MINISTRY OF EDUCATION AND SCIENCE OF UKRAINE
National Aviation University

Anna V. Yakovlieva, Sergii V. Boichenko,
Kazimierz Lejda, Oksana O. Vovk

MODIFICATION OF JET FUELS COMPOSITION WITH RENEWABLE BIO-ADDITIVES

Monograph

Kyiv – 2019

UDC 656.7.064:665.7.032.5(02)
DOI
M 78

Recommened
by the Scientific Board
of the National Aviation University
Minutes No 7 on 31 October 2018

Authors:

Anna V. Yakovlieva – PhD, Associate Professor, National Aviation University
Sergii V. Boichenko – Dr. Sc., Professor, Rzeszow University of Technology;
Kazimierz Lejda – Dr. Sc., Professor, Rzeszow University of Technology;
Oksana O. Vovk – Dr. Sc., Professor, National Aviation University

Reviewers:

Yurii M. Tereshcnenko – Dr. Sc., Professor, National Aviation University
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CONTENT

THE LIST OF ABBREVIATIONS AND DESIGNATIONS

The list of abbreviations

AF – alternative fuel,
AFR – air/fuel ratio,
AFTF – Alternative Fuels Task Force,
ASTM – American Society for Testing and Materials,
AtJ – Alcohol-to-jet,
BtL – biomass to liquid,
CAAFI – Commercial Aviation Alternative Fuels Initiative,
CAEP – Committee on Aviation Environmental Protection,
CamO – camelina oil,
CFPP – cold filter plugging point,
C_xH_y – hydrocarbons,
CO – carbon monoxide,
CO_2 – carbon dioxide,
CORSIA – Carbon Offsetting and Reduction Scheme for International Aviation,
CtL – coal to liquid,
EU ETS – European Union Emission Trading Scheme.
FAEE – fatty acids ethyl esters,
FAME – fatty acids methyl esters,
FAM – fuel-air mixture,
FF – fuel flow,
FFP – Fit-For Purpose,
FP – freezing point,
FlP – flash point,
GtL – Gas to Liquid,
HEFA – hydroprocessed esters and fatty acids,
IATA – International Air Transport Association,
ICAO – International Civial Aviation Organization,
IEA – International Energy Agency,
ILUC – Indirect Land Use Change,
ISA – International Standard Atmosphere
JE – jet engine,
JF – jet fuel,
LAQ – local air quality,
NO_X – nitrogen oxides,
OEM – Original Equipment Manufacturers,
PM – particulate matter,
PP – pour point,
RED – Renewable Energy Directive,
RO – rapeseed oil,
SAF – sustainable aviation fuel,
SFF – specific fuel flow,
SKA – synthetic kerosene with aromatics,
SIP – synthetic Iso-paraffin,

SO_X – sulfur oxides,
SPK – synthetic paraffinic kerosene,
TCL – throttle control lever,
TLO – take-off – landing cycle,
UCO – used cooking oil,
UNFCCC– United Nations Framework Convention on Climate Change,
USAF – Uniited States Air Forces,
USN – Uniited States Navy,

The list of designations

B_0 – standard barometric pressure [mm Hg],
c – concentration [%],
EI – emission index [g/kg of fuel],
G – fuel flow [kg/s],
G_s – spesific fuel flow [kg/N h],
M – mass of emitted poluttant [g],
n – relative rotor speed [%],
P_s – scuffing load [N],
Q_m – net heat of combustion [kJ/kg],
Q_v – energy value [kJ/l],
$R_\mathrm{t.th.}$ – take-off thrust [N],
$\bar{R}$ – relative thrust,
t – temperature [°C],
t_cfpp – cold filter plugging point [°C],
$t_\mathrm{fl.p.}$ – freezing point [°C],
$t_\mathrm{fl.p.}$ – flash point [°C],
$t_\mathrm{p.p.}$ – pour point [°C],
$t_\mathrm{t.in.}$ – turbine inlet temperature [°C],
$t_\mathrm{j.p.}$ – jet pipe temperature [°C],
t_0 – standard atmospheric temperature [°C],
$V_\mathrm{rec.}$ – volume of recovery [%],
α – air/fuel ratio,
ρ – density [kg/m^3],
ν – kinematic viscosity [mm^2/s],
η_c – completeness of fuel combustion,
τ – duration of aircraft operation regime [s],
τ_c – fuel-air mixture residence time in the combustion chamber before combustion [ms].

INTRODUCTION

Today aviation is a service not just for the wealthy. It is accessible to the vast majority of the global population and serves a varied and valuable contribution to the global societal fabric from connecting friends and families, populating ideas and cultural sharing as well as enabling vital business through physical interaction and efficient cargo movement. Modern transport sector is developing constantly. The world volume of aircraft transportation increases on 4–5 % annually. Transport predominantly relies on a single fossil resource, petroleum that supplies 95 % of the total energy used by world transport. Along with the situation in exhausting of crude-oil deposits, the state of environment causes a special concern. According to the report by *Intergovernmental Panel on Climate Change*, transport is responsible for 23 % of world energy-related greenhouse gases emissions with about 17 % coming from road vehicles and 2 % from aviation. Over the past decade, transport's and aviation's in particular, greenhouse gases emissions have increased at a faster rate than any other energy using sector. And according to some forecasts air traffic will be responsible for about 20 % of harmful emissions by 2020.

Rapid growth of motor transport fleet apposes scientists two important problems of modern world. Rising demand in motor fuels faces task of providing energy resources for transport means on one hand and decreasing negative impact of fuels and its exhaust gases on environment on other hand.

The world transport energy use is projected to increase at the rate of about 2 % per year, and total transport energy use and carbon emissions is projected to be about 80 % higher than current levels by 2030. Thus, increasing attention is paid to the question of traditional energy sources replacement with its alternative analogues. The question is particularly acute for transport sector and aviation in particular. That's why numerous developed countries work on developing of alternative aviation fuels and improving its properties. Today alternative aviation fuels are related to renewable energy resources, have lower price and possess better environmental properties. A recent *International Energy Agency* analysis stated that biofuels' share of transport fuel should increase up to about 10 % in 2030.

At the same time rising of air traffic causes the need in improvement of fuel efficiency and decreasing exhaust gases emissions from aircrafts. Numerous states around the world took a responsibility for creating conditions for safe and effective flights according to standards and practices recommended by ICAO. Countries- EU members are planning to reduce by 2030 levels of greenhouse emissions by 40 % comparing to the level of 1990. It is considered that starting from 2021 maximal level of allowed greenhouse gases emissions will be decreased annually by 2.1 %. One of the main instruments for reaching this aim is implementing and using of alternative fuels for aviation. Alternative jet fuels should possess high level of chemmotological reliability. This is stipulated by the intensive development of air transport: risinf of flight altitudes, speed and flying range (flight duration). It is known that on of the main requirements to alternative fuels, set by *International Civil Aviation Organization (ICAO)*, *International Air Transport Association (IATA)* and other leading organizations in sphere of civil aviation, is its environmental safety and energy efficiency at all stages of life cycle (starting from producing feedstock up to exhaust gases emissions).

Significant progress in the development and deployment of alternative aviation fuels has been achieved over the last ten years. When the first feasibility studies for the use of biofuel as a sustainable alternative to petroleum-based jet fuel were conducted in the mid-2000s, few people would have envisioned that by 2014 over twenty airlines would have flown more than 1700 commercial passenger flights powered by alternative aviation fuels, and continuous alternative aviation fuels supply for airlines and airports would be imminent for 2015. While a wide variety of alternative aviation fuels production pathways have been developed and solutions to most technical challenges to alternative aviation fuels implementation still can be found, the political and economic boundary conditions still require further development to allow the large-scale production of alternative aviation fuels at affordable prices for airline customers. As far ahead as 2040 to 2050, new fuels and energy sources such as “solar jet fuel”, produced from CO_2 and water using solar energy, and aircraft using electric energy for propulsion will likely play an increasing role in the aviation industry commitment to reduce its global carbon footprint by 50 % compared to 2005. However, considerable development efforts will have to be deployed before these technologies, which are today at lab scale, reach maturity. Bio-based fuels will therefore remain the only sustainable alternative to fossil jet fuels for at least two to three decades.

Today the idea of producing bio-based aviation fuels became also important in Poland. The promising biofuel feedstock is plant biomass (corn, rapeseed, soybean, camelina, algae, etc), animal fats, industrial, household and municipal waste, etc. Poland is related to energy deficient countries. The dependence on crude oil import is considered to be a question of national and energy safety of the state. At the same time the use of oil products as a source of energy poses a significant environmental danger. One of the main tasks in the field of production and use of aviation fuels and lubricants is to expand the resource base and to develop progressive technologies for its production. At the same time, alternative aviation fuels must meet a number of requirements related to efficiency, reliability and durability of transport vehicles. These factors stipulate an intensive search for energy efficient and environmentally safe alternative motor fuels.

Taking into account the abovementioned, the idea of this study is development of alternative aviation fuels composition with bio-additives produced from renewable plant feedstock and selection of optimal composition of new jet fuels. These blended fuels should possess quality parameters, which satisfy technical requirements of modern specification related to fuel efficiency and environmental safety of aviation fuels.

Analyzing modern situation in oil processing industry and constant worsening of world’s environmental situation, transition to alternative JFs is seemed to be obvious. The absence of practical experience on the use of alternative JFs requires the development of advanced technologies of JFs production from environmentally safe, accessible and relatively cheap renewable raw materials. At the same time, new alternative JFs should possess the following characteristics:

- worldwide distribution on account of intercontinental flights requiring the implementation of alternative fuel production criteria with a consistent quality at international level,

- great life span of aircraft (over 30 years on average) requires the compatibility of alternative fuels and existing fuels without any need to make significant changes to the engine or aircraft construction,
- alternative fuels must undergo stringent certification procedures with a view to demonstrating its full compatibility with all engine parts and materials in contact with the fuel (from logistics and distribution to combustion),
- alternative fuels must provide an incredibly restrictive operating mode, since fuel is consumed by aircraft in a wide range of conditions of use such as varying temperatures and varying pressures.

Object of the study – is modifying the composition of JF by blending with bio-additives of plant origin.

Subject of the study – is physical-chemical, exploitation and environmental properties of JFs blended with bio-additives of plant origin and operational parameters of JE powered with blended JFs.

For solving the set tasks the algorithm of studies realization and general scheme of experimental researches fulfillment have been developed (Fig. 1.1). We have analyzed the wide range of literature sources in the field of scientific researches methodology and studied the existing methods for solving similar tasks.

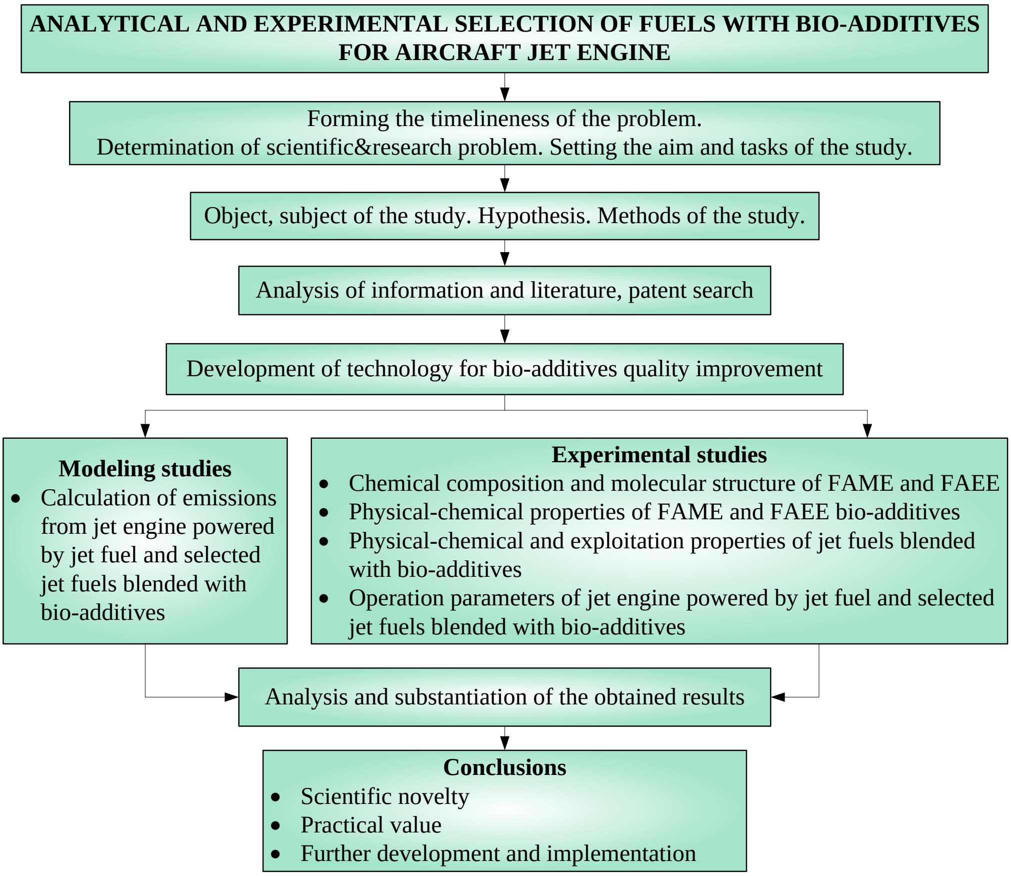


Fig. 1.1. The general scheme of fulfillment scientific studeies

In order to reach the main aim of the work it was necessary to develop the criteria for selecting alternative JFs and to fulfill complex experimental studies for testing and checking these criteria. The criteria for selecting fuels with optimal content of bio-additives for using in aircraft JEs were developed basing on literature analysis, requirements of standards and specifications and results of previous studies on alternative blended JFs. Thus, the complex of physical-chemical, operation and environmental criteria, which were developed for the scope of this work and characteristics corresponding to these criteria, are presented at Fig. 1.2. JF and its blends with bio-additives were tested for satisfying the presented criteria.

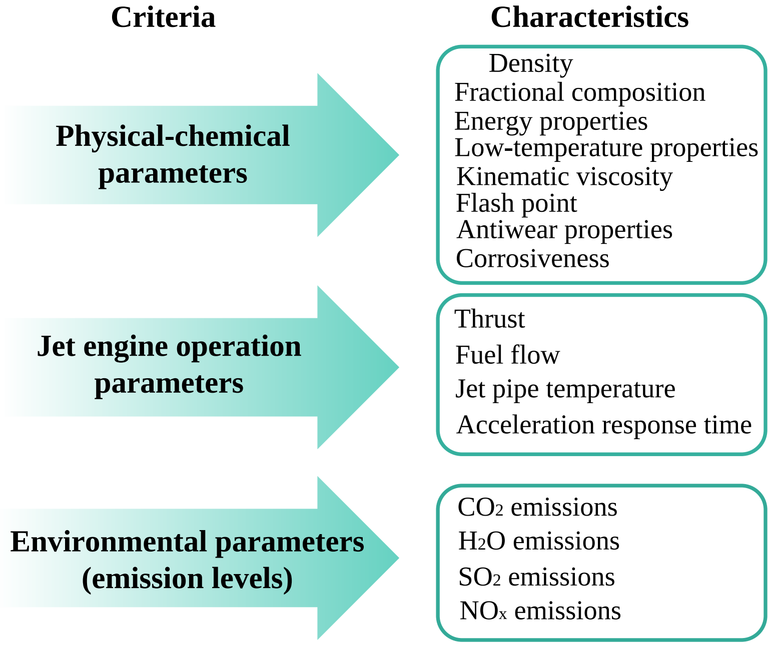


Fig. 1.2. The criteria for selecting fuels with optimal content of bio-additives for JEs

This study has an applied, experimental character. However, for reaching the set aim it requires significant theoretical grounds. That is why during fulfillment the work, both empirical and theoretical methods of scientific cognition were used.

CHAPTER 1

THE CURRENT STATUS OF JET FUELS PRODUCTION AND USE

Modern civil aviation is developing constantly. Each year, about 20 thousand commercial aircraft carry 3 billion passengers over 3 trillion passenger-miles, connecting 35 thousand city pairs with 30 million aircraft movements. These aircraft also carry more than $6 trillion in air cargo, about 35 % of world trade by value. As a result during last decade consumption of fuels for air-jet engines has increased on 21 %. About 5.5 thousand barrels of jet fuel is produced and consumed in the world daily. Commercial aircraft now consume more than 70 billion gallons of jet fuel per year. Thus, today aviation is one of the most significant consumers of oil-derived jet fuels. Fig. 1.3 demonstrates that more than 90 % of global aviation fuel consumption is related to large commercial aircrafts.

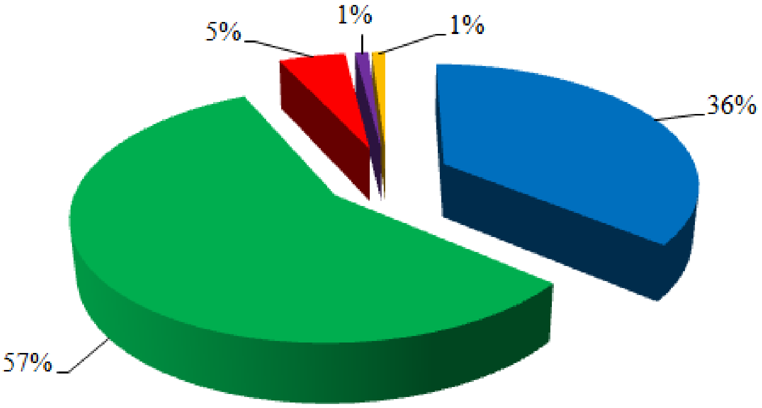


Fig. 1.3. Global civil aviation fuel consumption:
single aisle – 36 %, twin aisle – 57 %, regional jet – 5 %, business – 1 % and turboprop – 1 %

As commercial aviation continues to grow in terms of revenue-passenger miles and cargo ton miles, CO_2 emissions are expected to increase. To reduce the contribution of aviation to climate change, it is essential to improve the effectiveness of ongoing efforts to reduce emissions and initiate research into new approaches. Although aviation CO_2 emissions are a small part of total CO_2 emissions, action to reduce them is urgent for the reasons stated above and because it takes new technology a long time to propagate into and through the aviation fleet.

Over the last years, increasing attention is paid to the question of traditional energy sources replacement with their alternative analogues. The question is particularly acute for transport sector and aviation in particular. One of the main tasks in the field of production and use of aviation fuels and lubricants is to expand the resource base and to develop progressive technologies for the production of aviation fuels. At the same time, alternative aviation fuels must meet a number of requirements related to efficiency, reliability and durability of aviation technics.

1.1. Jet fuel production technologies

At the modern stage of development the main raw material for JFs production is still crude oil. For today, the alternative kinds of raw material comparing to crude oil are pit, brown coal, oil-shales and natural gas. These materials are also related to fossil fuels. Fuels derived from coal, natural gas, oil-shales, etc became widely popular in some countries. Technologies for jet fuel production using coal and gas are already known for a long time, quit well studied and have been already implemented into production scales. This fact is stipulated mainly by the presence of certain raw material at the territory of producing country. Fig. 1.4 gives basic representation of existing technologies for jet fuel production according to involved feedstock.

As it is seen from the scheme, the bigger part of existed technologies is still directed for the processing of various fossil fuels, such as oil, coal, natural gas, oil-shales and some others. However, during several decades various renewable resources are being investigated to be processed into jet fuel. The main advantages of renewable energy is that it is of natural origin, can be quickly renewed, do not form extra CO_2 in the atmosphere, pose less negative impact on environment and it can be easily decomposed in nature.

1.1.1. Jet fuels production by crude-oil refining

Traditionally JFs are obtained via direct straight-run cut distillation of crude oil. Destructive methods of oil processing are also applied. The generalized proceess of JFs manufacturing from crude-oil is presented below.

Oil, extracted from the oil wells contains dissolved gases, mechanical impurities in the form of sand and clay (approximately 1.5 %), water (up to 50 % or more), various salts and other chemical compounds injected to the oil well in order to increase oil recovery from strata. All of these products can partially come into JFs, produced by direct straight-run distillation, and affect their quality. Because of this, oil passes preparatory processes both in the oil fields and in the manufacturing enterprise. They include stabilization with the purpose of removing the above-mentioned components in order to protect equipment from corrosion and favours obtaining of high-quality products.

Then oil is divided into fractions. JFs are represented by middle distillation oil fractions with boiling range that partially overlaps with diesel one (140÷280 ^{o}C). They contain different classes of hydrocarbons, heteroatom compounds and inorganic impurities. Fractions of JF are obtained at the atmospheric columns. Oil is divided into a large number of fractions, including gasoline, diesel, kerosene, ligroin, and others. As a result of the considerable diversity of the processed oil and its quality, facilities for oil processing also vary greatly. Depending on the composition of crude oil, enterprise's equipment and the required amounts of final products (gasoline, jet and diesel fuels), boiling range of fractions and number of factions involved in JF, is not the same.

