,5 to 5. The ASTM color of the base fuel of red-dyed samples with concentration levels equivalent to 0,1 to 20 mg/L of Solvent Red 26 is estimated for the ASTM color range from 0,5 to 5. The ASTM color of undyed samples is estimated over the ASTM color range of 0.5 to 5. The test method provides a means to indicate conformance to contractual and legal requirements.

1	*2*	*3*
	ASTM D 6258 – Determination of Solvent Red 164 Dye Concentration in Diesel Fuels	Because the natural color of diesel fuels varies from nearly colorless to amber, red dye concentration cannot be measured accurately by simple visible absorption spectroscopy. This method effectively eliminates interference from the background color of the fuel by using the second derivative of the absorption spectrum. The amplitude difference between the second derivative spectrum maximum at 538 nm and the minimum at 561 nm is used to determine red dye concentration.
Conductivity	ASTM D 2624 – Electrical Conductivity of Aviation and Distillate Fuels (IP 274)	ASTM D 2624 covers the use of portable conductivity meters and in-line conductivity meters to determine the electrical conductivity of aviation and distillate fuels with and without a static dissipator additive. The test methods normally give a measurement of the conductivity when the fuel is uncharged, that is, electrically at rest (known as the rest conductivity). A voltage is applied across two electrodes in the fuel and the resulting current expressed as a conductivity value.
	ASTM D 2624 – Electrical Conductivity of Aviation and Distillate Fuels (IP 274)	With portable meters, the current measurement is made almost instantaneously upon application of the voltage to avoid errors due to ion depletion. Ion depletion or polarization is eliminated in dynamic monitoring systems by continuous replace- ment of the sample in the measuring cell. The procedure, with the correct selection of electrode size and current measurement apparatus, can be used to measure conductivities from 1 pS/m or greater. Please see the sidebar on page 47 for the definition of conductivity.

1	2	3
	ASTM D 4308 – Electrical Conductivity of Liquid Hydrocarbons by Precision Meter	This test method applies to the determination of the “rest” electrical conductivity of aviation fuels and other similar low-conductivity hydrocarbon liquids in the range from 0,1 to 2000 pS/m and can be used in the laboratory or in the field. A sample of liquid hydrocarbon is introduced into a clean conductivity cell which is connected in series to a battery voltage source and a sensitive dc ammeter. The conductivity, automatically calculated from the observed peak current reading dc voltage and cell constant using Ohm’s law, appears as a digital value in either the manual or auto- matic mode of meter operation.
Alcohol Control	EN 14110 –Determination ofMethanol Content ASTM D 93 – Flash-Point byPensky-Martens Closed Cup Tester(IP 34)	Alcohol control is to limit the level of unreacted alcohol remaining in the finished fuel. This can be measured directly by the volume percent alcohol or indirectly through a high flash point value. The flash point specification, when used for alcohol control for biodiesel, is intended to be 100 °C minimum, which has been correlated to 0,2 vol % alcohol. Typical values are over 160 °C. Due to high variability with Test Method D 93 as the flash point approaches 100 °C, the flash point specification has been set at 130 °C minimum to ensure an actual value of 100 °C minimum. Improvements and alternatives to Test Method D 93 are being investigated. Once complete, the specification of 100 °C minimum may be reevaluated for alcohol control.

Biodiesel Fuel Test Methods

Property	Standard Test Method	Description
1	*2*	*3*
Sulfated Ash	ASTM D 874 – Sulfated Ash from Lubricating Oils and Additives (IP 163)	Ash-forming materials may be present in biodiesel in three forms: (1) abrasive solids, (2) soluble metallic soaps, and (3) unremoved catalysts. Abrasive solids and unremoved catalysts can contribute to injector, fuel pump, piston and ring wear, and also to engine deposits. Soluble metallic soaps have little effect on wear but may contribute to filter plugging and engine deposits. The sample is ignited and burned until only ash and carbon remain. After cooling, the residue is treated with sulfuric acid and heated at 775 °C until oxidation of carbon is complete. The ash is then cooled, retreated with sulfuric acid, and heated at 775 °C to constant weight.
Carbon Residue	ASTM D 4530 – Determination ofCarbon Residue (Micro Method)	Carbon residue gives a measure of the carbon depositing tendencies of a fuel oil. While not directly correlating with engine deposits, this property is considered an approximation. Although biodiesel isin the distillate boiling range, most biodiesels boil at approximately the same temperature, and it is difficult to leave a 10 % residual upon distillation. Thus, 100 % sample is used toreplace the 10 % residual sample, with the calculation executed as if it were the 10 % residual.