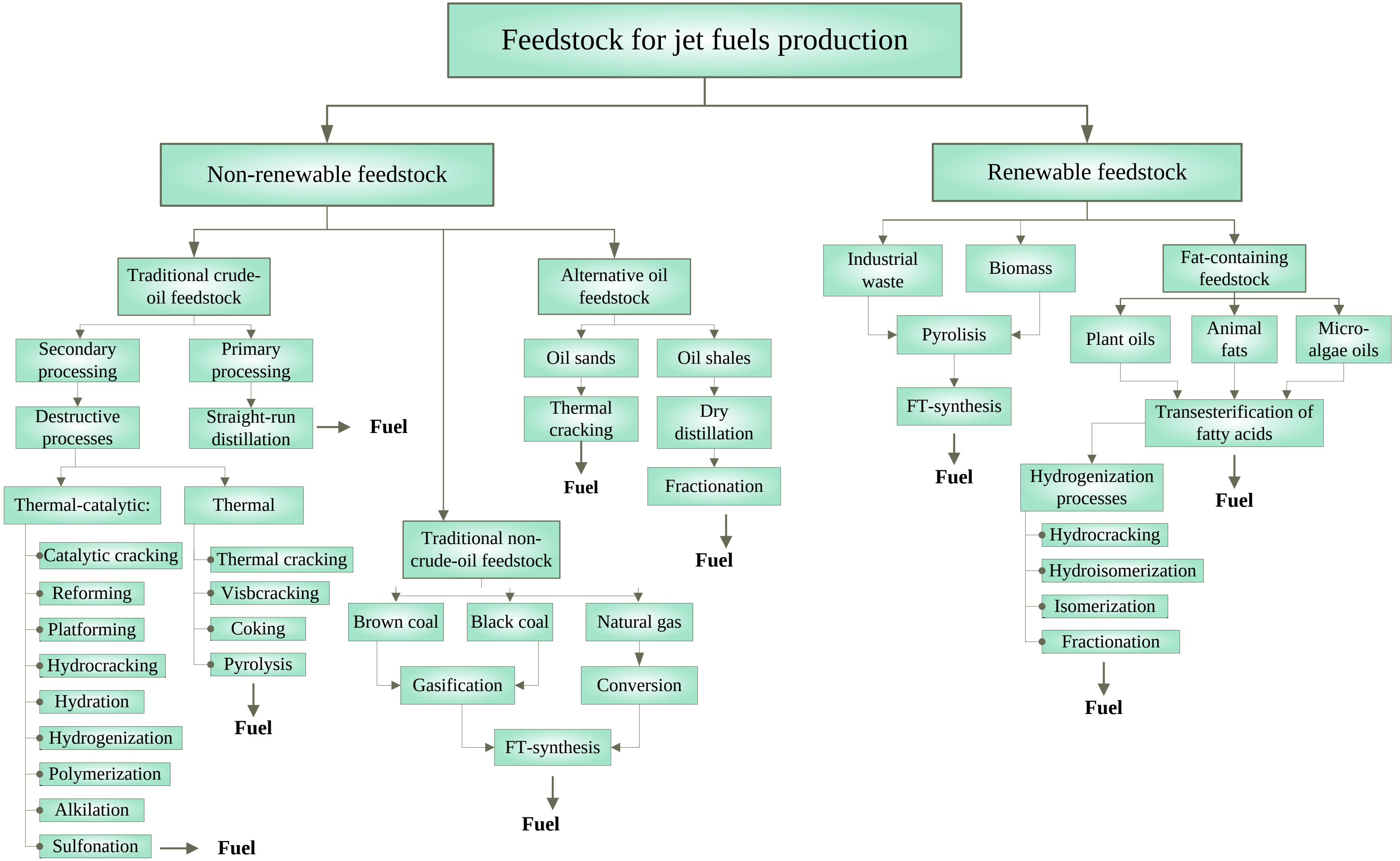


Fig. 1.4. Classification of technologies for jet fuel production according to the feedstock used

Crude oil fractions of the direct straight-run distillation are purified from the compounds affecting the quality of JFs. In order to remove some of these compounds, fractions are treated with a solution of sodium hydroxide and washed with water. This allows removing of naphtenic acids, phenols, as well as hydrogen sulphide and mercaptanes. Alkaline salts of petroleum acids and sodium phenolates, created during the purification, show a tendency to hydrolysis, so they are not completely removed. Sodium hydroxide reacts with hydrogen sulphide forming sulphides and sulphates when there is a lack of alkali. Mercaptans react forming sodium mercaptides. Mercaptides, especially macromolecular, are easily hydrolyzed, preventing their retrieval during kerosene fractions' cleaning. Therefore, for removal of mercaptans out of JF alkaline cleaning is almost never used. Further step is washing of kerosene fraction after treatment with sodium hydroxide. As it was said, as a result of alkaline treatment naphtenic acids are removed from JF, then it lead to a deterioration of anti-wear properties. Mercaptans are the most undesirable compounds in the gasoline and kerosene fractions that are used for JF manufacturing. For removal of mercaptans the following processes are applied: plumbating cleaning, purification with copper chloride and process "Merox".

Effective method for the removal of heteroatomic compounds from JF is hydrotreatment. It means catalytic purification in the presence of hydrogen and catalyst. In those cases, where it is sufficient to remove only mercaptans out of fuel, the treatment is carried out in a "soft" regime, if it is necessary to reduce the total amount of sulphur compounds (hydrodesulfurization), fuel is purified in a "harder" regime. But in this case, a lower yield of liquid products and a greater consumption of hydrogen are observed. During hydrotreatment compounds that play a role of natural oxidation inhibitors, and surface-active substances improving the anti-wear properties of fuels are also removed along with undesirable substances. Therefore hydrotreated JFs are injected with antioxidant and anti-wear additives. Or hydrotreated component (up to 70 %) is mixed with the factions of direct distillation. The further increasing of hydrotreating regime hardness leads to partial hydrogenation of aromatic hydrocarbons (hydrodearomatization process). Reactions of condensation and coke formation during hydrodearomatization are not observed almost. Liquid products yield during hydrodearomatization is about 94÷95 %. However, nowadays, this process is not used almost, as it became possible in some cases to increase the permissible content of aromatic hydrocarbons in JF.

In order to increase the yield of higher quality light oil from crude oil the secondary oil refining processes are used. This involves oil processing with cracking (destruction) of heavy hydrocarbons into lighter ones. Such processes are known as destructive ones. They include *thermal* processes, based on the ability of organic compounds to break down and chemically change under the influence of high temperatures (thermal cracking, visbcracking, coking, pyrolysis). *Thermal-catalytic* processes are also used; they are based on the application of different catalysts to speed up the chemical reactions (catalytic cracking, reforming, platforming, hydrocracking, hydration, hydrogenation, polymerization, alkylation, sulfonation, etc.). Let us consider some of them in details.

One of the destructive oil refining processes is hydrocracking. The given process is used to produce JFs from high-boiling vacuum oil distillates. Hydrocracking catalysts contain metals of platinum group, as hydrogenation components, such as nickel, molybdenum, tungsten, cobalt placed on amorphous and crystalline aluminosilicates. Due to such catalysts the increased amounts of iso-form alkanes are produced during hydrocracking, which makes it possible to get jet and diesel fuels out of heavy distillates without deparafinization process. In a result of hydrocracking of the same raw material, gasoline, or predominantly (not less than 70 %) jet or diesel fuels are produced. This peculiarity of the process is especially important, as it allows varying the volume of produced fuel taking into account necessity, including seasonal one. As a result of hydrocracking JFs have freezing point below minus 60 °C and contain few (≈ 10 %) aromatic hydrocarbons. Similarly to hydrotreated fuels, they virtually have no heteroatomic compounds. To reduce the tendency of fuels to oxidation and improvement of their anti-wear properties it is better to introduce the appropriate additives.

During the deep hydrogenation process JF is obtained from kerosene-gasoil distillates of straight-run distillation of selected oils or products of catalytic cracking, containing more than 60 % of aromatic hydrocarbons. During the process, aromatic hydrocarbons are converted into naphthenes. Appropriate selection of raw material allows receiving a JF that contains mainly naphthenes of high density (840 kg/m^3 at 20 °C), low sulphur content (<0.01 %), alkenes (iodine value <0.2 g I_2/100 g) and existent gums (<3 mg/100 ml). There is an assumption [165] that almost all heteroatomic compounds and alkenes are subjected to hydrogenation. Due to the low content of natural antioxidants in the products of hydrogenation, there is a need to introduce additives into the fuel. Despite the absence of surfactants, product possesses satisfactory anti-wear properties due to its relatively high viscosity.

Currently the most popular grade of JF around the world is “Jet A-1”. JFs of grades “RT” and “TS-1” are still widely used at the territory of post-soviet countries.

Jet A-1 fuel. JF of grade Jet A-1 is derived by purification of straight-run components and hydrogenated components of oil fractions with boiling temperatures 205÷300 ^{o}C and addition of complex of functional additives. Technological process of jet fuel “Jet A-1” production is schematically shown at Fig. 1.5.

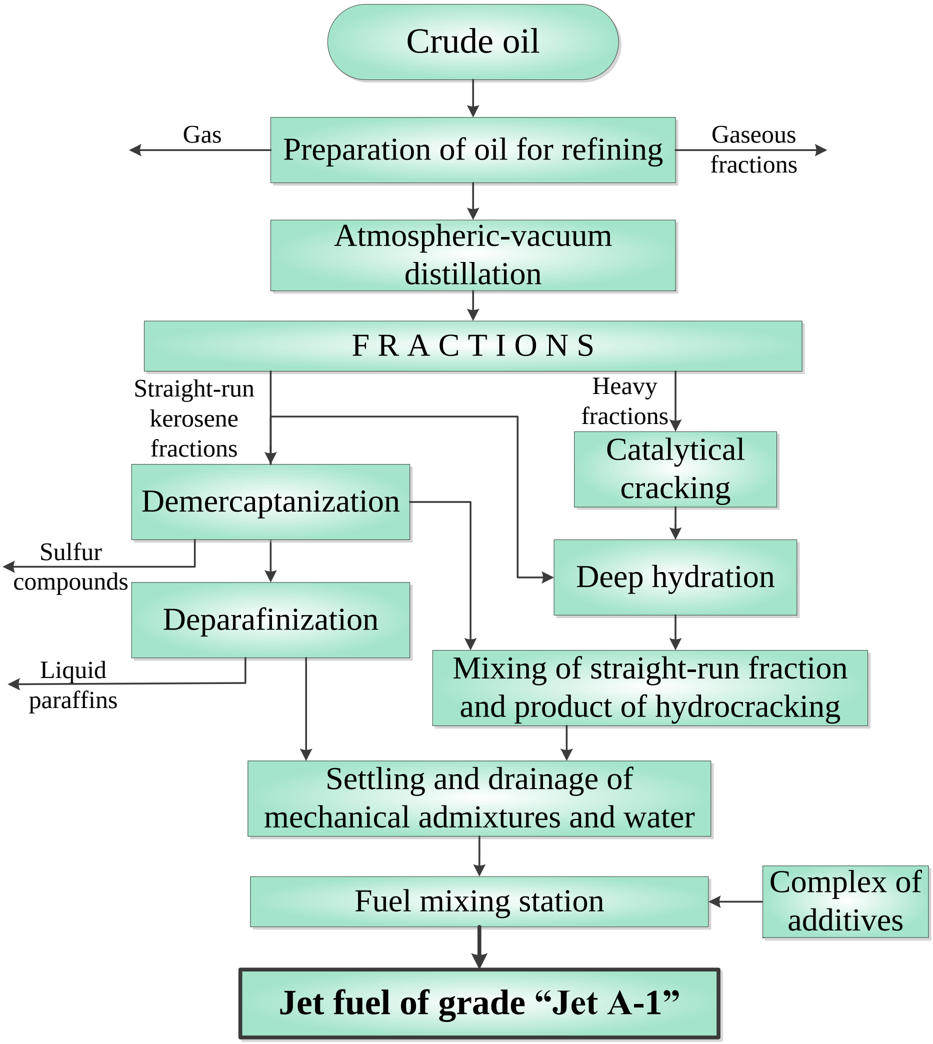


Fig. 1.5. Technological scheme of JF of grade Jet A-1 production

TS-1 fuel. This kind of fuel is usually used in subsonic and supersonic aircrafts with a limited duration of supersonic flight. It is produced both as a straight-run and mixed fuel with hydrotreated component. In the latter case, hydrotreated component is added to the oil straight-run fraction. It is known that hydrotreatment and demercaptanisation processes are applied in case when the content of total sulfur and mercaptans in kerosene distillates is to high. Hydrodeparaffinization is used for hydroconversion and improvement of low-temperature properties of kerosene fractions. Technological process of JF “TS-1” production is schematically shown at Fig. 1.6.

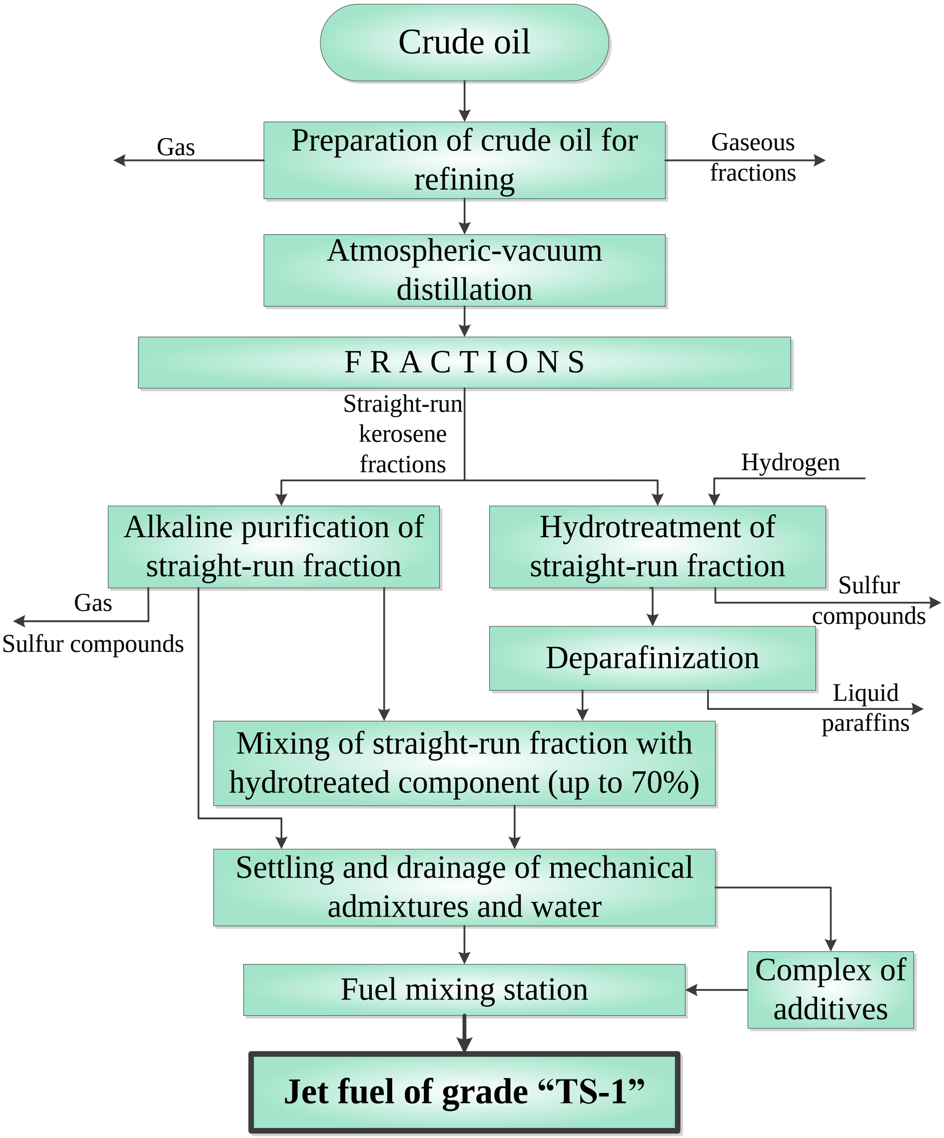


Fig. 1.6. Technological scheme of jet fuel of grade “TS-1” production

RT fuel. “RT” fuel is usually produced by hydrotreatment of straight-run fraction with boiling temperatures 135÷280 ^{o}C from various oil and also by adding different additives to straight-run kerosene fraction after deparaffinisation. Distillate fractions that can not be used for TS-1 fuel production because of high sulphur and mercaptans content, are used for hydrotreatment for RT-fuel production. The aggressive and unstable compounds, which contain sulfur, oxygen and nitrogen are extracted from oil distillate during hydrotreatment. Thus, thermal stability of fuel increases and corrosiveness decreases. Technological process of JF “RT” production is schematically shown at Fig. 1.7.

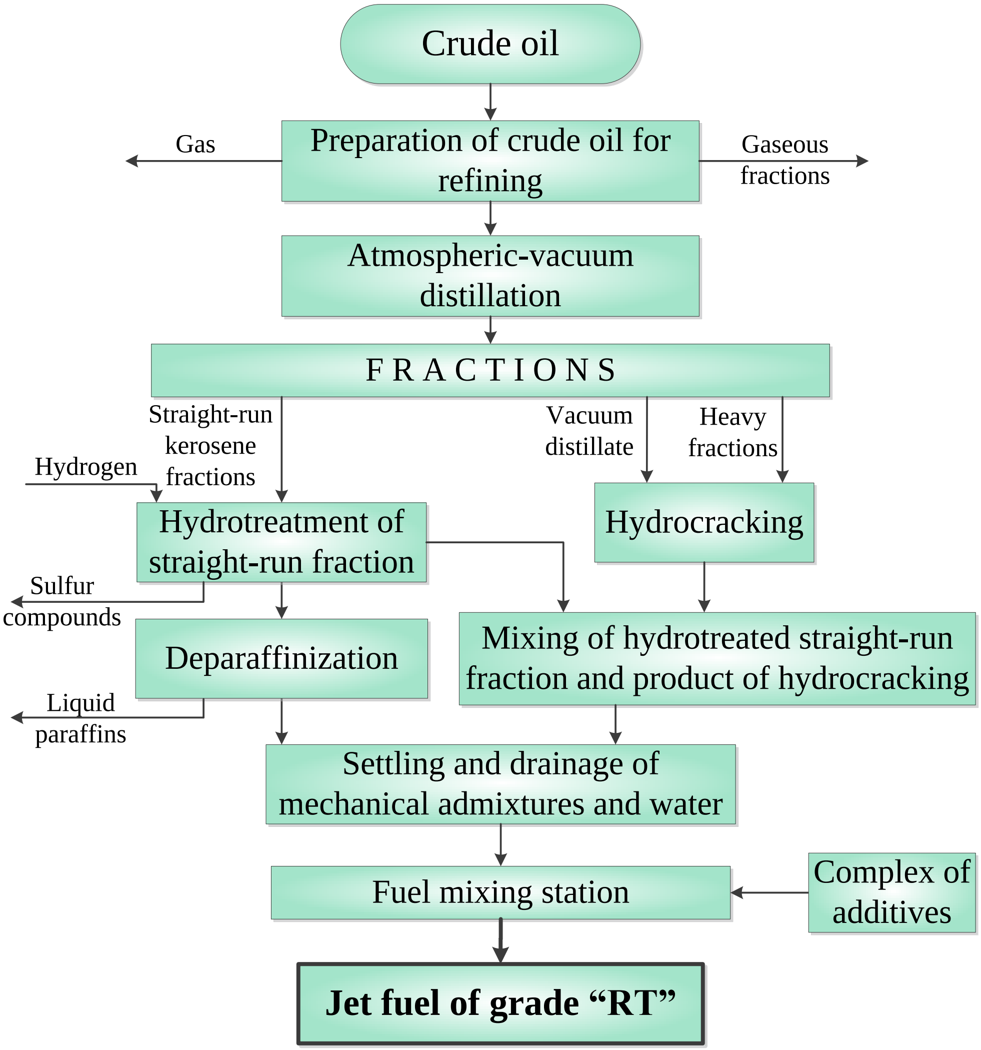


Fig. 1.7. Technological scheme of JF of grade "RT" production

1.1.2. Jet fuel production by oil-shale refining

During last decades scientific literature pay much attention to the technology of JFs production from oil-shales. This technology did not become popular in Poland and Ukraine because of the absence of oil-shales deposits. They 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 after their 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.

It is known that the most widely used technology of oil-shale processing today is fractionation, slow coking and hydrocracking (Fig. 1.8). 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.

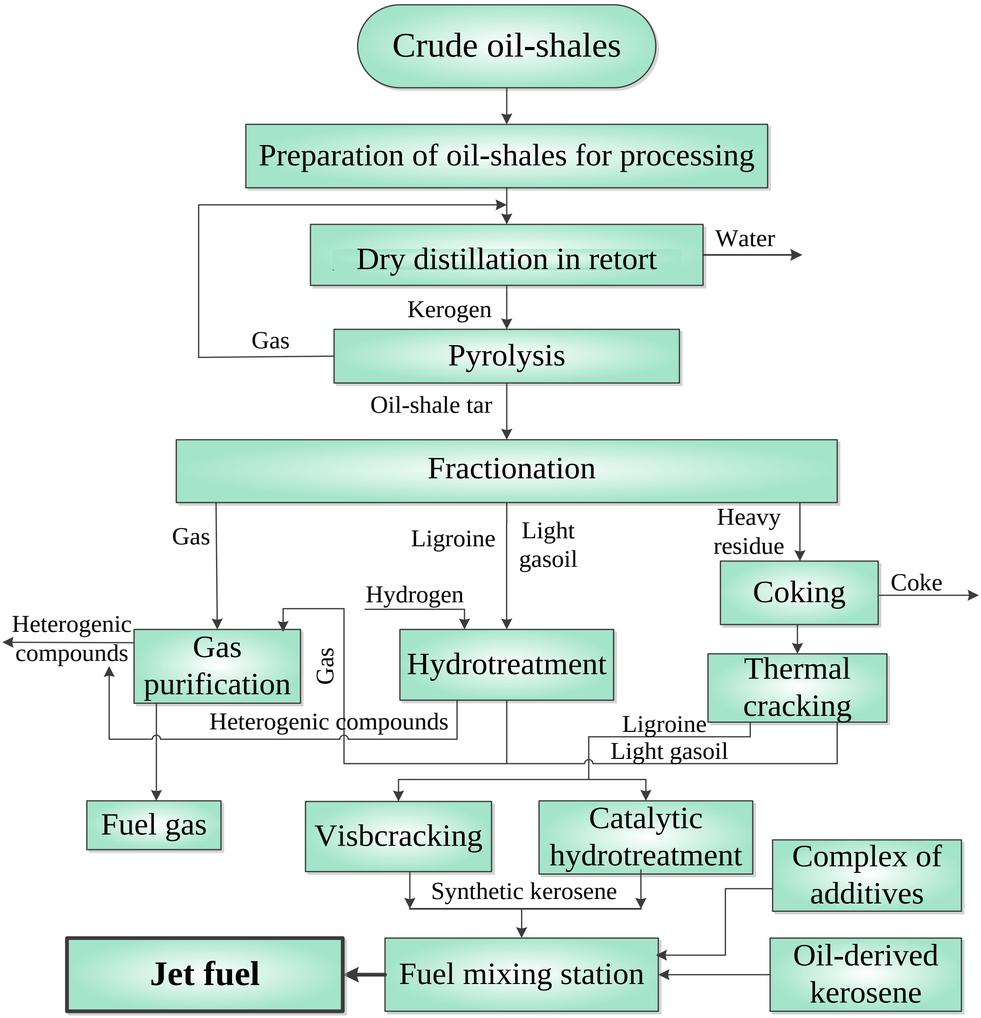


Fig. 1.8. Technologe of JF production by oil-shales processing

Shale tar is applicable for JFs 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 JFs from oil-shales requires hydrotreating to reduce the content of mentioned organic compounds and to improve its quality. In general, production of JF from oil-shales of appropriate quality requires deeper processing and higher expenses than production of JFs from crude oil.

JFs obtained by processing of oil-shales possess the average content of aromatic hydrocarbons (10÷25 %) and does not cause problems associated with lubricating properties. Moreover, it shows a high level of stability during long-term storage.

1.1.3. Jet fuel production by coal processing

Fisher-Tropsh method or process (FT-process) is a widely known technology of JF production since the World War II. The main feedstock, used for this technology is black and brown coal. Moreover, natural gas and biomass are also successfully used today. Principal stages of FT-process are presented at Fig. 1.9.

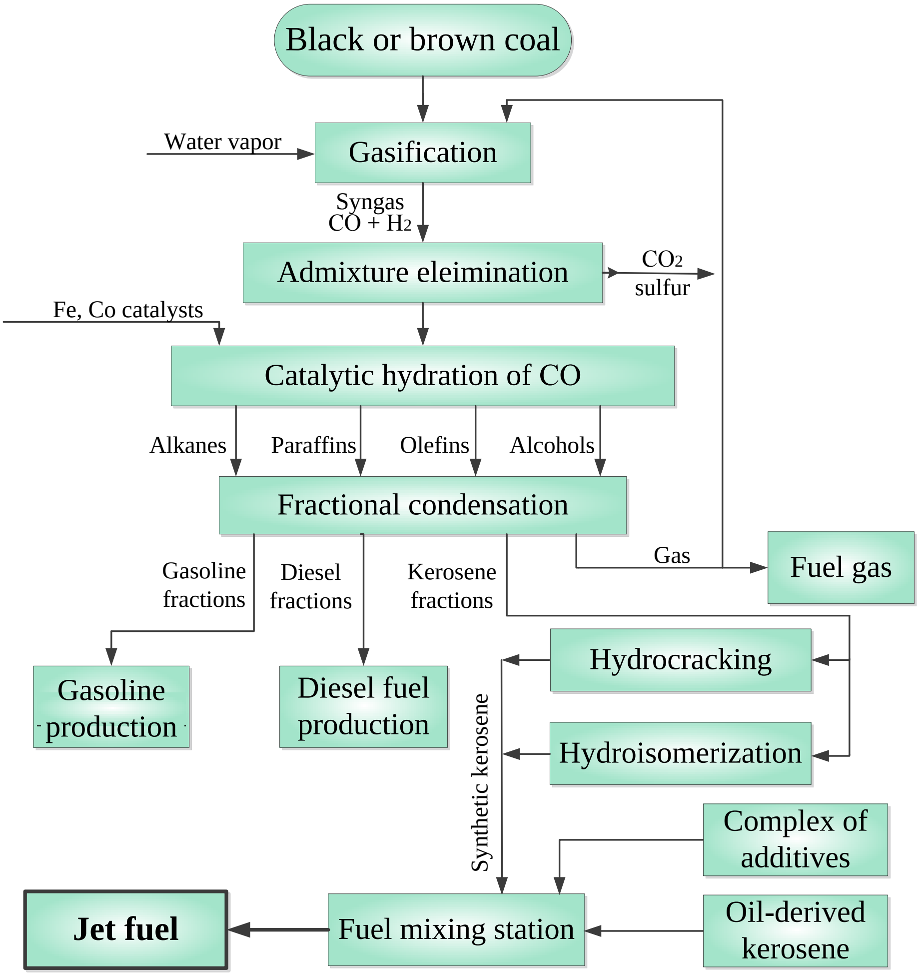


Fig. 1.9. Technological scheme of JF production by coal processing

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 elemination 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.

As it was already mentioned, natural gas is widely used along with coal for JF production by FT-process. The main component of natural gas is methane. Technological scheme of fuel production for air jet engines 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, JF 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.

1.2. Factors stipulating implementation of alternative jet fuels

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 1.1).

Table 1.1

The world energy balance for 2010÷2050, %

Kind of energy source	Years			
	2010	2020	2030	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

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. *International Energy Agency (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 [63]:

$$EROEI = \frac{energy\ delivered\ (usable\ energy)}{energy\ required\ to\ deliver\ that\ energy} \qquad (1.1)$$

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 1.2). Rising of prices for crude-oil is connected to the decrease of its EROEI.

Table 1.2

EROEI values for certain energy sources [63]

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

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.

It is well known that aviation industry ingeneral and aircrafts in particular cause stong impact on environment. As depicted in Fig. 1.10, the environmental impacts arising from the operation of an aviation are diverse and include.

- Local air quality in the vicinity of the airport,
- Noise nuisance,
- GHG (Greenhouse Gases) emissions from energy consumption and vehicle use,
- Resource use including water, energy and other consumables,
- Waste production, prevention and management of solid and liquid waste,
- Soil contamination, groundwater and surface water pollution,
- Habitat and biodiversity losses.

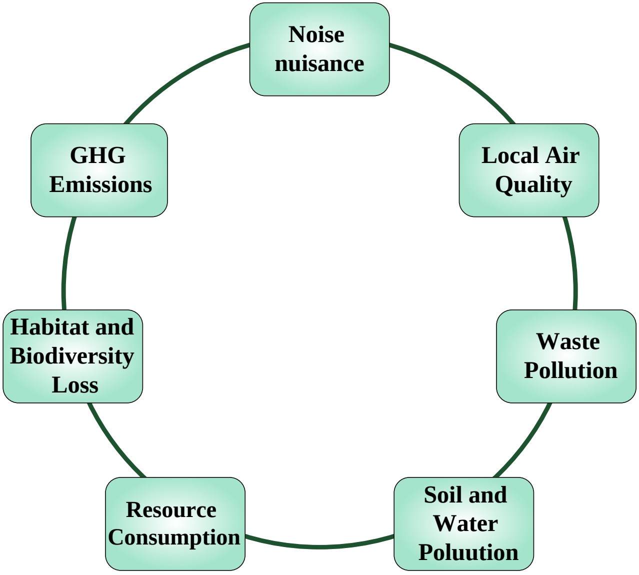


Fig. 1.10. Environmental impacts of aviation industry’s activity

According to another literature sources the modern environmental impact of aviation can be divided into three categories:

1) in-flight operations,
2) airport operations,
3) manufacturing and disposal.

In-flight operation impact includes noise, emissions affecting local air quality at ground level, and emissions at altitude contributing to climate change. Airport operations impact is related to power consumption associated with the operation of the airport itself, emissions during taxiing, byproducts of aircraft and engine maintenance, and contamination resulting from the use of deicing fluid. Finally, the impact of manufacturing and disposal is associated with materials of concern, contaminants, and energy use.

LAQ quality at and near airports is similarly a health concern associated with pollutants emitted by aircraft at ground level during taxiing, take-off, and landing, including ozone, carbon monoxide, sulphate aerosols, and soot aerosols (particulate matter). A promising approach toward alleviating local air quality concerns is electric taxiing either by powering the aircraft’s wheels with an electric motor or through an electric tractor that tows the aircraft to and from the gate.

Turning to the impact of aviation on climate change, this is associated with aircraft emissions in the upper troposphere and lower stratosphere. This includes the direct effect of CO_2 emissions, which have a lifetime of 50÷200 years. Today, more than 90 % of CO_2 emissions from global commercial aircraft operations are generated by large aircraft (twin-aisle and single-aisle airplanes with more than100 passengers).

The main products of fuels, including 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 JFs consumption. Today about 5.5 thousand barrels of JF 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* states that the share of CO_2 produced by air transport is about 2 % (Fig. 1.11) and may reach 3 % in the nearest future.

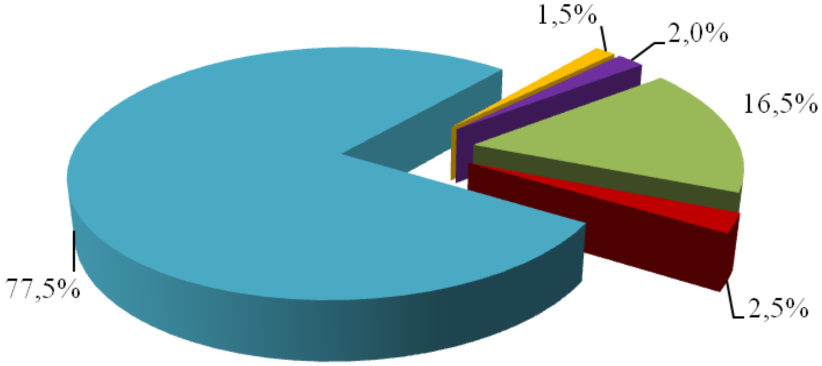


Fig. 1.11. The share of CO_2 emissions from air transport comparing to other kind of transport: 1.5 % – international aviation, 2 % – international marine transport, 16.5 % – motor transport, 2.5 % – other kinds of transport, 77.5 % – other energy sources

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. 1.12).

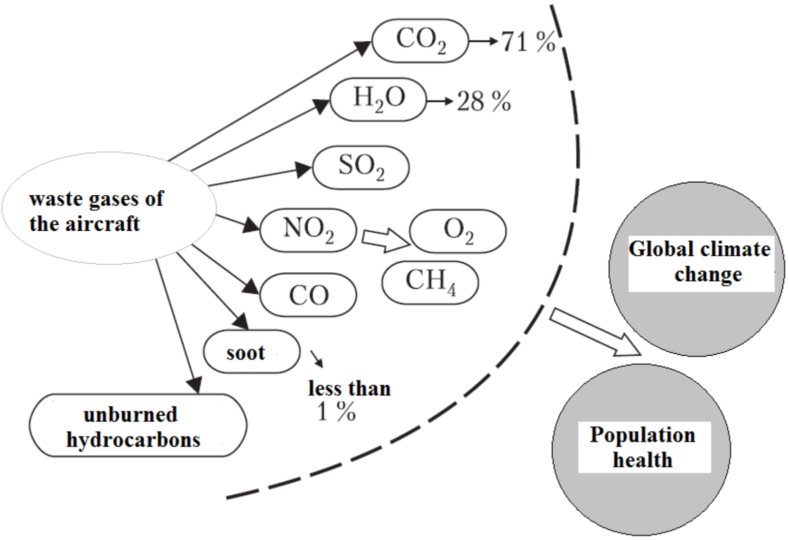


Fig. 1.12. Average composition of aircrafts' exhaust gases

In addition, emissions of NO_x cause an indirect effect on climate change by causing changes in O_3 and CH_4concentrations 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 vapour 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 vapour emissions.

Quantitative and qualitative composition of aircrafts emissions determines ecological properties of JFs, which are determined by the quality of crude-oil. Except that, amount of greenhouse gases formation during JFs production from natural gas is in 1.8 times lower and from coal is in 2.4 times higher comparing to crude-oil.

Processing of bituminous coal is accompanied with CH_4 emissions that are also one of the greenhouse gases. At the same time SO_x emissions are absent during combustion of fuel made of natural gas.

The special attention to the question of civil aviation “greening” is traditionally paid by *ICAO (International Civil Aviation Organization)*. During the 38-th session of ICAO Assembly that was held in November 2013 there was a proposal on “… collecting information about development of alternative JFs … and estimating the progress in reaching global tasks of the modern civil aviation”. In a result the *AFTF (Alternative Fuel Task Force) Group* was created. Its main task is review and analysis of AFs, available feedstock, technologies and volumes of its production.

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 alternatve JFs. Otherwords, 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).

Thus, we can see that the search in methods and technologies of alternative JF production from renewable feedstock was acknowledged as a key direction for solving such questions as energy and resource saving and environmental protection in aviation.

1.4. Production and use of alternative jet fuels of the first, the second and the third generation

The search and widening of new feedstock, development of progressive technologies of AFs production and their rational use in air 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 JFs from renewable feedstock must meet the requirements connected to efficiency, reliability and durability of aviation equipment.

Today there is a great variety of renewable feedstock or biomass for alternative JFs production. Biomass-derived JFs can provide a near-term and even a long-term solution to the airline industry and the military with a lower environmental impact than petroleum fuels.

Potential feedstocks for producing biojet fuel are 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 biojet fuel 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 biojet fuel conversion processes and, therefore, would allow the industry and government to assess and address the feedstocks' 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. 1.13).

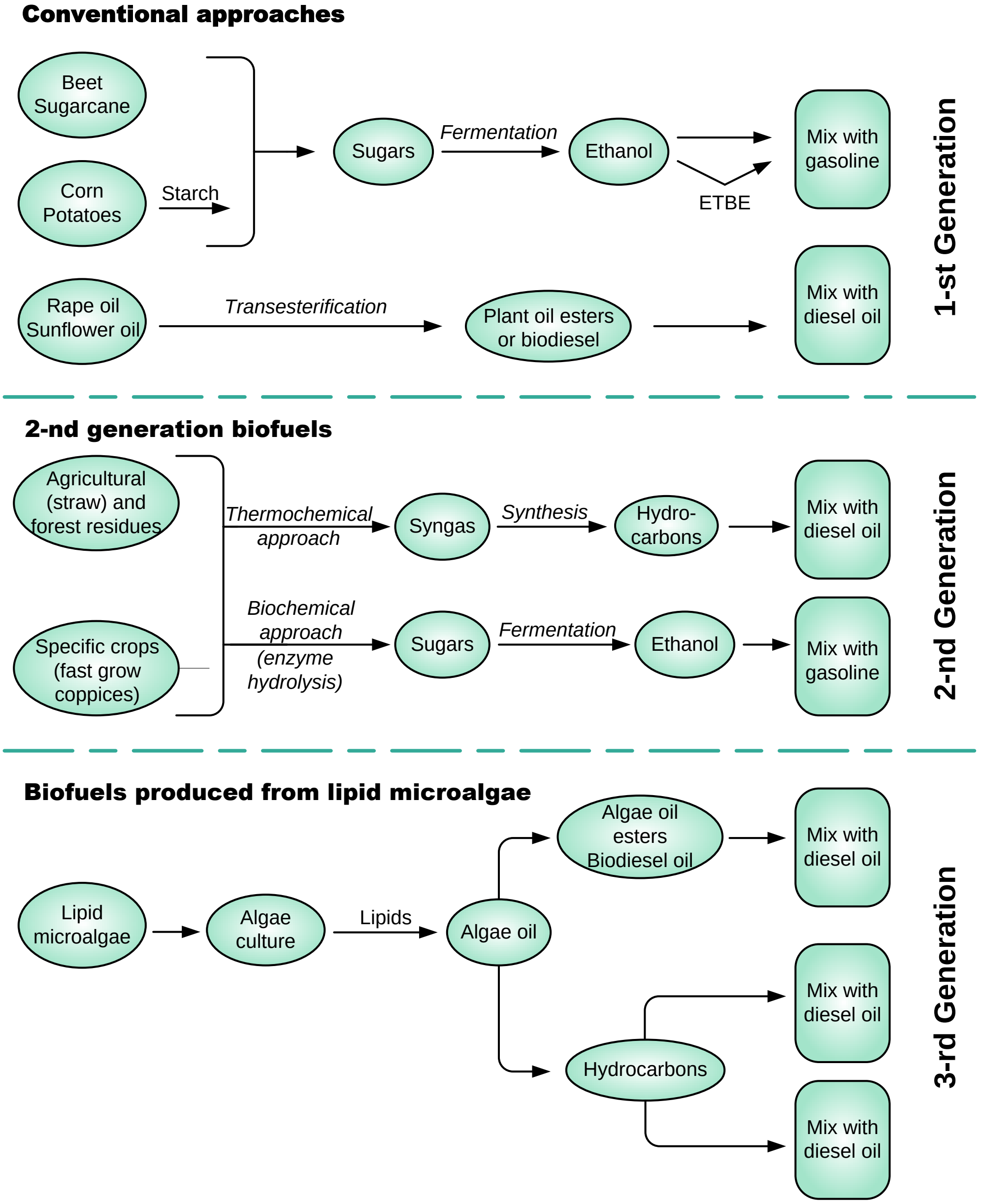


Fig. 1.13. Development of technologies for biofuels production

First generation of AFs (biofuels), which are widely popular today, are produced from traditional agricultural plants. Plant oil-derived biofuels are produced by esterification of traditional oil-containing plants (rape, soya, sunflower, palm, etc). Ethanol is produced by fermentation of the sugar or starch contained in plant biomass.

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. Two processes are being studied: biochemical conversion and thermochemical conversion.

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). 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).

Fourth generation biofuels (Fig. 1.14) 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. 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 greenhouse gas 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.

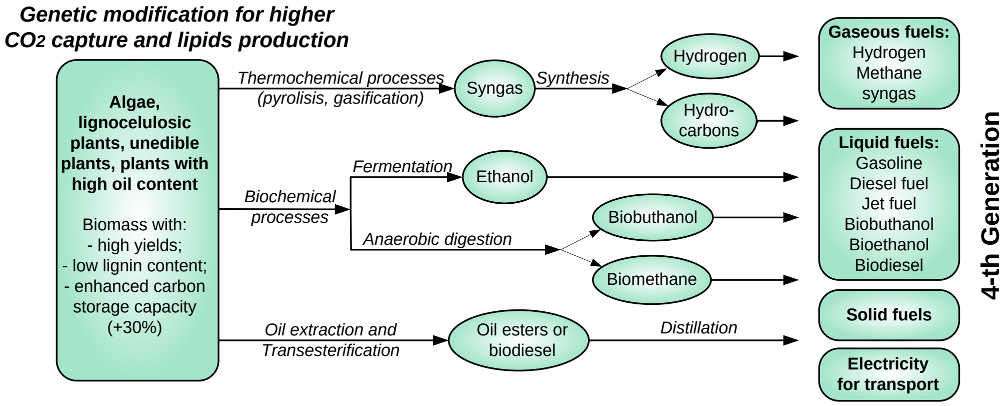


Fig. 1.14. Technologies for 4th generation alternative fuels production

Many biojet fuel conversion technologies, whether in the research and development, demonstration, or commercial stages, are described in the literature.

The production pathways are classified as one of four types, based on the feedstocks and conversion processes (Table 1.3):

1. *alcohol-to-jet (ATJ),*
2. *oil-to-jet (OtJ),*
3 *gas-to-jet (GtJ),*
4. *sugar-to-jet (StJ*).

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 (FT) 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.

Table 1.3

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

Many process technologies that convert biomass-based materials into JF 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 JF 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. 1.15. The most perspective and promising technologies for biomass processing into alternative JFs will be considered in details.