1	*2*	*3*
Phosphorus	ASTM D 4951 – Determination of Additive Elements in Lubricating Oils by Inductively Coupled Plasma Atomic Emission Spectrometry	Phosphorus can damage catalytic converters used in emissions control systems and its level must be kept low. This specification was added to ensure that all biodiesel, regardless of the source, has low phosphorus content. A sample portion is weighed and diluted by mass with mixed xylenes or an other solvent. An internal standard, which is required, is either weighed separately into the test solution or is previously combined with the dilution solvent. Calibration standards are prepared similarly. The solutions are introduced to the Inductively Coupled Plasma (ICP) instrument by free aspiration or an optional peristaltic pump. By comparing emission intensities of elements in the test specimen with emission intensities measured with the calibration standards and by applying the appropriate internal standard correction, the concentration of phosphorus in the sample is calculable.
Distillation	ASTM D 1160 – Distillation of Petroleum Products at Reduced Pressure	Biodiesel exhibits a narrow boiling range rather than a distillation curve. The fatty acids chains in the raw oils and fats from which biodiesel is produced are mainly comprised of straight chain hydro- carbons with 16 to 18 carbons that have similar boiling temperatures. The atmospheric boiling point of biodiesel generally ranges from 330 to 357 °C, thus the specification value of 360 °C maximum at 90 % recovered. This specification was incorporated as an added precaution to ensure the fuel has not been adulterated with high boiling contaminants. The sample is distilled at an accurately controlled pressure

1	*2*	*3*
		between 0,13 and 6,7 kPa (1 and 50 mm Hg) under conditions that are designed to provide approximately one theoretical plate fractionation.Data are obtained from which the initial boiling point, the final boiling point, and a distillation curve relating volume percent distilled and atmospheric equivalent boiling point temperature can be prepared.
Metals	EN 14538 – Determination of Ca, K, Mg, and Na Content by Optical Emission Spectral Analysis with Inductively Coupled Plasma ICP OES)	Calcium, potassium, magnesium, and sodium may be present in biodiesel as abrasive solids or soluble metallic soaps. Abrasive solids can contribute to injector, fuel pump, piston, and ring wear and also to engine deposits. Soluble metallic soaps have little effect on wear, but they may contribute to filter plugging and engine deposits. High levels of these metals may also collect in diesel particulate filters and are not typically removed during passive or active regeneration. They can create increased back pressure and reduce the service maintenance period.
Stability	EN 14112 – Determination of Oxidation Stability (Accelerated Oxidation Test), 743 Rancimat	Determines the oxidation stability of biodiesel fuel. The sample is exposed to a stream of heated air. The volatile oxidation products are transferred to a measuring vessel by the air stream where they are absorbed into distilled water. The conductivity of the water is continuously measured. The time (in hours) between the start of the test and when the conductivity begins to increase rapidly is the induction period. This test provides an indication of the oxidation stability of the sample.

AvgasTest Methods

Property	Standard Test	Method Description
1	*2*	*3*
Density	ASTM D 1298 / IP 160 – Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method ASTM D 4052 – Density and Relative Density of Liquids by Digital Density Meter	Fuel is transferred to a cylindrical container and a hydrometer is carefully lowered into the cylinder and allowed to settle. After temperature of sample has equilibrated, value on hydrometer scale positioned at the surface of the sample and the sample temperature are recorded. The hydrometer value is converted to density at 15,6 °C or API gravity at 60°F using standard tables. Small volume of sample is introduced into oscillating tube held at constant temperature. Change in oscillation frequency caused by change in mass of tube is related to density of the sample.
Vapor Pressure	ASTM D 323 / IP 69 – Vapor Pressure of Petroleum Products (Reid Method)	A special cylinder with separate vapor and liquid chambers that can be joined together is used. The liquid chamber is filled with chilled sample and then immediately connected to the vapor chamber, which has been heated to 38 °C (100 °F). The assembled apparatus is immersed in a bath held at 38° C (100 °F) until a constant pressure is observed. This pressure includes a contribution from air and water dissolved in the fuel.
	ASTM D 5191 – Vapor Pressure of Petroleum Products (Mini Method) Referee Method	A chilled sample is introduced into an evacuated, thermostatically controlled chamber. The chamber and sample are heated to 38 °C (100 °F) and the resulting rise in pressure is measured. The sample size and chamber volume are chosen to duplicate the conditions of the Reid Method.