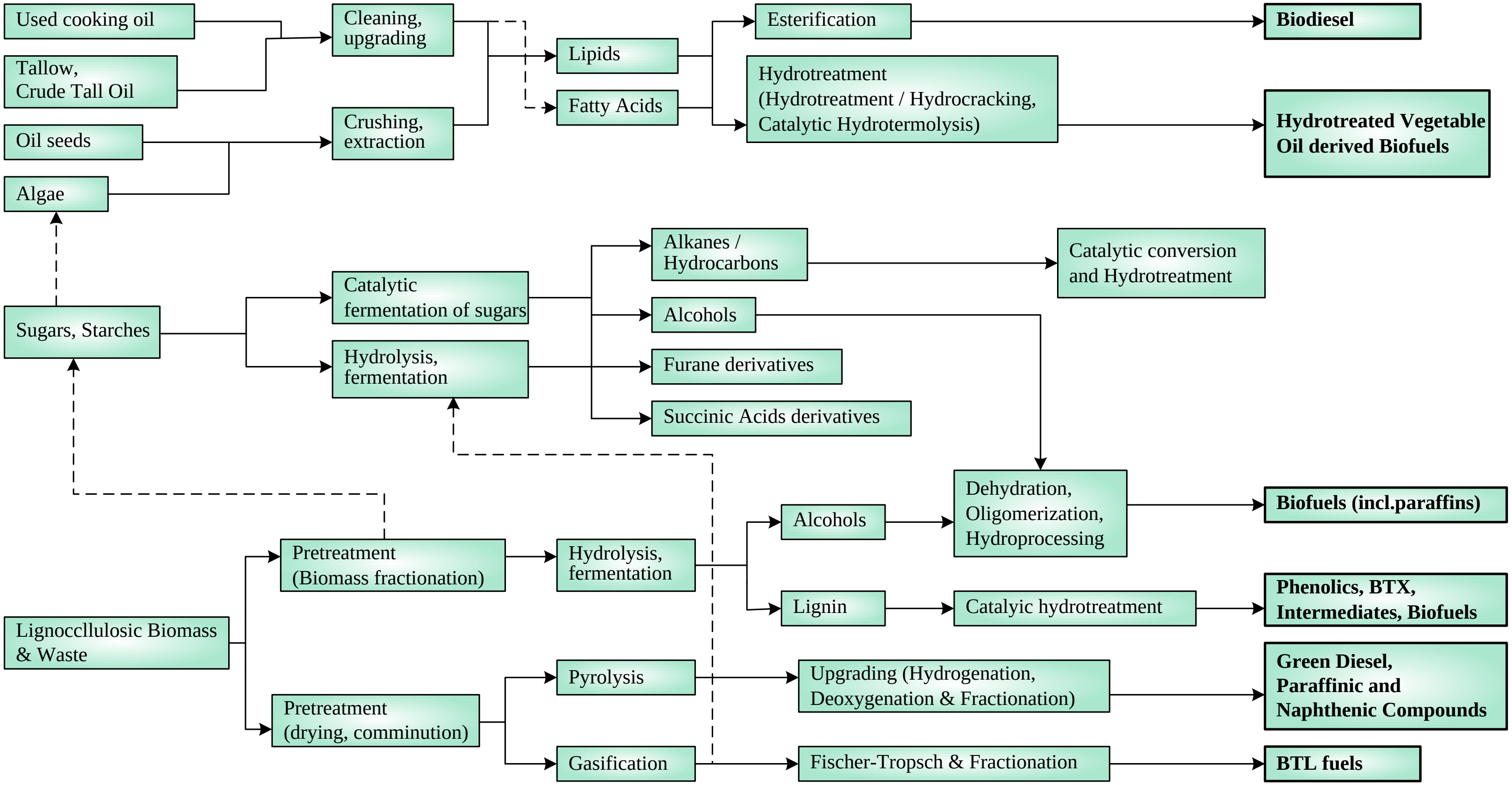


Fig. 1.15. Main possible pathways to aviation biofuels

1.4.1. Technology of biokerosene production

One of the first, who started studying and development of alternative JFs, was the group of scientist from Brazil leaded by Dr. E. Parente. In 1980's he proposed using biokerosene as an alternative to conventional JF. 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 (Fig. 1.16).

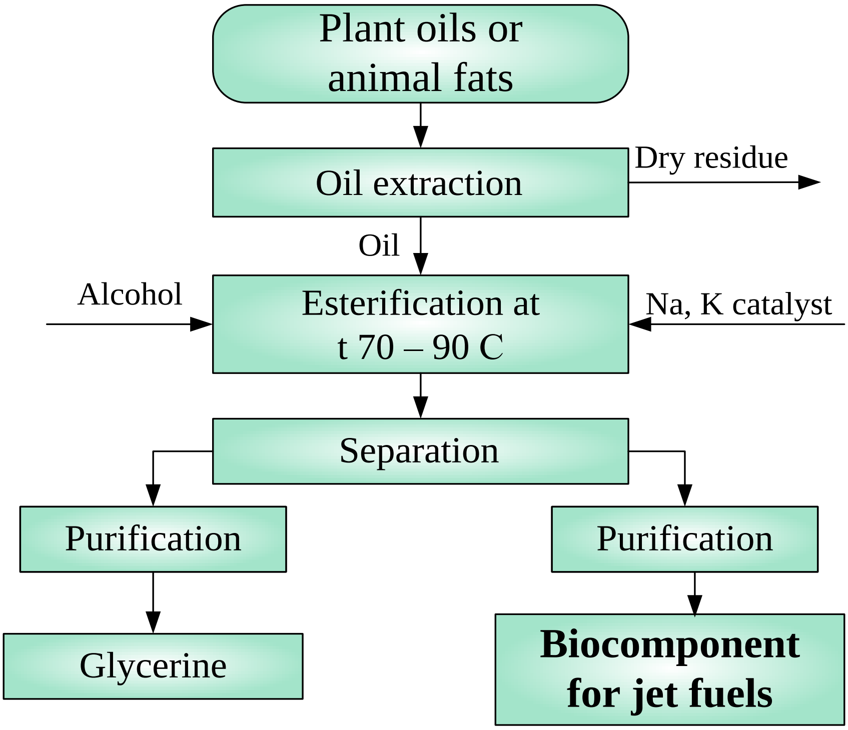


Fig. 1.16. Technology of biokerosene components production

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 JF developments numerous experimental studies have been done. A number of technologies, which allows production of high quality JF 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 *American Society for Test Material (ASTM)* as technologies for production of JF 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.

1.4.2. 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 (Fig. 1.17). The result is hydrogenated synthetic paraffinic kerosene *(SPK or Bio-SPK)*. The new product is used as a component of conventional JF 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.

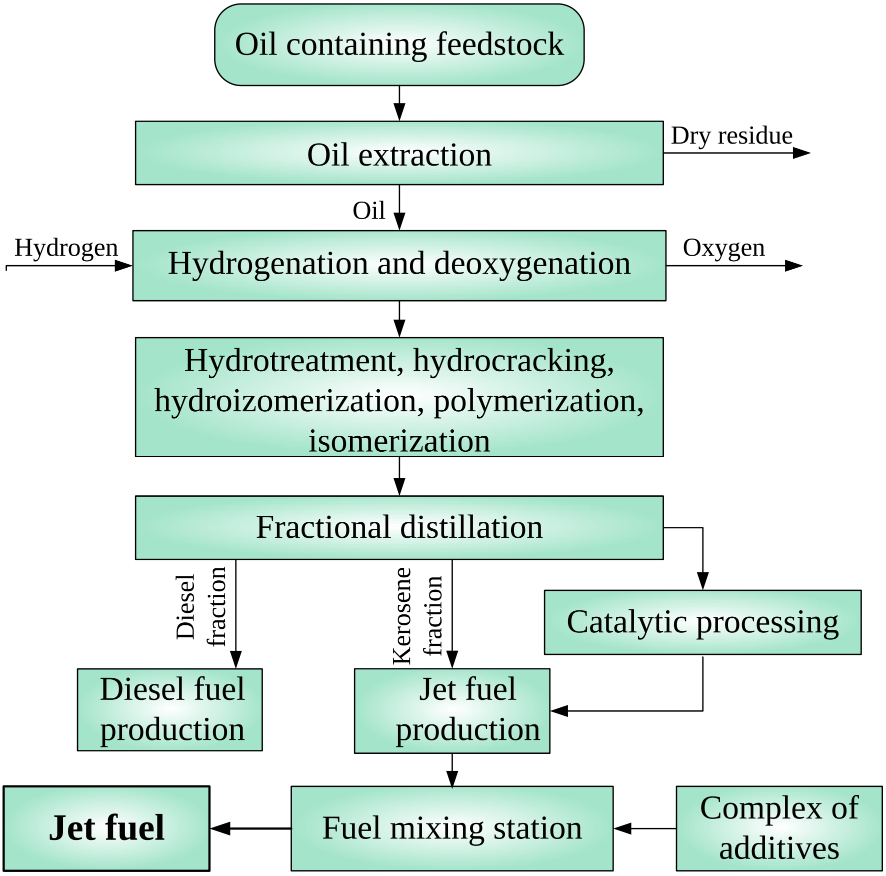


Fig. 1.17. Technology of jet fuel producion via hydrotreatment of fat-containing feedstock

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.

1.4.3. Jet fuel production by biomass processing

BtL technology is another commonly approved technology of JF 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 JF produced by this technology is completely synthetic and its properties are similar to JF made of coal (Fig. 1.18).

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)* – JF made of alcohols. One of the aapproaches is convertion of agricultural waste by bacteria or yeasts into JF 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.

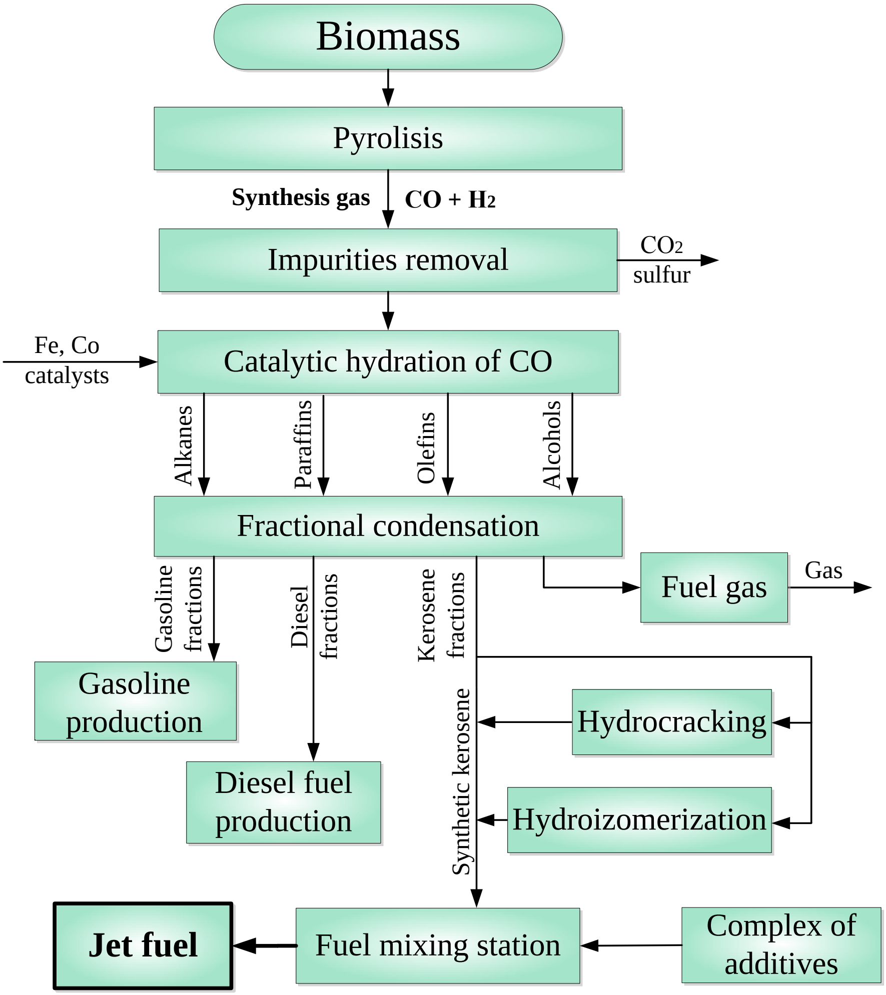


Fig. 1.18. Technology of jet fuel producion via biomass pyrolisis

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 JFs 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 (FT) 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.

1.5. Perspective plant-derived components for alternative jet fuels production

This diversity of technologies provides the ability for JF production using various feedstocks. Scientists believe that the most promising feedstocks are plants with high oils content, algae and some types of industrial and household waste.

Camelina relates to energy crops with high oil content. 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 .

Rape 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 (RO) were Canada, the US and European countries such as Germany, France, Czech Republic, Poland, UK. The chemical composition and basic characteristics of RO are well suited for alternative fuels. But then the question arose about the necessity of rape 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 RO 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.

It should be noted that for Poland rape is a typical culture, and in the last 8÷10 years the massive producing was noticed. The most rapid increase of production volumes of rape occurred in the period 2004÷2008 years, which coincided with the growing of global demand for RO as raw material for the production of biofuels. This allows us to consider RO as the most promising raw materials for JE biofuels .

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 AF. This culture is not a depending on soil quality and can give good yields in dry uncultivated areas, leaving fertile soils for agriculture. However, the factor that limits the widespread use of jatropha, is the possibility of growing only in warm climates.

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 Fatty AcidMethyl Ester (FAME) 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 transesterification 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). 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.

Household and industrial wastes 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 JFs 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 (JF), do not harm the environment, or involve any negative socio-economic impacts. Not all biomass feedstock are 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 1.5 presents a summary of the emissions 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 1.5

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 1.4 shows a selection of the wide range of variables influencing feedstock, logistics and pre-processing costs.

Table 1.4

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.

CHAPTER 2

INFLUENCE OF FUELS PARAMETERS ON OPERATION AND EXPLOITATION OF JET ENGINES

Introduction of the JE and the turbojet principle into aircraft propulsion more than 70 years ago led to a revolutionary change in transport technology. As a result of this transformation supersonic flight became possible, the cost of air travel and cargo transport was greatly reduced, and significant improvements in aircraft safety were achieved. The cost reductions were realized as a result of a combination of increasing flight speed and the ability to build much larger aircraft. Prior to introducing gas turbine engines into aircraft propulsion, aircraft had piston engines to drive the propeller. As the performance and efficiency of JEs began to exceed those of piston engines, gas turbines became the dominant engines in aircraft. The adaptations of turbine engines in the form of turbojet, turbofan, and turboprop engines came with the different needs for thrust at various speeds.

The JE (gas turbine engine) is a heat engine using air as a working fluid to provide thrust. To achieve this, the air passing through the engine has to be accelerated; this means that the velocity or kinetic energy of the air is increased. To obtain this increase, the pressure energy is first of all increased, followed by the addition of heat energy, before final conversion back to kinetic energy in the form of a high velocity jet efflux.

A simple way to compare the performance of the three main engine types is to look at their thrust specific fuel flow (FF). This parameter gives the amount of fuel by weight required to provide a specific amount of jet thrust over a certain period of time. Thrust specific FF characteristics of typical aircraft engines as a function of aircraft Mach number are given in Fig. 2.1.

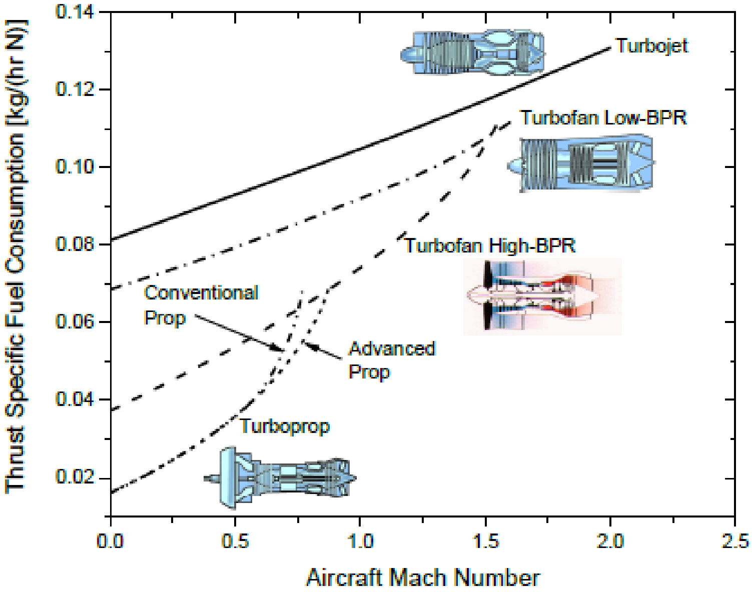


Fig. 2.1. Thrust specifc fuel consumption characteristics of typical aircraft engines

It is clear that turboprops have superior fuel efficiency over turbofans and turbojets, but they are disadvantaged by the limitation of the flight speed. This limitation is induced by the tip speed of the propeller which should be below the sonic speed, hence limiting the engine shaft speed. The solution to this problem seems to be a geared-propeller that is a geared transmission between the propeller and engine shafts. The gearbox is typically massive and requires extensive development effort to ensure reliability and durability; most of the time substantial speed reduction is necessary. The massiveness of the required gearbox becomes the limiting factor for relatively larger turboprop engines. However, for long range subsonic aircraft high bypass ratio turbofan engines are still the only choice. The latest design of this type of engine incorporates a geared turbofan which provides significant efficiency improvements. Another concept is the open rotor engine design that has the potential to provide appreciable fuel burn savings for single aisle aircraft as compared to that of an equivalent high bypass ratio turbofan engine. This concept is a follow up on known designs of unducted fans or fanprops which have not been commercially produced. Open rotor engines are likely to be noisier than turbofan engines as there is no nacelle to absorb and attenuate the noise generated by the engine. Other approaches that could improve the efficiency of jet engines are to find solutions to increase the compression ratio and the turbine inlet temperature. Both parameters directly influence the fuel efficiency. Today, the turbine inlet temperatures are limited by the blade materials available and the blade cooling technologies. Advances in these areas will further improve the fuel efficiency of aviation gas turbine engines. The issue of high compression ratios and higher turbine inlet temperatures also has some negative implications since nitrogen oxide (NO_x) emissions increase with increasing pressure and temperature.

Generally, in the JE, combustion occurs at a constant pressure. The processes of induction, compression, combustion and exhaust of gas occur constantly in the JE (Fig. 2.2).

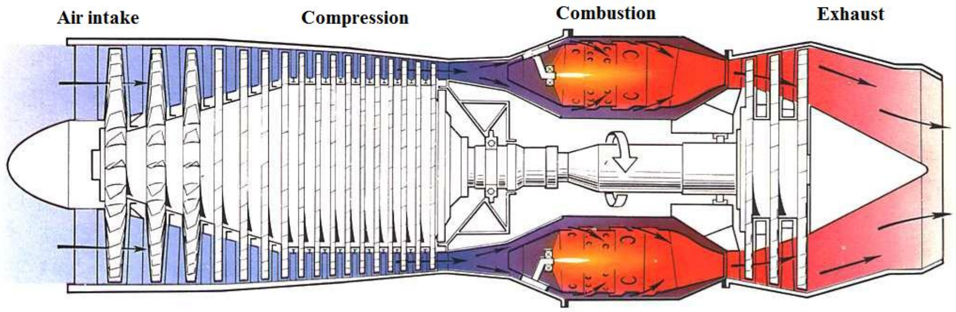
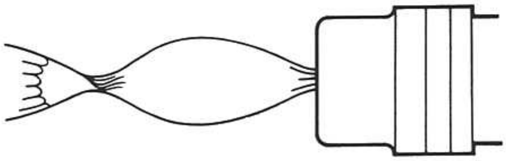


Fig. 2.2. Working cycle of the jet engine

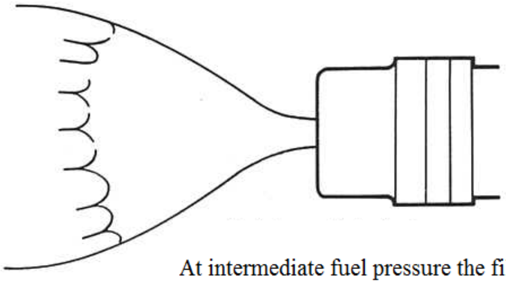
Due to the continuous action of the turbine engine and the fact that the combustion chamber is not an enclosed space, the pressure of the air does not raise during combustion but its volume increases. This process is known as heating at constant pressure.

2.1. Fuel spraying process

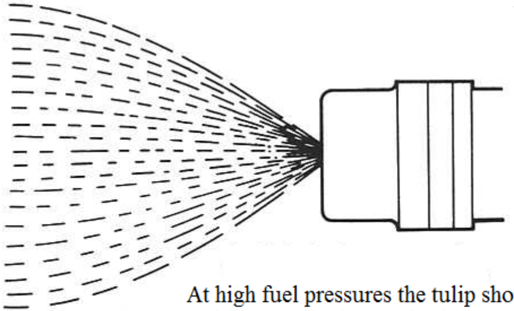
Fuel spray nozzles are the final components of the JE fuel system, which task is atomizing or vaporizing the fuel to ensure its rapid burning. An early method of atomizing the fuel is to pass it through a swirl chamber where tangentially disposed holes or slots imparted swirl to the fuel by converting its pressure energy to kinetic energy. In this state, the fuel is passed through the discharge orifice which removes the swirl motion as the fuel is atomized to form a cone-shaped spray. This is called *pressure jet atomization*. The rate of swirl and pressure of the fuel at the fuel spray nozzle are important factors in good atomization. The shape of the spray is an indication of the degree of atomization as shown in Fig. 2.3.



At low fuel pressures a continious fuel film is formed, called "bubble"



At intermediate fuel pressure the film breaks up at the edges to form a "tulip"



At high fuel pressures the tulip shortens towards the orifice and forms a finely atomized spray

Fig. 2.3. Various stages of fuel atomization

Later fuel spray nozzles use the airspray principle, which employs high velocity air instead of high velocity fuel to cause atomization. This method allows atomization at low fuel flow rates thus providing an advantage comparing to the pressure jet atomizer by allowing fuel pumps of a lighter construction to be used.

Processes of fuel supply and preparing of FAM in the combustion chambers of JEs are crucial for burning. In particular, the process of atomization and evaporation of liquid fuels during FAM formation highly depend on properties of combustion chambers. Taking into account low volatility of modern fuels, it requires fuel atomization into large number of droplets in order to increase the evaporation surface and thus to accelerate evaporation of the droplets. The smaller the size of a drop, the greater the ratio of liquid surface to its volume, and thus more evaporation rate.

The quality of fuel atomization affects the completeness of combustion, emissions of soot, CO and C_nH_m, verge of steady burning and particularly strongly ignition characteristics. It is advisable to supply fuel in the form of a hollow spray cone that is adjacent outside to areas of return jets, where the speed gradient is maximal.

Fuel atomization happens due to the velocities difference between liquid and air flow (gas), where it is supplied. This speeds difference can be achieved in two cases: when liquid fuel flow from nozzles at high speed in the relatively slow-moving gas, or when in the fast air flow blows slowly moving liquid. The first principle is used in various types of mechanical nozzles, where fuel is supplied under pressure or due to the nozzle rotation. The second principle may include: gas spraying with an internal flows; atomization using auxiliary air, pneumatic atomization. The requirement to obtain a large spray cone angle is caused by the need to reduce the length of the flame tube. The atomizing spray nozzle has been developed in five fairly distinct types; the Simplex, the variable port (Lubbock), the Duplex or Duple, the spill type and the airspray nozzle.

Taking into account strengthening of requirements to JEs – increasing completeness of fuel combustion, decreasing of exhaust gases emissions, possibility to use alternative fuels, the more attention is paid to the questions of fuel preparation and supply into the JEs.

2.2. Fuel-air mixture formation

The combustion chamber has to burn large quantities of fuel, supplied through the fuel spray nozzles, with extensive volumes of air, supplied by the compressor, and release the heat in such a manner that the air is expanded and accelerated to give a smooth stream of uniformly heated gas at all conditions required by the turbine. This task must be accomplished with the minimum loss in pressure and with the maximum heat release for the limited space available.

The amount of fuel added to the air will depend upon the temperature rise required, with a limit within the range of 850÷1700 °C. The air is heated between 200÷550 °C by the work done during compression, giving a temperature rise requirement of 650÷1150 °C from the combustion process. Since the gas temperature required at the turbine varies with engine thrust the combustion chamber must also be capable of maintaining stable and efficient combustion over a wide range of engine operating conditions.

Air from the engine compressor enters the combustion chamber at a velocity up to 150 m/s, but because at this velocity the air speed is far too high for combustion, the first thing that the chamber must do is to decelerate it and raise its static pressure. Since the speed of burning JF at normal mixture ratios is only a few feet per second, any fuel lit even in the diffused air stream, which now has a velocity of about 25 m/s, would be blown away.

In normal operation, the overall AFR of a combustion chamber can vary between 45:1 and 130:1, however, JF will only burn efficiently at, or close to, a ratio of 15:1, so the fuel must be burned with only part of the air entering the chamber, in what is called a primary combustion zone. This is achieved by means of a flame tube (combustion liner) that has various devices for metering the airflow distribution along the chamber.

Approximately 20 % of the air mass flow is taken in by the snout or entry section. Immediately downstream of the snout are swirl vanes and a perforated flare, through which air passes into the primary combustion zone. The swirling air induces a flow upstream of the centre of the flame tube and promotes the desired recirculation.

Through the wall of the flame tube body, adjacent to the combustion zone, are a selected number of secondary holes through which a further 20 % of the main flow of air passes into the primary zone (Fig. 2.4). The air from the swirl vanes and that from the secondary air holes interacts and creates a region of low velocity recirculation. This takes the form of a toroidal vortex, similar to a smoke ring, which has the effect of stabilizing and anchoring the flame. The recirculating gases hasten the burning of freshly injected fuel droplets by rapidly bringing them to ignition temperature.

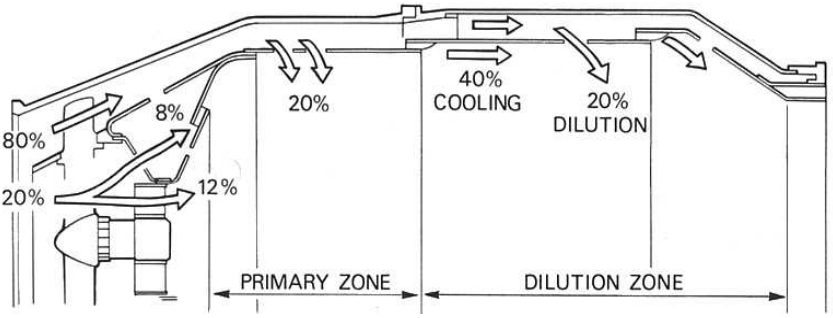


Fig. 2.4. Apportioning the airflow]

It is arranged that the conical fuel spray from the nozzle intersects the recirculation vortex at its centre. This action, together with the general turbulence in the primary zone, assists in breaking up the fuel and mixing it with the incoming air.

The temperature of the gases released by combustion is about 1800÷2000 °C, which is too hot for entry to the nozzle guide vanes of the turbine. The air not used for combustion, which amounts to about 60 % of the total airflow, is therefore introduced progressively into the flame tube. Approximately a third of this is used to lower the gas temperature in the dilution zone before it enters the turbine and the remainder is used for cooling the walls of the flame tube. This is achieved by a film of cooling air flowing along the inside surface of the flame tube wall, insulating it from the hot combustion gases (Fig. 2.5).

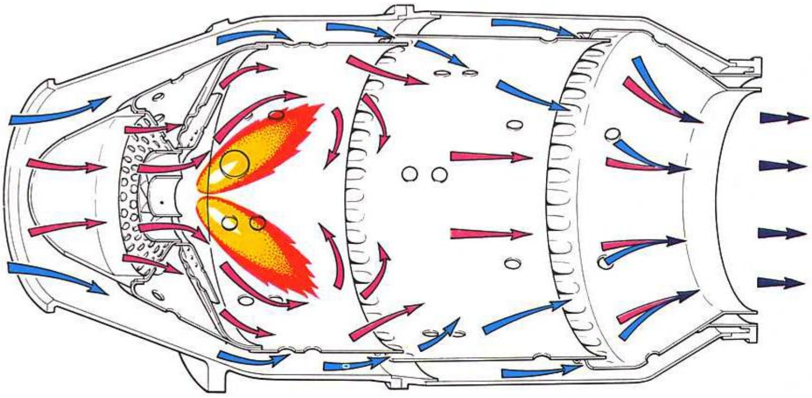


Fig. 2.5. Flame stabilizing and general airflow pattern

A recent development allows cooling air to enter a network of passages within the flame tube wall before exiting to form an insulating film of air; this can reduce the required wall cooling airflow by up to 50 %. Combustion should be completed before the dilution air enters the flame tube, otherwise the incoming air will cool the flame and incomplete combustion will result. An electric spark from an igniter plug initiates combustion and the flame is then self sustained.

2.3. Fuel combustion process

There are three main types of combustion chamber in use for gas turbine engines. These are the multiple chamber, the tubo-annular chamber and the annular chamber.

Multiple combustion chamber. This type of combustion chamber is used on centrifugal compressor engines and the earlier types of axial flow compressor engines. The chambers are disposed around the engine (Fig. 2.6) and compressor delivery air is directed by ducts to pass into the individual chambers. Each chamber has an inner flame tube around which there is an air casing. The air passes through the flame tube snout and also between the tube and the outer casing. The separate flame tubes are all interconnected. This allows each tube to operate at the same pressure and also allows combustion to propagate around the flame tubes during engine starting.

Tubo-annular combustion chamber. The tubo-annular combustion chamber bridges the evolutionary gap between the multiple and annular types. A number of flame tubes are fitted inside a common air casing (Fig. 2.7). The airflow is similar to that already described. This arrangement combines the ease of overhaul and testing of the multiple system with the compactness of the annular system.

Annular combustion chamber. This type of combustion chamber consists of a single flame tube, completely annular in form, which is contained in an inner and outer casing (Fig. 2.8). The airflow through the flame tube is similar to that already described, the chamber being open at the front to the compressor and at the rear to the turbine nozzles.

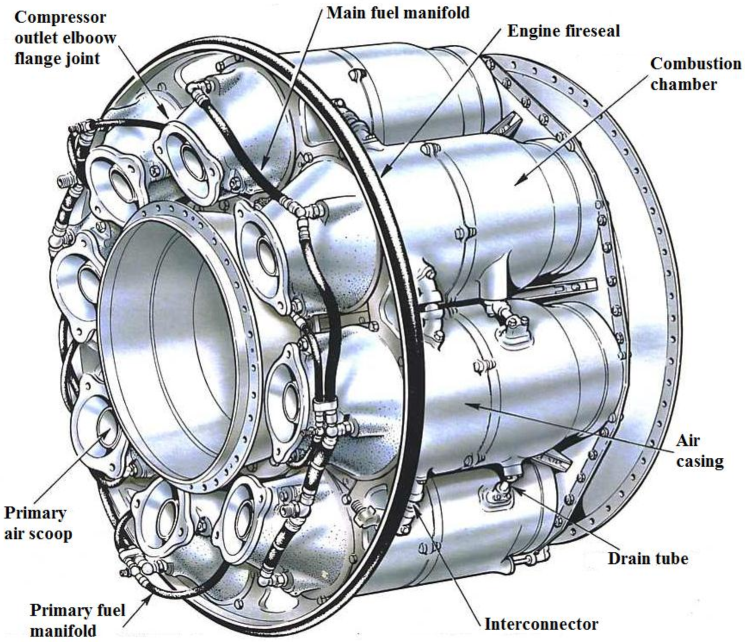


Fig. 2.6. Multiple combustion chamber

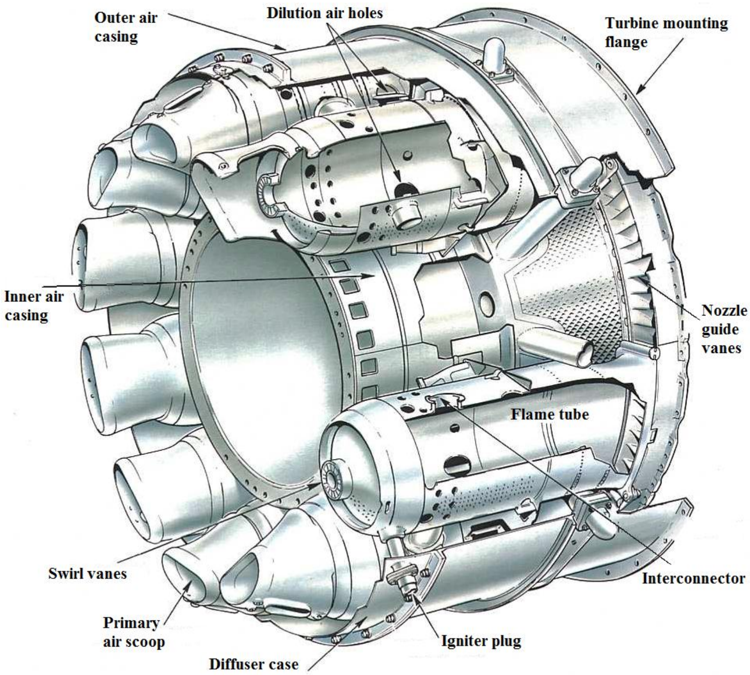


Fig. 2.7. Tubo-annular combustion chamber

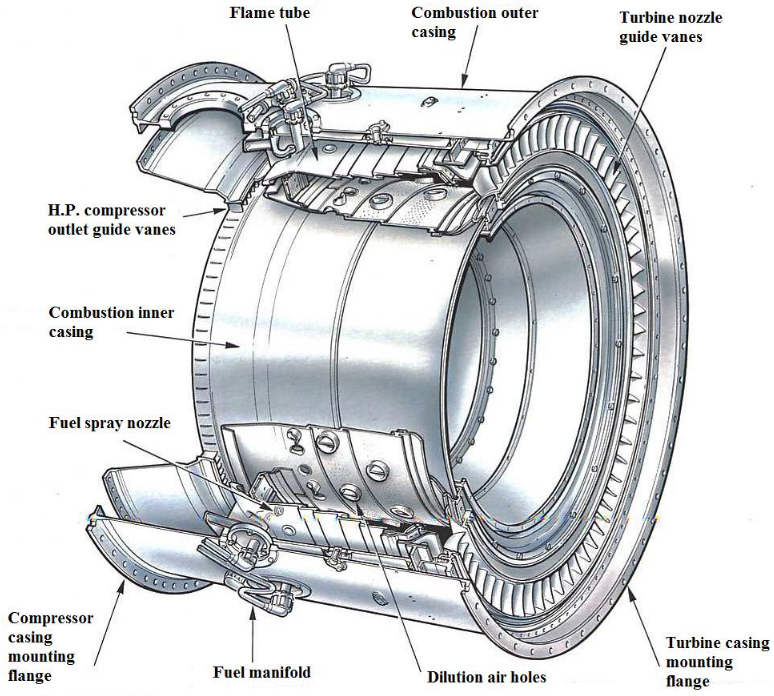


Fig. 2.8. Annular combustion chamber

The main advantage of the annular chamber is that, for the same power output, the length of the chamber is only 75 % of that of a tubo-annular system of the same diameter, resulting in considerable saving of weight and production cost. Another advantage is the elimination of combustion propagation problems from chamber to chamber.

In comparison with a tubo-annular combustion system, the wall area of a comparable annular chamber is much less; consequently the amount of cooling air required to prevent the burning of the flame tube wall is less, by approximately 15 %, This reduction in cooling air raises the combustion efficiency to virtually eliminate unburnt fuel, and oxidizes the carbon monoxide to non-toxic carbon dioxide, thus reducing air pollution.

A combustion chamber must be capable of allowing fuel to burn efficiently over a wide range of operating conditions without incurring a large pressure loss. In addition, if flame extinction occurs, then it must be possible to relight. In performing these functions, the flame tube and spray nozzle atomizer components must be mechanically reliable.

The gas turbine engine operates on a constant pressure cycle; therefore any loss of pressure during the process of combustion must be kept to a minimum. In providing adequate turbulence and mixing, a total pressure loss varying from about 3÷8% of the air pressure at entry to the chamber is incurred.

The combustion efficiency of most gas turbine engines at sea-level take-off conditions is almost 100 %, reducing to 98 % at altitude cruise conditions, as shown in

Fig. 2.9. Combustion stability means smooth burning and the ability of the flame to remain alight over a wide operating range.

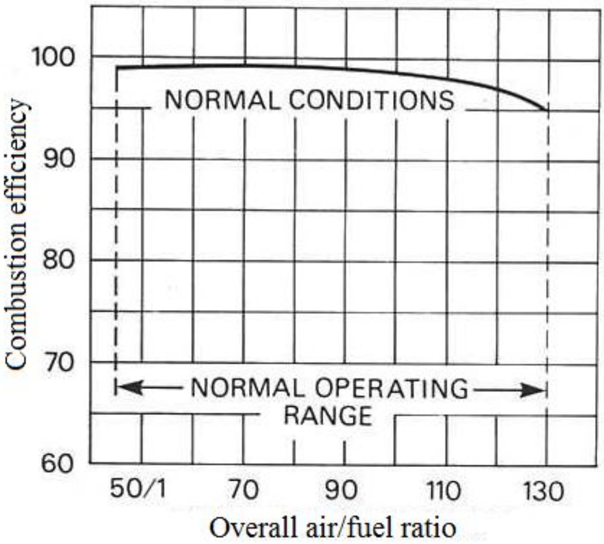


Fig. 2.9. Combustion efficiency and air/fuel ratio

For any particular type of combustion chamber there is both a rich and weak limit to the AFR, beyond which the flame is extinguished. An extinction is most likely to occur in flight during a glide or dive with the engine idling, when there is a high airflow and only a small fuel flow, i.e. very weak mixture strength.

The range of air/fuel ratio between the rich and weak limits is reduced with an increase of air velocity, and if the air mass flow is increased beyond a certain value, flame extinction occurs. A typical stability loop is illustrated in Fig. 2.10. The operating range defined by the stability loop must cover the AFRs and mass flow of the combustion chamber.

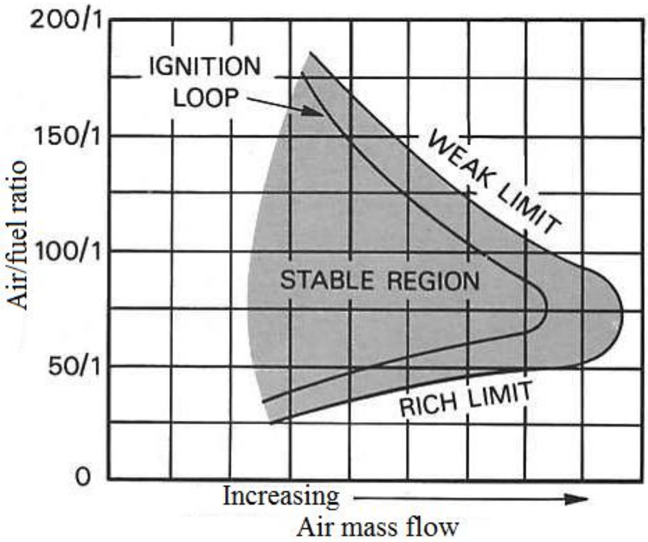


Fig. 2.10. Combustion stability limits

The ignition process has weak and rich limits similar to those shown for stability in Fig. 2.10. The ignition loop, however, lies within the stability loop since it is more difficult to establish combustion under ’cold’ conditions than to maintain normal burning.

2.4. Exhaust gases emissions

Approximately 99.5÷99.9 % of the molar content of typical JE exhaust gases consists of N_2, O_2, CO_2, and H_2O. The substances that compose the remaining 0.1÷0.5 % exist in trace amounts. This trace exhaust component consists primarily of NO_x, CO, C_xH_y (including CH_4, soot), the hydroxy family (HO_x, H_2O_x), the sulfur oxide family (SO_x), and elemental species such as O (Fig. 2.11).

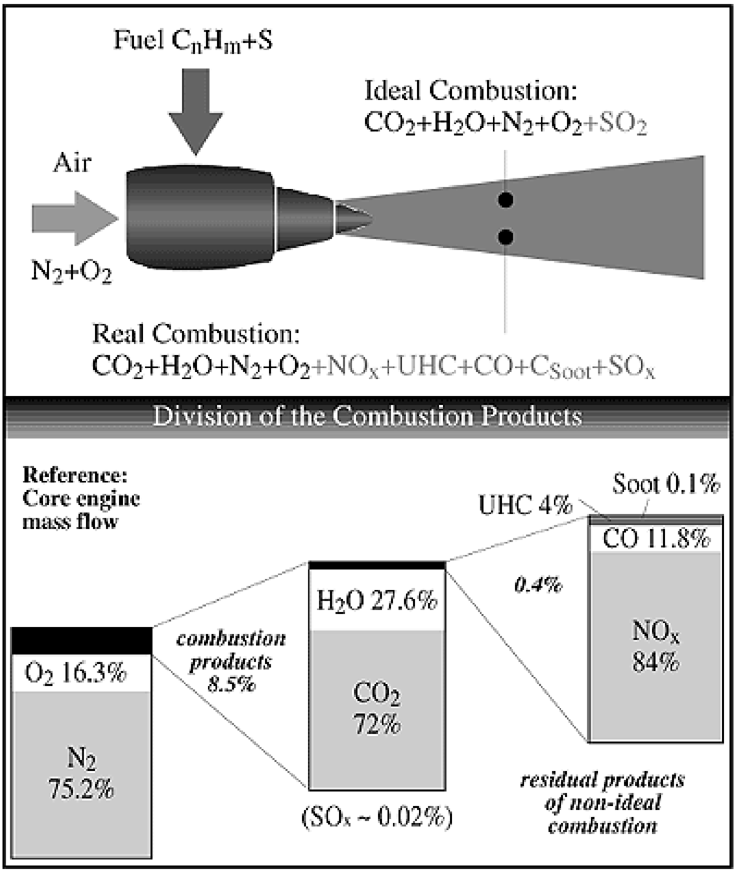


Fig. 2.11. Mechamism of exhaust gases formation

For complete understanding the problem of aircrafts emissions and the necessity of it reduction we need to understand specifically the mechanism of exhaust gases formation and its negative effect on components of environment (Table 2.1).