1	*2*	*3*
Freezing Point	ASTM D 2386 / IP 16 – Freezing Point of Aviation Fuels	A sample is placed in a special jacketed tube fitted with a stirring rod and a thermometer. The tube is placed in a low-temperature bath and stirred as the sample cools. When crystals of hydrocarbon appear, the tube is removed from the cooling bath and allowed to warm up slowly with continuous stirring. Temperature at which the last hydrocarbon crystals are completely melted is recorded as the freezing point.
Sulfur	ASTM D 2622 – Sulfur in Petroleum Products by X-Ray Spectrometry	A sample is placed in a wavelength-dispersive X-ray spectrometer and the intensity of the sulfur X-ray fluorescence is measured and used to calculate the sulfur content of the sample.
	ASTM D 1266 / IP 107 – Sulfur in Petroleum Products (Lamp Method)	A sample is burned in a glass lamp equipped with a cotton wick. Burning converts sulfur in the sample to sulfur oxides, which are subsequently converted to sulfuric acid by bubbling the combustion gases through solution of hydrogen peroxide. The amount of sulphuric acid formed is determined either by barium precipitation or titration.
Copper Strip Corrosion	ASTM D 130 / IP 154 – Detection of Copper Corrosion from Petroleum Products by the Copper Strip Tarnish Test	A polished copper strip is immersed in a sample for two hours at 100 °C (212 °F) and then removed and washed. The condition of the copper surface is evaluated qualitatively by comparing it to standards.
Net Heat of Combustion	ASTM D 3338 – Estimation of Net Heat of Combustion of Aviation Fuels	The net heat of combustion of a sample is estimated from its API gravity, aromatic content, and distillation profile. The estimate relies on a correlation developed for a wide range of fuels.

1	*2*	*3*
	ASTM D 4529 – Estimation of Net Heat of Combustion of Aviation Fuels	The net heat of combustion of a sample is estimated from its aniline point, density, and sulfur content. The estimate relies on a correlation developed for a wide range of fuels.
	ASTM D 4809 – Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter Referee Method	A weighed sample of fuel is placed in an oxygen bomb calorimeter under specified conditions. The fuel is ignited and the temperature ncrease of the calorimeter is used to calculate the heat of combustion.
Oxidation Stability	ASTM D 873 / IP 138 – Oxidation Stability of Aviation Fuels (Potential Residue Method)	A 100 mL sample is placed in a tared beaker inside a pressure vessel and heated to 100 °C (212 °F) under 700 kPa (100 psi) of oxygen forfive hours. The bomb is then cooled to room temperature and the pressure is released. The oxidized fuel is filtered through a tared sintered glass crucible. The residue in the crucible is weighed and reported as insoluble gum in mg/100 mL. The fuel is then evaporated to dryness in a tared beaker and any residue is weighed and reported as soluble gum in mg/100 mL. The potential gum is the sum of the soluble gum and insoluble gum.
Water Reaction	ASTM D 1094 / IP 289 – Water Reaction of Aviation Fuels	A sample is shaken with an aqueous buffer solution in a clean glass cylinder at ambient temperature and then allowed to stand to let the mixture separate into hydrocarbon and aqueous phases. After fiveminutes of standing, the change in volume of the aqueous layer is measured. The appearance of the hydrocarbon/aqueous interface is also examined for the presence of bubbles or film.

1	*2*	*3*
Electrical Conductivity	ASTM D 2624 / IP 274 – Electrical Conductivity of Aviation and Distillate Fuels	A sample is placed in a cell containing two electrodes. A voltage is applied across the electrodes and the resulting current is expressed in terms of the conductivity of the sample.
Lead Content	ASTM D 3341 / IP 270 – Lead in Gasoline – Iodine Monochloride Method	A sample is shaken with aqueous iodine monochloride solution, which converts tetraalkyl lead compounds to water-soluble dialkyl lead compounds. The aqueous phase is separated from the fuel and evaporated. Digestion with nitric acid converts the dialkyl lead compounds to inorganic lead compounds. The digestion residue is dissolved in a buffer and the lead content is determined by titration with EDTA using xylenol orange indicator.
	ASTM D 5059 – Lead in Gasoline by X-Ray Spectrometry	A sample is placed in an X-ray beam and the intensity of the lead X-ray fluorescence is measured. The concentration of lead is determined by a previously prepared calibration curve. Bismuth may be used as an internal standard to improve precision.
Color	ASTM D 2392 – Color of Dyed Aviation Gasolines	A sample's hue and color intensity are compared to those of colored-glass standards.