Table 2.1

Composition of aircraft's exhaust gases

Compound	Mechanism of formation	Impact on environment
1	*2*	*3*
CO_2	CO_2 is product of complete jet fuel combustion. Carbon in fuels is oxidized by oxygen from the air up to CO_2.	CO_2 is a main greenhouse gas with long life-cycle (50 – 200 years). Its share in total aircraft's emissions is about 70%. While spreading in the atmosphere CO_2 causes direct heating of the troposphere under the solar radiation.
NO_x	NO_x are formed when air gets to combustion zone with high temperature and pressure. Molecular nitrogen combines with oxygen and NO_x are formed.	NO_x promote formation of photochemical smog and destruction of ozone layer in higher parts of the atmosphere. NO_x cause irritation of mucous shells and disorders of central nervous system in the human organism.
C_xH_y	Unburned hydrocarbons are emitted in a result of incomplete jet fuel combustion in conditions of lack of oxygen in fuel-air mixture.	Unburned hydrocarbons are the source of environmental pollution with carcinogenic substances. They cause carcinogenic, mutagenic, narcotic and other effects in human organism.
Soot and particulate matter	During the combustion of fuel formed unburned particles of fuel. Soot is formed by incomplete combustion of fuel.	Fractions of particles up to 10 μm stay in the atmosphere and decrease air transparency thus reduce the access of ultraviolet radiation and make microclimate of some regions worse. Particulate matter negatively influence on respiratory system and mucous shells of the human organisms.
SO_x	SO_x are formed when sulfur-containing compounds are oxidized by oxygen from the air during fuel combustion.	SO_x form in air water solutions of sulfuric acid that later gets onto earth's surface. It decreases fertility of soil and destroys plants' chlorophyll. It causes metals corrosion, decreases persistence of paint coatings, durability of constructions and buildings.
H_2O	H_2O vapor is another product of complete jet fuel combustion. In a result of burning hydrogen is oxidized to H_2O.	H_2O vapor makes about 29% from in total aircraft's emissions. It doesn't make some significant danger to the state of environment.

2.4.1. Mechanisms of CO and C_xH_y emissions formation

CO is formed in the primary zone on combustion chamber at rich FAM, because of the lack of oxygen for complete carbon oxidation to CO_2. When FAMs are stohiometric of comparatively poor CO is formed in a result of CO_2 dissociation.

Low levels of CO formation can be achieved by providing coefficient of air excess in a combustion zone $\alpha=1.1\div1.4$. At the same time CO emissions increase compared to the thermodynamic equilibrium, especially at idling regime because of several reasons:

- heterogenity of the FAM,
- low rate of combustion in the primary zone,
- insufficient FAM residence time in the combustion zone for complete CO oxidation,
- “freezing” of products of incomplete combustion, which are thrown by cooling air in the parietal layer of a flame tube.

When FAM is heterogeneous the CO concentration increases because of the lack of oxygen in local areas with rich FAM, and – because of slow combustion in areas with very poor FAM.

C_xH_y include both gaseous and liquid particles of initial fuel and products of its decomposition into hydrocarbons of smaller molecular weight. The main reasons for their release are the same as for the formation of CO: insufficient spraying and mixing, low rate of combustion and “freeze” in the parietal layer of cooling air. Therefore, the same measures are applied to reduce emissions of CO and C_xH_y:

- improving of fuel atomization to speed up evaporation and creation of a homogenous FAM,
- optimal distribution of air in the combustion chamber for providing $\alpha=1.4$ in a primary zone at all operation regimes by means of optimal regulation (use of multimode nozzles or its partial switching off, special preparation of FAM etc.),
- increasing volume of the primary zone and the fuel duration time in this zone,
- afterburning of CO, C_xH_y and soot in the intermediate zone,
- reducing air flow for the film cooling of a flame tube at the site of the primary zone through the use of thermal barrier coatings or specially designed flame tubes.

Increasing of C_xH_y and CO emissions during change of JE operation regime toward idling is explained not only by worsening of fuel atomization, but decrease of chemical reactions rate due to decrease of pressure and temperature at the combustion chamber inlet.

2.4.2. Mechanisms of NO_X emissions formation

NO_X is formed in the form of NO and NO_2 in a result of the exothermal oxidation of atmospheric nitrogen and also oxidation of nitrogen contained in the fuel at relatively high temperatures (T *> 1527 °C).

Generally three mechanisms of nitrogen oxide NO are found.

1) *Atmospheric thermal NO* is formed in a result of chain reactions of atmospheric nitrogen oxidation:

$$O_2 \leftrightarrow 2O; \qquad O + N_2 \leftrightarrow NO + N; \qquad N + O_2 \leftrightarrow NO + O;$$

$$N + OH \leftrightarrow NO + H. \tag{2.1}$$

Under the assumption of a fixed concentration of nitrogen and hydrogen atoms the rate of NO formation is determined by the ratio:

$$\frac{dNO}{d\tau} = 2K_1 \cdot O \cdot \frac{N_2 - K_{-1}K_{-2}NO^2/K_1K_2O_2}{1 + K_{-1}NO/(K_2O_2 + K_3OH)} \tag{2.2}$$

where NO, O, N_2, O_2, OH – concentration of substances, g·mol/cm^3; K_j– constants of reaction rates:

$$O+N_2 \rightarrow NO+N, \quad K_1 = 1.439 \cdot 10^{14} \cdot e^{-17910/RT};$$
$$NO+N \rightarrow O+N_2, \quad K_1 = 3.09 \cdot 10^{13} \cdot e^{-79/RT};$$
$$N+O_2 \rightarrow NO+O, \quad K_2 = 6.427 \cdot 10^{9} \cdot T \cdot e^{-1490/RT};$$
$$NO+O \rightarrow N+O_2, \quad K_2 = 1.45 \cdot 10^{9} \cdot T \cdot e^{-9160/RT};$$
$$N+OH \rightarrow NO+H, \quad K_3 = 4{,}2 \cdot 10^{13}.$$

where T – stoichiometric adiabatic flame temperature (temperature, which may be reached by the flame, if all the energy of a chemical reaction of converting new FAM into combustion products would be used for heating of these products);
τ – time of gas duration in the combustion chamber, ms.

Calculated equilibrium concentration of NO rises with increasing of α at $T = const$ and also with increasing of burning temperature at $\alpha = const$. Since α and T in the combustion chamber are interconnected, NO production reaches its maximum at $1{,}0 < \alpha < 1{,}2$ from a "poor" side of stoichiometric ration.

Increase gas duration time at high temperature promotes the release of NO. Furthermore, as already noted, the high temperature (above 1527 °C) causes dissociation of complete combustion products CO_2 and H_2O to simpler components CO, H_2, O, H, OH with energy expenses. This leads to a significant reduction in the maximal (adiabatic) flame temperature. The impact of pressure within the range of 0.5÷3.0 MPa for NO formation is not found, that is explained the constant volume of gases in the reaction $N_2 + O_2 = 2NO$.

2) *Over equilibrium (“fast”) NO* is formed in the front of a flame, that is, when $\tau \rightarrow 0$ (at the early stages of combustion of rich FAM at relatively low temperatures). However, this mechanism is not fully defined yet, it is assumed that the concentration of such NO may be in the range of $0 \div 30 \cdot 10^{-6}$ and makes up to 30 % of total NO_x emissions.

3) *The third mechanism of NO describes the oxidation of organic nitrogen in fuel*, which content is up 1.8 % in heavy distillates. Moreover, when the content of nitrogen in fuel is low (< 0.5 %) it is fully converted to NO during combustion of poor FAMs, but with increasing nitrogen content in the fuel the share of its conversion to NO decreases, especially during burning of rich FAM. However, with rising temperature of flame, this share is slowly increasing. The increase of nitrogen content in fuel up to 1 % (m/m) leads to NO emissions rise approximately in 1.5 times, but increasing of nitrogen content in fuel more than 2 % doesn’t lead to NO_x rise.

NO_2 is formed is a result of further oxidation of NO in areas with significant excess air at temperatures lower than during NO formation. That’s why the share of NO_2 is low at maximal regime of engine operation at high temperatures in the combustion chamber, at the same time it may reach 50 % at idling regime. At low temperatures NO_2 is more stable than NO.

The main measure for reduction NO_x emissions is decreasing the flame temperature in the combustion zone by making pre-prepared FAM poorer. Emissions of NO_x increase when stoichiometric FAM has uniform composition and vice versa, when the composition is non homogeneousemissions decreases. For decreasing NO_x emisions it is necessary to decrease fame temperature by adding more air into primary zone. Thus, homogenization of combustion is reasonable, however lowering of temperature in the primary zone for decreasing NO_x emissions is limited because C_nH_m and CO emissions rise in this case.

Except lowering temperature in the reaction zone, reduction of NO_x may be also facilitated by reducing duration time of gas at high temperature. Reducing the flame temperature and duration time is achieved by increasing the air flow through the primary zone, but it keads to increase of CO and C_nH_m emissions. That's why most of the methods for reducing harmful emissions are a compromise between emissions of CO and C_nH_m on the one hand and NO_x emissions on the other.

Except that adding of hydrogen or propane in FAM shifts the border of "poor" flameout towards high values of α, thus contributing to a significant reduction in NO_x emissions without worsening the completeness of fuels' combustion.

2.4.3. Mechanisms of soot emissions formation

Smoking of aircraft exhaust gases is associated with the formation of small particles of soot that is composed of 96 % carbon and 4 % of mixtures of compounds with hydrogen and oxygen. Smoking accompanied with soot formation happens in areas rich fuel, where $\alpha < 0.8$ – for example, in the center of reversed streams area. Most of the soot, formed in the primary zone, is combusted at high temperature areas along the stream. Thus we can consider smoking of the combustion chamber like a two-stage process: the formation of soot in the primary zone and its combustion in the intermediate and dilution zones.

Depending on what stage is dominating, different concentration of soot is obtained at the combustion chamber outlet. The formation of soot depends on the way of fuel supply and the quality of its atomization, pressure and temperature in combustion chamber, distribution of α and fuel properties. As the content of hydrogen in fuel increases, the tendency to soot formation rises (Fig 2.12).

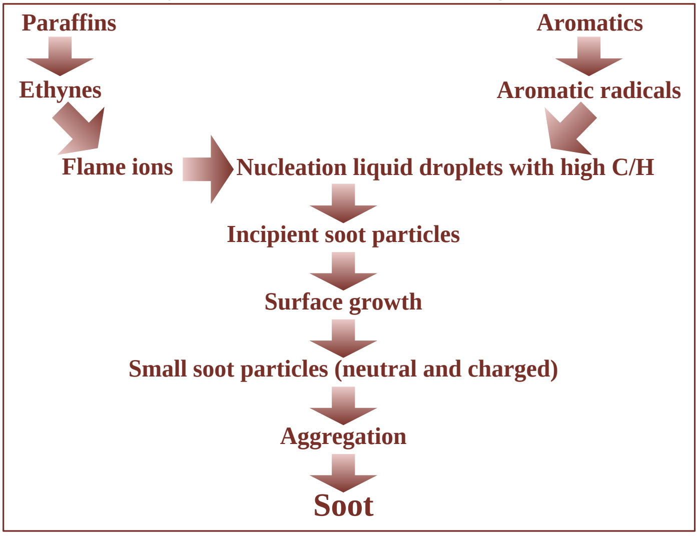


Fig. 2.12. The scheme of soot particles formation

With a decrease of pressure in the combustion chamber soot formation decreases, and at pressure lower than 0.6 MPa of homogeneous FAM no soot is formed at any values of α (even in rich mixtures). If $P > 0.6$ MPa and $\alpha < 0{,}8$ both pressure increase and α decrease lead to increased soot formation.

Increasing temperature at the combustion chamber inlet leads to increased smoking, especially in rich FAMs ($\alpha < 0{,}6$), and increasing temperature at the combustion chamber outlet, vice versa reduces smoking due to expanding areas of soot combustion before mixing zone with excess of air for combustion.

Except improving preparation of FAM and increasing α in the combustion zone, water injection into the combustion zone or using of additives in the fuel are recommended for reducing smoking and NO_x emissions. However, application of additives may lead to emission of new toxic substances or carbon formation on the turbine blades.

One of the proposed mechanisms of formation one of the strongest carcinogenic substances – benzapyrene (Fig. 2.13) is described by the equation:

$$C_6H_2 + 3C_2H_2 + 4C_2H = C_{20}H_{12},$$

where semi radical C_6H_2 is a soot nucleous.

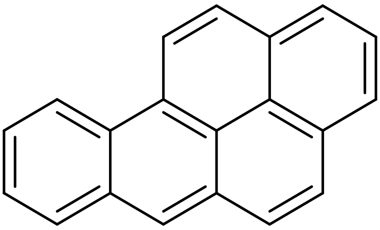


Fig. 2.13. Molecular structure of benzapyrene

Realization of measures for reducing harmful emissions into environment led to creation of new types of combustion chambers: dual-zone, double-deck, variable geometry, catalytic, etc. Its peculiarity is fulfillment of requirement on temperature change in the combustion zone in a very narrow range in all operating regimes of the engine. This requirement results from condition of allowable concentrations of CO and NO_x set by ICAO standards. Another way for decreasing levels of emissions is application of alternative JFs, especially produced from renewable feedstock.

2.5. Jet engine performance

The turbine has the task of providing the power to drive the compressor and accessories. It does this by extracting energy from the hot gases released from the combustion system and expanding them to a lower pressure and temperature. High stresses are involved in this process, and for efficient operation, the turbine blade tips may rotate at speeds over 460 m/s, The continuous flow of gas to which the turbine is exposed may have an entry temperature between 850÷1700 °C. and may reach a velocity of over 760 m/s in parts of the turbine.

The turbine depends for its operation on the transfer of energy between the combustion gases and the turbine. This transfer is never 100 % because of thermodynamic and mechanical losses. When the gas is expanded by the combustion process, it forces its way into the discharge nozzles of the turbine. At the same time the gas flow is given a “spin” or “whirl” in the direction of rotation of the turbine blades by the nozzle guide vanes. On impact with the blades and during the reaction through the blades, energy is absorbed, causing the turbine to rotate at high speed and so provide the power for driving turbine shaft and compressor.

JEs have an exhaust system which passes the turbine discharge gases to atmosphere at a velocity, and in the required direction, to provide the *thrust*. The design of the exhaust system exerts a considerable influence on the performance of the engine. The areas of the jet pipe and propelling or outlet nozzle affect the turbine entry temperature, the mass airflow and the velocity and pressure of the exhaust jet. The temperature of the gas entering the exhaust system is 550÷850 °C. According to the type of engine it can be 1500 °C or higher. It is necessary to use materials and a form of construction that will resist cracking, and prevent heat conduction to the aircraft structure. A basic exhaust system is shown in Fig. 2.14.

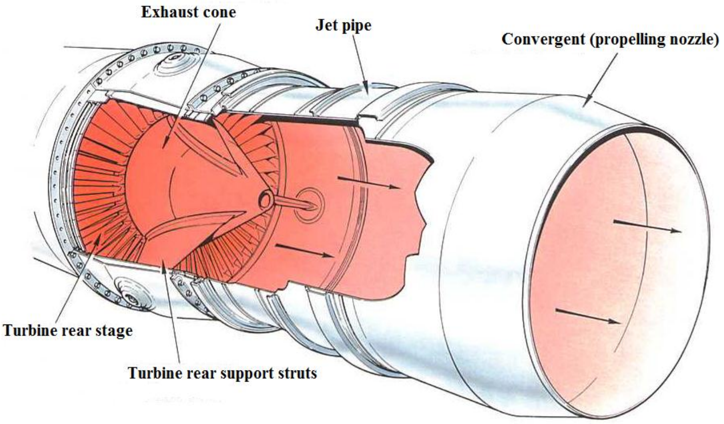


Fig. 2.14. Basic JE exhaust system

The performance requirements of JEs are obviously dictated by the type of operation for which the engine is designed. The power of the JEs is measured in thrust, produced at the propelling nozzle or nozzles. The power is assessed on the amount of thrust they develop for a given weight, FF and frontal area. Since the thrust developed is dependent on the mass of air entering the engine and the acceleration imparted to it during the engine cycle, it is influenced by such variables as the forward speed of the aircraft, altitude and climatic conditions, These variables influence the efficiency of the air intake, the compressor, the turbine and the jet pipe; consequently, the gas energy available for the production of thrust also varies.

In the interest of fuel economy and aircraft range, the ratio of FF to thrust should be as low as possible. This ratio, known as the specific fuel flow (SFF), is expressed in kilograms of fuel per hour per kilogram of thrust and is determined by the thermal and propulsive efficiency of the engine. In recent years considerable progress has been made in reducing SFC and weight.

Whereas the thermal efficiency is referred to as the internal efficiency of the JE, the propulsive efficiency is referred to as the external efficiency. The thermal and the propulsive efficiency also influence the size of the compressor and turbine, thus determining the weight and diameter of the engine for a given output.

To enable comparing the performance of similar engines it is necessary to standardize in some conventional form the variations of air temperature and pressure that occur with altitude and climatic conditions. For this purpose standard atmospheric conditions that are known as International Standard Atmosphere (ISA) are used. ISA are considered to be:

- barometric pressure B_o = 760 mm Hg,
- external temperature t_o = 15 °C.

Performance of the JE is not only concerned with the thrust produced, but also with the efficient conversion of the heat energy of the fuel into kinetic energy, as represented by the jet velocity, and the best use of this velocity to propel the aircraft forward, i.e. the efficiency of the propulsive system.

The efficiency of conversion of fuel energy to kinetic energy is termed thermal or internal efficiency and is controlled by the cycle pressure ratio and combustion temperature. Unfortunately, this temperature is limited by the thermal and mechanical stresses that can be tolerated by the turbine.

The efficiency of conversion of kinetic energy to propulsive work is termed the *propulsive or external efficiency* and this is affected by the amount of kinetic energy wasted by the propelling mechanism. Briefly, propulsive efficiency may be expressed as:

$$Propulsive\ efficiency = \frac{Work\ done\ by\ the\ aircraft}{Energy\ imparted\ to\ engine\ airflow} \qquad (2.3)$$

or

$$Propulsive\ efficiency = \frac{Work\ done}{Work\ done + work\ wasted\ in\ exhaust} \qquad (2.4)$$

Work done is the net thrust multiplied by the aircraft speed.

Primary engine design considerations, particularly for commercial transport porposes, are those of low SFF and weight. Considerable improvement has been achieved by use of the bypass principle, and by advanced mechanical and aerodynamic features, and the use of improved materials, resulting in a lighter and more compact engine. SFF is directly related to the thermal and propulsive efficiencies and thus, the overall efficiency of the JE.

2.6. Problem of engine parts contamination

It is well known that fuel quality plays one of the key roles in providing proper operation of JEs. At the same time low-quality fuel or presence of certain components or contaminants in fuel may be the reason influencing durability and reliability of the engine.

One of the most usual JF contaminants is *water*. It can be dissolved into fuel or entrained. Entrained water can be detected by a cloudy appearance to the fuel. Water can enter a fuel system via condensation. The water vapor in the space above the liquid fuel in a fuel tank condenses when the temperature changes. Large amounts of water in JE can disrupt engine operation. Settled water in tanks can cause corrosion. This can be magnified by microorganisms that live in the fuel/water interface.

Solid particles that do not dissolve are common contaminants in JFs. Dirt, rust, dust, metal particles, and other materials are of concern. Filter elements are designed to trap these contaminants and some fall into the sump to be drained off. Preventing solid contamination of JF is critical. Coarse sediments, which are visible may pass beyond system filters and later can clog in fuel metering device orifices, sliding valves, and fuel nozzles. Fine sediments cannot be seen as individual particles. They may be detected as a haze in the fuel or they may refract light during fuel testing. Their presence in JFs controls and metering devices is indicated by dark shellac-like marks on sliding surfaces.

Surfactants are liquid chemical contaminants that naturally occur in JFs. They can also be introduced during the refining or handling processes. These surface active agents usually appear as tan to dark brown liquid when they are present in large quantities. They may even have a soapy consistency. Surfactants in small quantities are unavoidable and pose little threat to fuel system functioning. Larger quantities of surfactants reduce the surface tension between water and the fuel and tend to cause water and even small particles in the fuel to remain suspended rather than settling into the sumps. Surfactants also tend to collect in filter elements making them less effective.

The presence of *microorganisms* in JFs is a critical problem. There are hundreds of varieties of these life forms that live in free water at the junction of the water and fuel in a fuel tank. They form a visible slime that is dark brown, grey, red, or black in color. This microbial growth can multiply rapidly and can cause interference with the proper functioning of filter elements and fuel quantity indicators. Moreover, the slimy water/microbe layer in contact with the fuel tank surface provides a medium for electrolytic corrosion of the tank.

Common JFs usually contain some amounts of *sulfur compounds,* that when burned at high temperatures, emits varying amounts of gaseous SO_2. Sulfidation (sulfur corrosion) is accelerated by the presence of catalysts. Moisture in the air, present in JE reacts with sulfur compounds and form corrosive sulfuric acid. This substance attacks blade's metal and destroy it. Mechanical integrity is significantly affected with sulfur corrosion will. This process may lead to details failure unless the degraded parts should be removed from the engine.

Chapter 3

STANDARDS AND TECHNICAL REQUIREMENTS FOR JET FUELS

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 JFs.

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 JFs, 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, JFs have to be safe and not to influence negatively on human organisms.

However the real JFs 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 JFs production are to reach the desired properties, which provide satisfaction of the most important requirements to JFs.

Among the general technical requirements for JFs 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.