Jet Fuel Test Methods

Property	Standard Test	Method Description
1	*2*	*3*
Distillation	ASTM D 86 / IP 123 – Distillation of Petroleum Products	A 100 mL sample is placed in a round-bottom flask and heated at a rate specified for a sample with its vapor pressure characteristics. Vaportemperatures are recorded when the first drop of condensate is collected (initial boiling point) and at recovered volumes of 5 mL,10 mL,15 mL, 20 0mL, and every subsequent 10-mL interval to 80 mL,85 mL,90 mL, 95 mL,and at the end of the test (end point).The amount of sample remaining in the flask at the end of the test and the amount lost during the test – both in percent by volume – are,respectively,recorded and calculated.
	ASTM D 2887 / IP 406 – Boiling Range Distribution of Petroleum Fractions by Gas Chromatography	A small portion of sample is injected onto a non-polar GC column, which separates compounds by boiling point. Elution time is converted to a boiling point by analyzing a mixture of n-paraffins of known boiling points under identical conditions.
Thermal Stability	ASTM D 3241 / IP 323 – Thermal Oxidation Stability of Aviation Turbine Fuels (JFTOT Procedure)	Fuel is pumped over a heated aluminum alloy tube at a constant flow rate for 2,5 hours. After contacting the tube, the fuel is filtered to collect any solid decomposition products. The pressure drop across the filter is monitored during the test.At the end of the test,the tube is removed and visually examined for any stain or discoloration,which is rated by comparing it to a standard color scale.This visual tube rating and the pressure drop across the filter at the end of the test are reported as the test result.

1	*2*	*3*
Density	ASTM D 1298 / IP 160 – Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method	Fuel is transferred to a cylindrical container and a hydrometer is carefully lowered into the cylinder and allowed to settle. After the temperature of the sample has equilibrated, the value on the hydrometer scale positioned at the surface of the sample and the sample temperature are recorded. The hydrometer value is converted to density at 15,6 °C or API gravity at 60 °F using standard tables.
	ASTM D 4052 / IP 365 – Density and Relative Density of Liquids by Digital Density Meter	A small volume of a sample is introduced into an oscillating tube held at constant temperature. The change in oscillation frequency caused by the change in the mass of the tube is related to the density of the sample.
Viscosity	ASTM D 445 / IP 71 – Kinematic Viscosity of Transparent and Opaque Liquids	A sample is placed in a calibrated glass viscometer and held at a closely controlled temperature. The time required for a specific volume of the sample to flow through the capillary under gravity is measured.This time is proportional to the kinematic viscosity of the sample.
Vapor Pressure	ASTM D 323 / IP 69 – Vapor Pressure of Petroleum Products (Reid Method) Referee Method	A special cylinder with separate vapor and liquid chambers that can be joined together is used. The liquid chamber is filled with chilled sample and then immediately connected to the vapor chamber, which has been heated to 37,8 °C (100 °F). The assembled apparatus is immersed in a bath held at 37,8 °C (100 °F) until a constant pressure is observed. This pressure includes a contribution from air and water dissolved in the fuel.

1	*2*	*3*
	ASTM D 5191 – Vapor Pressure of Petroleum Products (Mini Method)	A chilled sample is introduced into an evacuated, thermostatically controlled chamber. The chamber and sample are heated to 37,8 °C (100 °F) and the resulting rise in pressure is measured. The sample size and chamber volume are chosen to duplicate the conditions of the Reid Method.
Flash Point	ASTM D 56 – Flash Point by Tag Closed Tester	A sample is placed in a lidded cup and heated at a slow, constant rate. At regular intervals, the lid is opened and an ignition source is directed into the cup. The lowest temperature at which the ignition source causes the vapor above the sample to ignite is the flash point.
	ASTM D 3828 / IP 303 – Flash Point by Small Scale Closed Tester	A sample is placed into a lidded cup and the cup is heated to a fixed temperature. After a specified time, the cup is opened, a test flame is applied, and an observation is made whether or not a flash occurs.The test is repeated with a fresh sample at other fixed temperatures until the flash point is established with the required precision [not greater than 0,5 °C (1 °F).
Net Heat of Combustion	ASTM D 3338 – Estimation of Net Heat of Combustion of Aviation Fuels	Net heat of combustion of a sample is estimated from its API gravity, aromatics content, and distillation profile. The estimate relies on a correlation developed for a wide range of fuels.
	ASTM D 4529 / IP 381 – Estimation of Net Heat of Combustion of Aviation Fuels	The net heat of combustion of a sample is estimated from its aniline point,density,and sulfur content.The estimate relies on a correlation developed for a wide range of fuels.
	ASTM D 4809 – Heat of Combustion of Liquid Hydrocarbon Fuels by BombCalorimeter Referee Method	A weighed sample of fuel is placed in an oxygen bomb calorimeter under specified conditions.The fuel is ignited and the temperature increase of the calorimeter is used to calculate the heat of combustion.

1	2	3
Freezing Point	ASTM D 2386 / IP 16 – Freezing Point of Aviation Fuels Referee Method	A sample is placed in a special jacketed tube fitted with a stirring rod and a thermometer. The tube is placed in a low-temperature bath and stirred as the sample cools.When crystals of hydrocarbon appear,the tube is removed from the cooling bath and allowed to warm up slowly with continuous stirring.The temperature at which the hydrocarbon crystals completely disappear is the freezing point.
	ASTM D 5972 / IP 435 – Freezing Point of Aviation Fuels (Automatic Phase Transition Method)	A small portion of fuel is cooled at a constant rate and monitored optically. When the formation of hydrocarbon crystals is detected by the optical system,the sample is then heated at a constant rate until the crystals redissolve.The temperature of the fuel at this point is the freezing point.
Naphthalenes Content	ASTM D 1840 – Naphthalene Hydrocarbons in Aviation Turbine Fuels by Ultraviolet Spectrophotometry	A sample is dissolved in isooctane at a known concentration and the absorbance of the solution at 285 nanometers is measured and used to calculate the naphthalenes content.
Luminometer Number	ASTM D 1740 – Luminometer Numbers of Aviation Turbine Fuels	A sample is burned in an ASTM-CRC Luminometer lamp to obtain a curve of flame radiation vs. temperature rise across the burner. The Luminometer number is calculated from the difference in temperature rise between the test fuel and tetralin, divided by the difference in temperature rise between isooctane and tetralin. Note: This method is no longer in the specification but is included here for historical reference.

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Sulfur	ASTM D 1266 / IP 107 – Sulfur in Petroleum Products (Lamp Method)	A sample is burned in a glass lamp with a cotton wick to oxidize the sulfur to sulfur dioxide. The combustion gases are bubbled though a solution of hydrogen peroxide to convert the sulfur dioxide to sulphuric acid. The amount of sulfuric acid formed is measured either by barium precipitation or titration.
	ASTM D 1552 – Sulfur in Petroleum Products (High-Temperature Method)	A sample is burned to oxidize the sulfur to sulfur dioxide. The sulphur dioxide is either absorbed by an acidic solution of potassium iodide and starch indicator and back titrated with standard potassium iodate solution, or collected in a cell where its infrared absorbance is measured. Note: This method is no longer in specification but included here for historical reference.
	ASTM D 2622 / IP 447 – Sulfur in Petroleum Products by Wavelength-Dispersive X-Ray Spectrometry	A sample is placed in an X-ray beam and the intensity of the sulfur X-ray fluorescence is measured and used to calculate the sulfur content of the sample.
	ASTM D 4294 / IP 336 – Sulfur in Petroleum Products by Energy-Dispers X-Ray Fluorescence Spectroscopy	A sample is placed in an X-ray beam and the resultant characteristic X radiation is measured and used to calculate the sulfur content of the sample.
	ASTM D 5453 – Determination of Total Sulfur in Light Hydrocarbons, Motor Fuels,and Oils by Ultraviolet Fluorescence	A sample is burned to oxidize the sulfur to sulfur dioxide.The combustion gases are irradiated with ultraviolet light and the fluorescence of the sulfur dioxide is measured.
Mercaptan Sulfur	ASTM D 3227 / IP 342 – Mercaptan Sulfur in Gasoline, Kerosine, Aviation Turbine,and Distillate Fuels (Potentiometric Method)	A hydrogen sulfide-free sample is dissolved in alcoholic sodium acetate and potentiometrically titrated with standard silver nitrate solution, which precipitates the mercaptan sulfur as silver mercaptide.