3.1. Review of specifications for jet fuels

Properties JFs, which were used since first turbojet aircraft has appeared, were primarily dictated by fuel system constraints, operational requirements and, ultimately, by availability. The first provisional jet JF specifications were published in 1943 in England (RDE/F/KER/210) and 1944 in the U.S. (AN-F-32a). As engines and specifications developed, it became apparent that several fuel properties such as fuel freeze point, higher fuel volatility/vapour pressure, etc. were key to bounding the envelope of JF characteristics. In 1944, the first fuel, specified by the US Army Air Corps for aviation gas turbines, was identified as "Jet Propellant No. 1" or simply JP-1 (the specification was MlL-F-5616). JP-1, JP-2 and JP-3 were unsuccessful attempts to balance the conflicting requirements of mentioned above properties. Two fuels emerged in the late 1940s and early 1950s from this chaotic situation:

1. A wide-cut naphtha / kerosene mixture called JP-4 in the United States (MIL-F-5624 in 1950),
2. A kerosene fuel with a minus 50 °C freeze point (DERD-2494 in England and Jet A-1 in ASTM D-1655 in the United States).

For the next four decades JP-4 would be the standard JF for the United States Air Forces (USAF). Meanwhile, due to safety reasons the Uniited States Navy (USN) rather than adopt JP-4 would adopt JP-5 which was deemed to be more suitable for ship borne operations. A kerosene fuel designated as Jet A (European Jet A-1) by the ASTM, became the baseline fuel specification for commercial jet aircraft in the early 1960s. Jet A, a kerosene fuel similar to JP-1, except for its freeze point, became the standard JF for all US and many international airlines. It was felt that for passenger safety, a pure kerosene fuel with a flashpoint above 38·°C was preferable to the highly flammable JP-4 or the availability limited JP-5. Civil aviation currently uses Jet A-1 (or its equivalent) throughout the world, except for domestic carriers in the US, who use Jet A to reduce the cost. Military aircraft have been using JP-8 since the 1980s. JP-8 (MIL-T-83133) is essentially Jet A-1 with three military-specified additives.

The possibility of using of JFs with satisfactory performance all over the world is a basic requirement of international aviation. In September, 1957, in Stockholm, a meeting of representatives of airlines and fuel suppliers, and at the next meeting on the 10th Technical Conference IATA released the IATA Guidance Document on JFs, used in civil aviation. The basic requirement of international aviation is the possibility to use JFs with satisfactory properties all over the world. On 4th March 2000 the IATA issued the Guidance Material on specifications for JFs.

Today, the basic requirements to civil aviation JFs form: IATA, ASTM, British specification (DERD) and "Check List". The most common JF in the world is known as *Aviation Turbine Fuel – Kerosene type (AVTUR)*. There are two grades of this fuel – Jet A (AVTUR-40) and Jet A-1 (AVTUR-50). Another type of JF is wide-cut fuel that contain not only basic kerosene fraction, but also gasoline one is known as *Aviation Turbine Fuel – Wide Cut (AVTAG)*, where letter G means "gasoline". The respective fuel grade is Jet B. Fuel of narrow fractional composition is known as *Aviation Turbine Fuel – High flash Point – Kerosene Type (AVCAT)*. The respective fuel grade is AVCAT-48.

The quality of JF of grade Jet A-1 is determined by the following standards:

- British standard Def Stan 91-91 Turbine fuel, Kerosene type, Jet A-1,
- American standard ASTM D1655 Standard Specification for Aviation Turbine Fuels,
- American standard ASTM D 7566 Standard Specification for Aviation Fuel Containing Synthesized Hydrocarbons.

British standard *Defense Standard 91-91* specifies requirements for one JF grade of kerosene-type, which is appropriate for use in gas turbine engines of aircrafts. Jet fuel, determined by this document should contain hydrocarbons obtained from traditional raw materials, including crude oil, heavy oil, oil sands and oil shales. Earlier this standard permits the use of fuels derived from crude oil only. Since December 2011, it has included fuels that contain hydrocarbons synthesized from some non-oil sources. According to this, synthetic paraffinic kerosene can be used as a component of traditional JF in the amount up to 50 % (v/v). Def Stan 91-91 doesn't define the process of synthetic fuel components production, but only the technical characteristics to be met by this kind of JF. The detailed requirements to JFs of grade Jet A-1, which are set by Def Stan 91-91 are given in Table 3.1.

American Standard *ASTM D1655* was firstly issued in 1959 and contained requirements to JFs of grades Jet A, Jet A-1 and Jet B. Similarly to standard Def Stan 91-91 it determines requirements to JF of kerosene type designated for use in gas turbine engines of aircrafts. This document defines quality of JF at all life cycle stages: from production to fuelling of aircrafts. This standard provides only two grades of JFs: Jet A and Jet A-1 – distillate fuels of kerosene type, with have relatively high flash point. Jet A and Jet A-1 are two brands of kerosene fuel, which have different freezing point. These fuels must consist primarily of hydrocarbons obtained from traditional raw materials, including crude oil, heavy oil, oil sands and shale oil. Use of hydrocarbons synthesized from other new raw materials is included into the standard ASTM D7566. The detailed requirements to JFs of grade Jet A-1, which are set by ASTM D1655 are given in Table 3.1.

American Standard *ASTM D7566* was firstly enacted in 2009. It covers the production of JFs, which consist of a mixture of conventional and synthetic components. It determines certain types of JFs for civil aviation that contain synthetic hydrocarbons, and that are satisfactory for use in aircrafts. It determines quality of JFs and its synthetic components at all life cycle stages: from production to fueling of aircrafts. This standard provides two grades of JFs: 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 (FT) 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.

Table 3.1

Requirements of standards for JF of grade Jet A-1

Parameter	Units of measurement	Values for standards		
		Def Stan 91-91	ASTM D 1655	ASTM D 7566
Density at *15*, ^{o}C	kg/m^{3}	775÷840	775÷840	775÷840
Distillation temperature:				
- 10% recovered, t	^{o}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:	% v/v		-	-
- Nonhydroprocessed components				
- Hydroprocessed components		report		
- Severely hydroprocessed components		report		
- Synthetic components		report		
Kinematic viscosity at -20 ^{o}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
Thermal stability (2.5 h at control temperature of *260* °C min):	mm Hg			
Filter pressure drop		<25	<25	<25
Tube deposits less than		<3	<3	<3
Aromatics, v/v	%	<25 (v/v)	<25 (v/v)	<25 (v/v)
Existent gums	mg/100 mL	<7	<7	<7
Sulfur, total, mass	%	<0.3	<0.3	<0.3
Doctor test		negative	-	-
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	mg/l			
Without electrical conductivity additive		>85	>85	>85
With electrical conductivity additive		>70	>70	>70
Specific electrical conductivity at 20 ^{o}C,	pS/m	50÷600	-	-
Particulate contamination, at point of manufacture		<1.0	-	-
Lubricity:	mm			
Wear Scar Diameter		0.85	0.85	0.85

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 JFs for commercial aviation. The allowable blending percentage is 10 % with the balance of 90 % fossil kerosene.

The detailed requirements to JFs of grade Jet A-1, set by ASTM D7566 are given in Table 3.1. Enlargement of feedstock for JFs 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 AFs 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 JF (i.e. can be used as JF without restrictions).

Further pathways (Fig. 3.1) 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.*

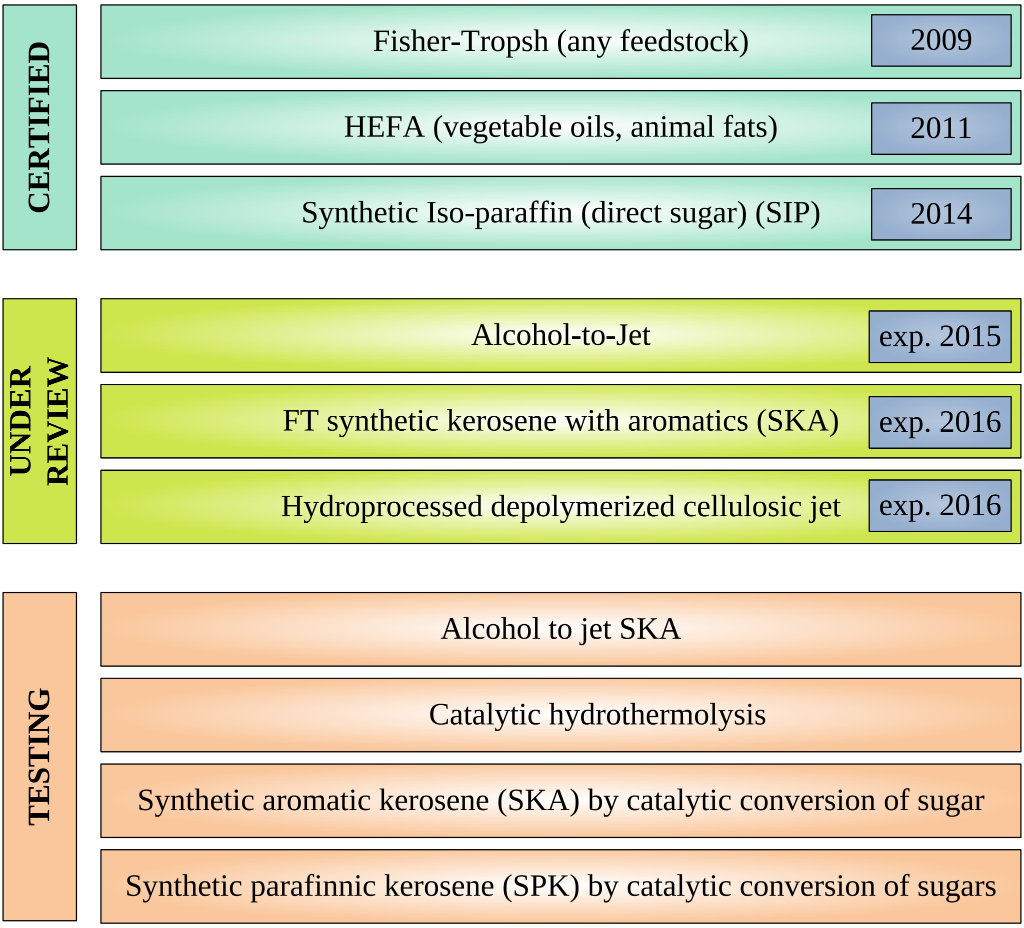


Fig. 3.1. ASTM certification and approval stages for diiferent SAF pathways

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.

3.2. Procedures of jet fuel qualification and approval

Speaking about the certification and approval of new alternative JFs one more standard and procedure have to be mentioned – ASTM D4054. Standard Practice for Qualification and Approval of New Aviation Turbine Fuels and Fuel Additives.

ASTM D4054-09 covers and provides a framework for the qualification and approval of new fuels and new fuel additives for use in commercial and military aviation gas turbine engines. The practice was developed as a guide by the aviation gas turbine engine Original Equipment Manufacturers (OEM) with ASTM International member support. Moreover, it must be noted that the OEMs are solely responsible for approval of a fuel or additive in their respective engines and airframes. Upon OEM and regulatory authority approval the fuel or fuel additive may be listed in fuel specification, manufacturers' manuals, etc. The qualification and approval process has been coordinated with airworthiness and certification groups within each company, the Federal Aviation Administration and the European Aviation Safety Agency. The main intent of this standard is to streamline the approval process and permit the new fuel (or additive) into field use in a cost effective and timely manner.

An overview of the approval process can be found in Fig.3.2; it comprises three parts as described below:

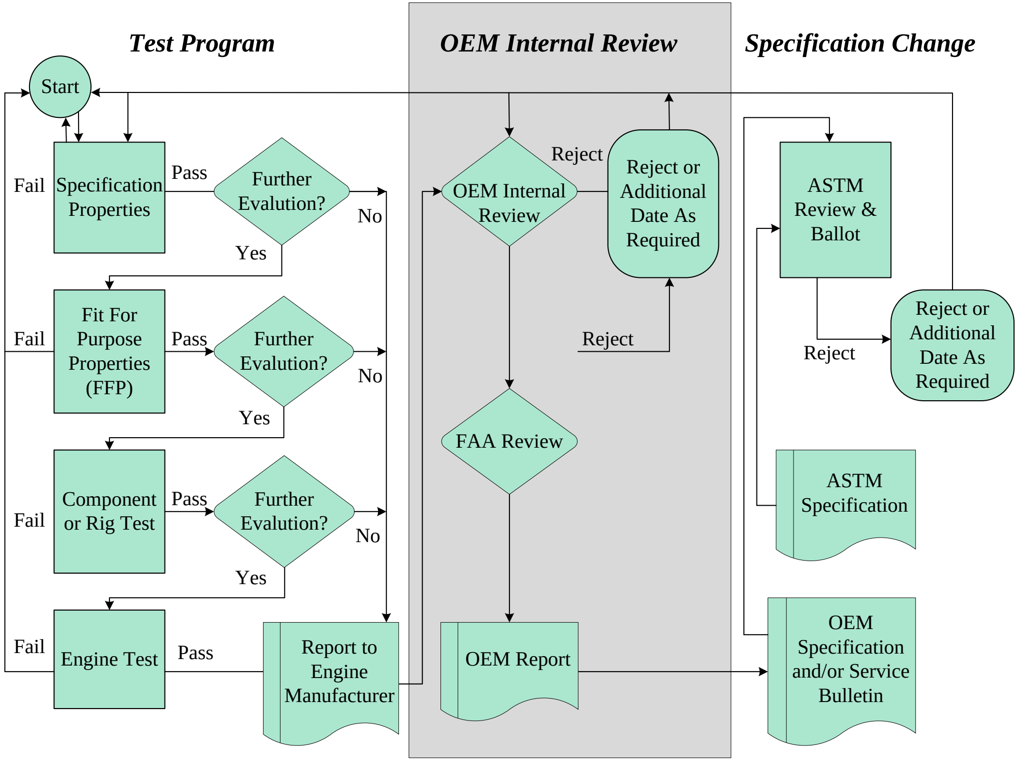


Fig. 3.2. Overview Fuel and Additive Approval Process

Test Program

The purpose of the test program is to ensure that the candidate fuel or additive will have no negative impact on engine safety, durability, or performance. This is accomplished by investigating the impact of the candidate fuel or additive on fuel specification properties, fit-for-purpose properties, fuel system materials, turbine materials, other approved additives, and engine operability Fig. 3.3 lists elements of the test program. During this process it is recommended that the OEMs should be consulted and will provide guidance on which tests are applicable. Applicability will be based on chemical composition of the new fuel or additive, similarity to approved fuels and additives, and engine manufacturer experience. The product of the test program is a research report submitted by the fuel or additive sponsor to the engine manufacturers. A complete chemical description of the candidate fuel or additive is required for defining the test program. The chemical nature of the fuel or additive defines criticality of the following issues:

- compatibility with fuel system seals and metallics,
- hot section compatibility,
- cold flow properties,
- thermal stability,
- rig tests for performance and operability,
- emissions,
- fuel handling.

The Test Program is comprised of four tiers as shown in Fig.3.3 Tier 1 consists of the Fuel Specification Properties. Tier 2 includes the Fit-For Purpose (FFP) Properties. Tier 3 is comprised of Component Tests. Tier 4 consists of Engine Tests.

Samples of both the neat synthetic blending component and the blended jet fuel will be required for evaluation. Most of the testing except for compositional and trace materials analyses are performed with the blended jet fuel. Fuel volumes that may be required are up to 38 l for the Specification Tests; 38 to 380 l for the FFP tests; 950 to 38,000 l for the Component and Rig Tests; and up to 852,000 l for the engine test. The aforementioned are rough estimates because the extent of required FFP tests is dependent upon the fuel chemistry and results of the Specification tests. Actual quantities could be higher or lower. Component and engine tests may or may not be required depending on results from the Specification Tests, the FFP tests, and at the evaluation of the OEM team. The quantity of fuel needed for Component and Rig Tests and Engine Tests, depends on the tests required and also the size of the rig or engine used for the test. Similarity of the new fuel chemistry or manufacturing process to one previously approved will also be considered when determining the extent of required D4054 testing.

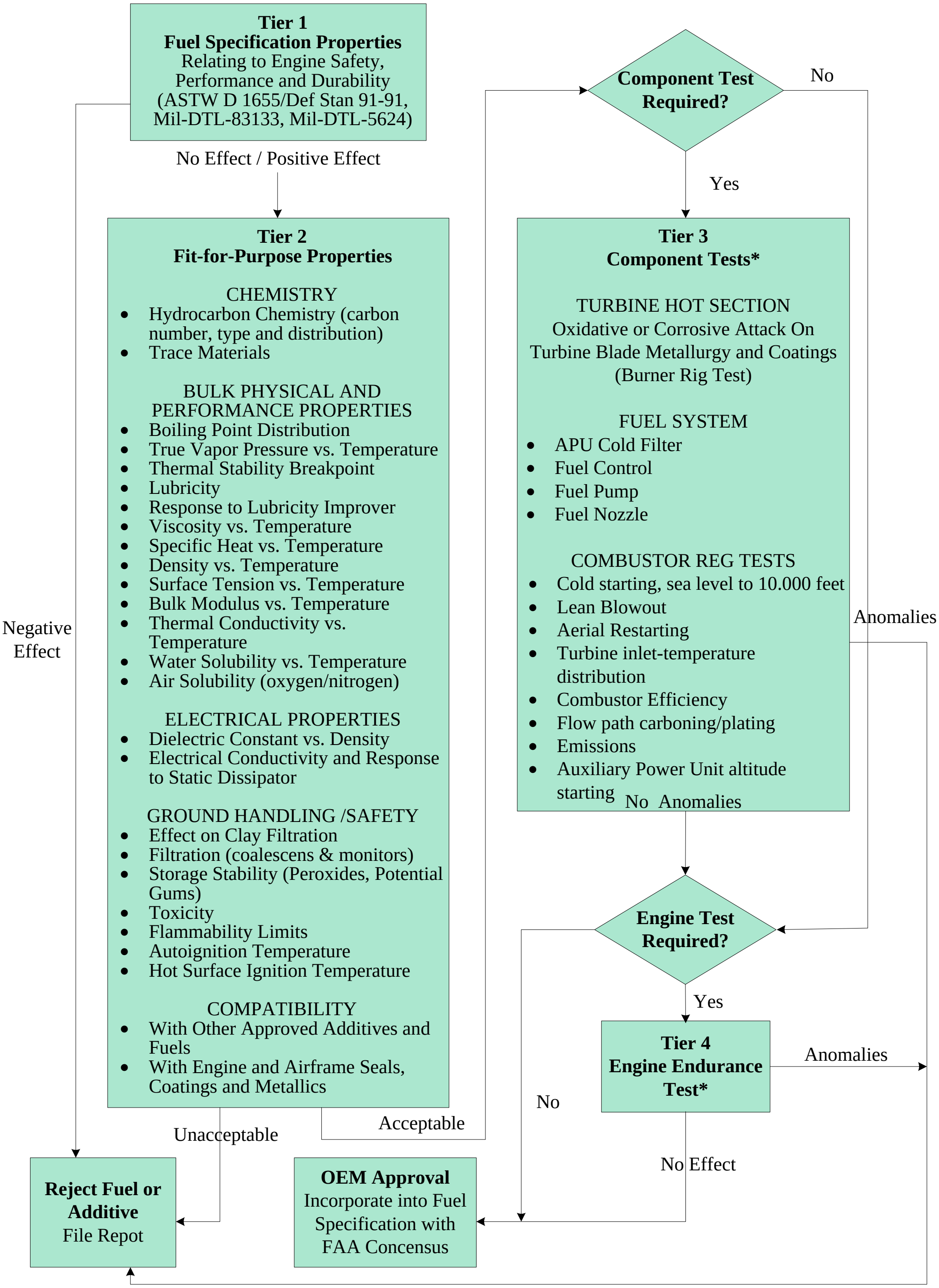


Fig. 3.3. Test Program elements of the Fuel and Additive Approval Process

The *first tier* requires measurement of the current JF specification properties of the blended JF. The new fuel progresses no further in the approval process if there is a negative impact on specification properties unless there is a compelling reason to do so. The fuel producer should be prepared to present the specification test results along with the proposed specification criteria and results for the neat synthetic blending component to the OEM team when initiating the dialog. In addition, a high level description of the new fuel process should also be included. It is important to note that the cumulative specification properties required for ASTM D1655, Def Stan 91-91, MIL-DTL-5624 and MIL-DTL-83133 must be presented for evaluation.

The *second tier* FFP properties address fuel properties that are not listed in the specification but are important to the OEM in the design and performance of gas turbine engines. These properties are not part of the jet fuel specification because they are relatively constant for all petroleum-derived kerosene fuels. However, this may not be the case for fuels derived from alternative sources. The OEM team will advise which FFP tests are required based on the specification test results, chemistry of the new fuel, and similarity to processes and fuels currently in ASTM D7566. Test methods, limits, and engine OEM scope of experience for each of the FFP tests are called out in table 2 of ASTM D4054.

The engine OEMs will determine what, if any, component tests must be performed under *the third tier* based on the specification and FFP test results and the chemistry of the new fuel. Typical component tests asked for by the engine OEMs include an atomizer cold spray test, an ignition test comprised of cold starts and altitude relight, a combustion rig test to measure lean blow-out, and emissions; a thermal stability fuel system simulator test, and an Auxiliary Power Unit (APU) cold start test.