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Copper Strip Corrosion	ASTM D 130 / IP 154 – Detection of Copper Corrosion from Petroleum Products by the Copper Strip TarnishTest	A polished copper strip is immersed in a sample for two hours at 100 °C (212 °F) and then removed and washed. The condition of the copper surface is qualitatively evaluated by comparing it to standards.
Acidity	ASTM D 3242 / IP 354 – Acidity in Aviation Turbine Fuel	A weighed amount of sample is dissolved in titration solvent and titrated with alcoholic potassium hydroxide to a colorimetric endpoint. The amount of acidity in the fuel is expressed as mg KOH/g.
Existent Gum	ASTM D 381 / IP 131 – Gum Content in Fuels by Jet Evaporation	A measured quantity of fuel is transferred to a weighed beaker, placed in a heated bath, and evaporated under a flow of steam. The resulting residue is weighed and reported as existent gum.
Aromatics Content	ASTM D 1319 / IP 156 – Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption	A small amount of sample is placed at the top of a special glass adsorption column packed with activated silica gel. Prior to this, the top layer of gel has been treated with fluorescent dyes. Isopropyl alcohol is used to transport the sample and the fluorescent dyes down the column. The hydrocarbons separate into bands of aromatics, olefins, and saturates because of their different affinities for the gel. The fluorescent dyes, which also selectively separate, make the boundaries of the aromatic, olefin,and saturate zones visible under ultraviolet light.
Aromatics Content (continued)	ASTM D 6379 / IP 436 – Aromatic Hydrocarbon Types in Aviation Fuels – High Performance Liquid Chromatography with Refractive Index Detection	A small amount of sample is injected onto a polar HPLC column which eparates the aromatics from the saturates. A refractive index detector is used to quantitate the aromatics by comparison to a previously prepared alibration curve.

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Smoke Point	ASTM D 1322 / IP 57 – Smoke Point of Kerosine and Aviation Turbine Fuel	The sample is burned in a wick-fed lamp. The smoke point is the maximum height of flame that can be achieved without smoking.
Electrical Conductivity	ASTM D 2624 / IP 274 – Electrical Conductivity of Aviation and Distillate Fuels	A sample is placed in a cell containing two electrodes. A voltage is applied across the electrodes and the resulting current is expressed in terms of the conductivity of the sample.
Water Reaction	ASTM D 1094 / IP 289 – Water Reaction of Aviation Fuels	A sample is shaken with an aqueous buffer solution in a clean glass cylinder at ambient temperature and then allowed to stand to let the mixture separate into hydrocarbon and aqueous phases. After five minutes of standing, the change in volume of the aqueous layer is measured. Appearance of the hydrocarbon/aqueous interface also is examined for the presence of bubbles or film. Note: This method is in the process of being removed from both the DEF STAN and ASTM specifications because it has been found ineffective in detecting surfactants that may disarm coalescers. It is being replaced by D3948.
Water Separability	ASTM D 3948 – Determining Water Separation Characteristics of Aviation Turbine Fuels by Portable Separometer	Using a semiautomatic Micro-Separometer instrument, a fuel sample is mixed with water, forced through a fiberglass coalescing medium, and rated. The MSEP rating indicates the relative ease of coalescing water from the sample.The instrument is calibrated with a water-free fuel sample.
Lubricity	ASTM D 5001 – Measurement of Lubricity of Aviation Turbine Fuels by the Ball-on-Cylinder Lubricity Evaluator (BOCLE)	A non-rotating steel ball is held against a cylindrical ring. The cylindrical ring is rotated at a fixed speed while partially immersed in the fuel. At the end of the test, the ball is removed and examined for wear. The size of the wear scar is related to the lubricity of the fuel (a large wear scar means poor lubricity).

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Particulate Matter	ASTM D 2276 / IP 423 – Particulate Contaminant in Aviation Fuel by Line Sampling	Fuel from a field sampler is fed through a membrane with a pore size of 0,8 micrometers. The membrane is compared to examples in a rating booklet to rate its color and color intensity.
	ASTM D 5452 – Particulate Contamination in Aviation Fuels by Laboratory Filtration	Fuel from a field sampler is fed through a pair of matched-weight membranes with a pore size of 0,8 micrometers. The membranes are dried under standard conditions and weighed. The weight difference between the two membranes is a measure of the particulate content of the sample.