The *fourth tier* engine test is the final gate in the test program. The OEMs will determine the need for an engine test based on the chemical make-up of the new fuel, specification, FFP, and component test results. The engine test may address the performance, operability, or durability of the engine when operating on the candidate fuel.

OEM Internal Review

Once the testing is completed, the data are compiled in an ASTM research report and submitted to the OEMs for an internal review. The research report should include a detailed description of how the process is going to be controlled such that the fuel that was tested and approved represents the fuel that will be produced at commercial volumes. Additionally, the research report should determine if the new fuel fits in an existing ASTM D7566 annex or if a new annex needs to be created. The OEMs, FAA, and ASTM International will make the final determination. The ASTM research report is prepared by the fuel producer, often with the assistance of an ASTM task force, and presented to the OEMs for review and comment.

During the OEM internal review, chief engineers and discipline chiefs within each OEM organization will review the ASTM research report to see that all concerns have been addressed and that there are no data gaps. The OEMs will discuss details of the research report with the fuel producer and task force and provide recommendations for the way forward. The way forward may include additional testing. The ASTM research report must contain all the data required to support a consensus by the OEMs, FAA, and other ASTM members that the new fuel will have no negative impact on engine and airplane safety, performance, and durability.

Specification Change Determination

Approval by the OEMs of a new fuel or additive may only affect OEM internal service bulletins and engine manuals and have no impact on the aviation fuel standard. If the OEM proposes changes to a given aviation fuel standard the proposed changes must then be reviewed and balloted by ASTM D02.J0. Requested changes could include listing the additive or fuel as acceptable for use, changes to published limits, special restrictions, or additional precautions. The OEMs and the regulatory agencies regard the ASTM review and balloting process, and the subsequent scrutiny of industry experts, as an additional safeguard to ensure that issues relating to safety, durability, performance, and operation have been adequately addressed. Although not a requirement, the OEMs typically wait for a successful ASTM ballot before changing their service bulletins and engine manuals to accommodate the new fuel or additive.

A research report shall be issued upon completion of the test program that formally documents all data and information compiled during the evaluation process. The report shall provide a conclusion regarding FFP. The report shall include a specification of the approved material with sufficient detail and limits to permit a purchaser to confirm receipt of OEM approved material.

3.3. Environmental requirements for jet fuels and worldwide policies on alternative jet fuels implementation

Modern environmental requirements also set additional requirements to quality of JF.

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 JF 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 JF, 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.

The increasing cost of conventional JF and the likely cost of meeting emission reduction targets, as well as an increasingly societal expectation, are driving the sector investigation on different pathways of fuel production. The public and political pressure on the sector to decrease GHG emission was continuously rising during last years, particularly in Europe after the extension of the European Union Emission Trading Scheme (ETS) to the air transport sector since January 2013 that will add another component to the overall cost of JF. Also for this reason the aviation industry has committed itself to reduce net CO_2 emissions of 50 % by 2050 compared with 2005 levels, and to achieve carbon–neutral growth by 2020, a really ambitious goal.

The European Parliament resolution on reduction of impact of aviation on climate change (INI/2005/2249) clearly states that: “The European Parliament promotes introduction of aviation biofuels, thereby reducing the effects on climate change”. IATA has set up the task to reduce the level of CO_2 emissions from air transport by 50 % by 2050. In addition, European Commision in 2011 has set a policy target of achieving a 60 % reduction of CO_2 by 2050. Low-carbon fuels in aviation should reach 40 % by 2050 (Proposals for Council Decision of the European Commission COM (2011) 811 final).

The ICAO, a United Nations agency that works with 191 member states and industry groups to develop policies, standards, and recommended practices for the civil aviation sector, has begun to implement policies to address the climate change impacts of international aviation. Under the *United Nations Framework Convention on Climate Change (UNFCCC),* GHG emissions from international aviation are not included in national GHG inventories or targets; therefore, these emissions are not regulated at a national level. Instead, the Kyoto Protocol to the UNFCCC specifies that industrialized countries shall pursue limitation or reduction of GHG emissions from aviation through the ICAO.

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.

ICAO’s *Committee on Aviation Environmental Protection (CAEP)* assessed trends in JF consumption and CO_2 emissions toward 2050, illustrated in Fig. 3.4. The calculations estimate the CO_2 emissions associated with JF combustion only, using an average CO_2 Emission Index (EI) equal to 3.16 kg CO_2 emitted per kg of fuel. The curve with the highest emissions represents the baseline fleet replacement scenario, based on a compound average annual growth rate of 5.3 % (2010 to 2030), and assuming that no technological or operational improvement takes place. The colored slivers cover different scenarios combining ICAO’s low to optimistic estimates for the evolution of technological and operational improvements. The projections illustrate different strategies to mitigate emissions and achieve carbon-neutral growth from 2020.

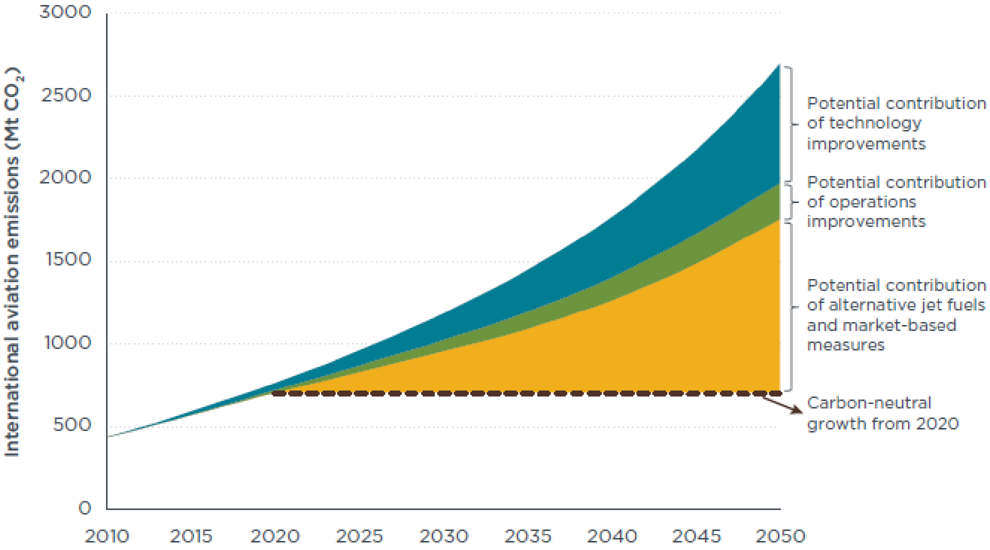


Fig. 3.4. International civil aviation emissions and mitigation strategies

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 JFs. AJFs do not necessarily generate lower carbon emissions than conventional petroleum-based fuels.

However, the contribution of alternative JFs to GHG mitigation rests on a variety of assumptions and is limited by two main considerations: the carbon intensity of alternative JFs 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.

Used cooking oils and animal fats are double counted but outside the percentage of 2.5 % of advanced biofuels. This proposal is under discussion vis a vis the European Council, which is elaborating its own position on the subject.

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. 3.5). 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.

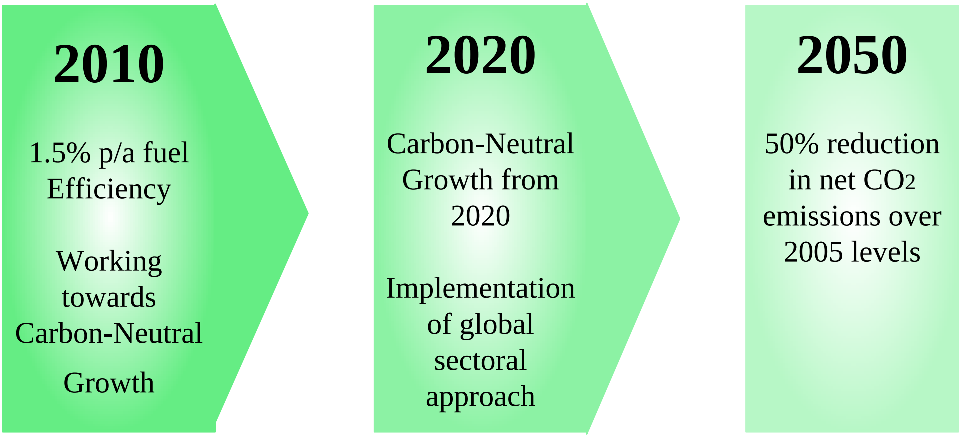


Fig. 3.5. Climate change targets for aviation industry

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.

Chapter 4

DEVELOPMENT OF JET FUELS' BIO-ADDITIVES

4.1. Technologies of jet fuels' bio-additives production

Analysis of the literature leads to the conclusion that today the most profitable for Poland is production of alternative JFs from renewable fat-containing feedstock of plant origin. The works substantiates the potential of production of alternative environmentally friendly aviation fuels from plant (technical oils). On the territory of Poland except rapeseed other oilseeds such as sunflower and soybean are also cultivated; in recent years, production of camelina is gaining popularity. From the works by V. Semenov, V. Kirichenko, E. Dankevich, G. Kovtun it is known, that in Poland there is sufficient experience of biofuels production, including biodiesel, both from rapeseed and sunflower oils. However, taking account number of factors (growing volumes, industries of oils use, their physical and chemical properties, and ensuring the sustainability of biofuels), RO is considered to be the most viable feedstock for alternative JFs production.

4.1.1. Technology of JFs' bio-additives production by oils hydrotreating

One of the most advanced technologies for the production of JFs bio-additives from fat-containing plant feedstock is hydrotreating of different oils and fats. This technology consists of several stages (Fig. 4.1). At the initial stage fat-containing feedstock is cleaned from different impurities by traditional methods of crude-oil treatment. Further, oils, which are triglycerides, and contain small amounts of free fatty acids pass processes of hydrogenization. They are transformed into shorter paraffinic hydrocarbons of diesel fraction. Due to the interaction with hydrogen deoxygenation of oils takes place, and olefins are converted into paraffins. Removal of oxygen atoms increases the heat of combustion, and the removal of olefins increases its thermal and oxidation stability.

At the last stage, obtained hydrocarbons are subjected to processes of hydrotreatment, hydrocracking, hydroisomerization and also polymerization. As a result, diesel hydrocarbon chains are broken into shorter and branched molecules, which are typical for kerosene fractions. The end product is synthetic paraffinic kerosene (Bio-SPK); it contains molecules similar to those, which are available in the conventional oil-derived JFs.

Bio-additives of JFs obtained by this technology is the recognized by manufacturers and aircraft operators. According to the standard ASTM D 7655 bio-additives can be added to conventional JF in an amount up to 50 %. Among the advantages of this component the developers of technology – J. Kinder, T. Rames and others indicate that the quality doesn't depend on the type and properties of initial feedstock. However, the described fuel component has certain disadvantages. According to the chemical structure it is a mixture of synthetic paraffinic hydrocarbons that are contained in conventional JFs, and therefore, when getting into the environment, have life cycle similar to traditional petroleum products, and causes a negative impact on the environment objects.

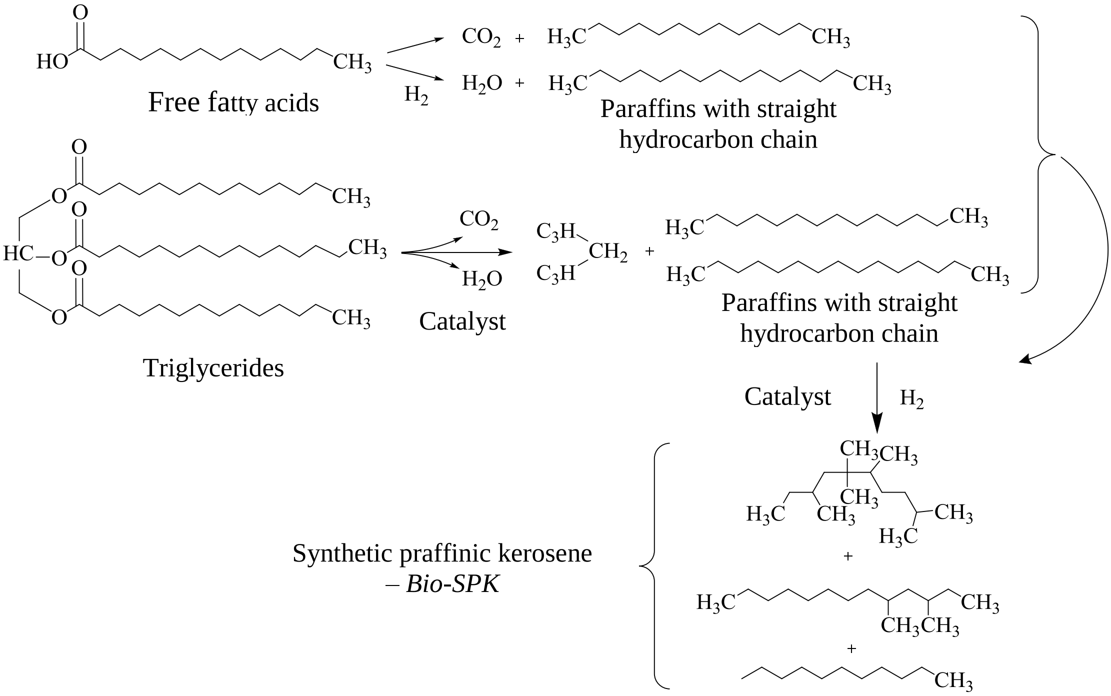


Fig. 4.1. The scheme of JFs' bio-additives production by plant oils and fats hydrotreatment

Technology of JFs' bio-additives production from fats and oils by hydrotreatment is usually realized on equipment, typical for crude-oil refineries. Implementation of the technology on industrial scale requires availability of large amounts of raw materials at enterprises to ensure its continuous operation. Other words, the implementation of considered technology requires construction of the plant for the production of this type of bio-additives, which will be similar to oil refineries scales.

Considering the economical issues, JFs' bio-additives production from fats and oils by hydrotreatment today is not economically feasible and difficult for implementation.

4.1.2. Technology of JFs' bio-additives production from plant oil fatty acids esters

The technology of JFs' bio-additives production from oil considers the reaction of its transesterification by simple alcohol (alcoholysis reaction). According to the studies of S. Nagornov, K. Patryliak, M. Stepanov, M. Ohrimenko today alcoholysis is the most effective comparing to other types of transesterification reactions.

The main components of oils are complete complex esters of glycerin and higher aliphatic (fatty) acids – triglycerides. The property of complex ester group of triglycerides is its ability to come into exchange reaction of acid or alcohol groups –

reaction of transesterification. In results of reaction between complex ester and simple alcohol, new complex esters of fatty acids and free glycerin are formed (Fig. 4.2).

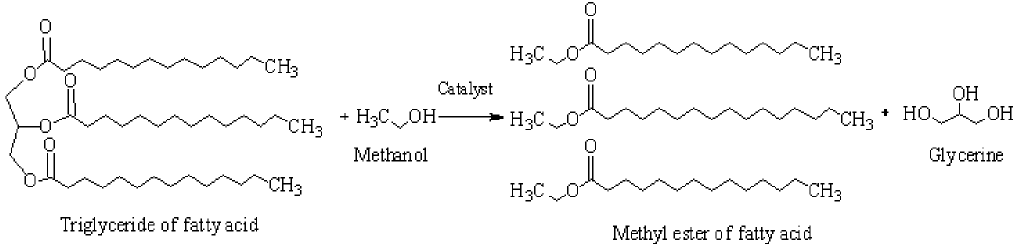
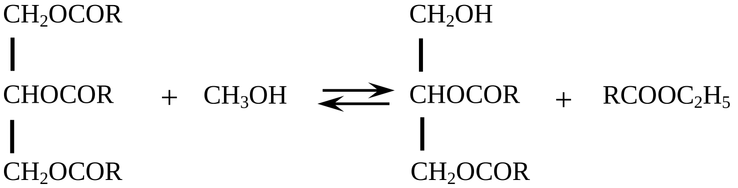


Fig. 4.2. The scheme of triglycerides transesterification by simple alcohol (ethanol)

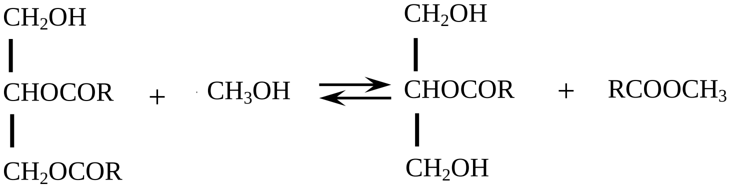
Newly-formed complex esters contain alcohol radical and acid radical of initial faty acid. Thus, during the reaction the transition of acyl radicals of ester to alcohol molecule takes place. This reaction may be promoted by both acids and bases. Transesterification consists of a series of step-by-step reactions with monoglycerides and diglycerides as intermediate products. The first stage is the formation of diglycerides and esters, second – monoglycerides and esters, the third – formation of esters and glycerol. All these stages are reversible, so the excess of alcohol should be used for provision the flow of reaction toward the formation of esters. Usually methyl or ethyl alcohols are used for conducting the reaction of alcoholysis; butyl alcohol may be used, but more rarely. Below the scheme of triglycerides alcoholysis, which is realized in three steps is presented. Methanol is used as an agent of transesterification.

Triglyceride + methanol → diglyceride + methyl esters of fatty acid:



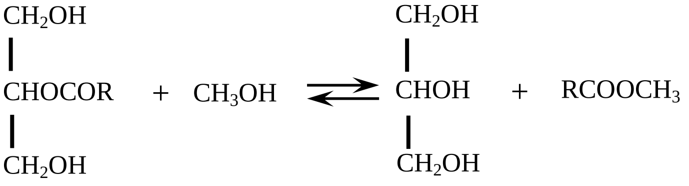
$$\begin{array}{l} CH_2OCOR \\ | \\ CHOCOR \\ | \\ CH_2OCOR \end{array} + CH_3OH \rightleftharpoons \begin{array}{l} CH_2OH \\ | \\ CHOCOR \\ | \\ CH_2OCOR \end{array} + RCOOC_2H_5$$

Diglyceride + methanol → monoglyceride + methyl esters of fatty acid:



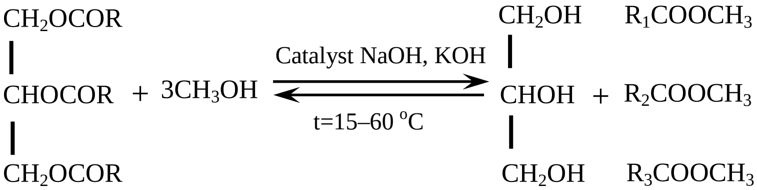
$$\begin{array}{l} CH_2OH \\ | \\ CHOCOR \\ | \\ CH_2OCOR \end{array} + CH_3OH \rightleftharpoons \begin{array}{l} CH_2OH \\ | \\ CHOCOR \\ | \\ CH_2OH \end{array} + RCOOCH_3$$

Monoglyceride + methanol → glycerin + methyl esters of fatty acid:



$$\begin{array}{l} CH_2OH \\ | \\ CHOCOR \\ | \\ CH_2OH \end{array} + CH_3OH \rightleftharpoons \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + RCOOCH_3$$

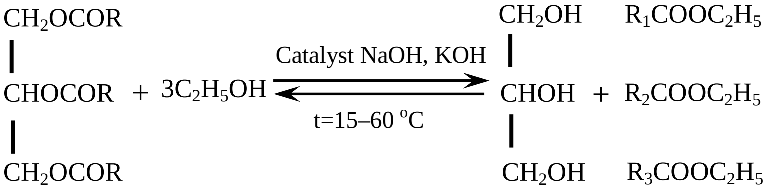
The overall equation of alcoholysis reaction:



$$\begin{array}{l} CH_2OCOR \\ | \\ CHOCOR \\ | \\ CH_2OCOR \end{array} + 3CH_3OH \underset{t=15\text{–}60\ ^{o}C}{\overset{\text{Catalyst NaOH, KOH}}{\rightleftarrows}} \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + \begin{array}{l} R_1COOCH_3 \\ \\ R_2COOCH_3 \\ \\ R_3COOCH_3 \end{array}$$

where R_1, R_2, R_3 – radicals of faty acids, which differ by number of carbon atom in chain and number of double bonds.

The overall equation of alcoholysis reaction using ethanol is analagous:



$$\begin{array}{l} CH_2OCOR \\ | \\ CHOCOR \\ | \\ CH_2OCOR \end{array} + 3C_2H_5OH \underset{t=15\text{–}60\ ^{o}C}{\overset{\text{Catalyst NaOH, KOH}}{\rightleftarrows}} \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + \begin{array}{l} R_1COOC_2H_5 \\ \\ R_2COOC_2H_5 \\ \\ R_3COOC_2H_5 \end{array}$$

Technology of fatty acid esters production from plant oils has gained considerable popularity during the last 10÷15 years mainly for biodiesel production. At present it is well established and successfully implemented both in the laboratory and in industrial facilities of various scale. There are many ways and methods of optimization parameters of fatty acids esters production, which are considered in numerous research papers. In general, all these methods are intended to obtain high-quality biofuels that meet modern requirements. So, today the quality of fatty acids esters as alternative to conventional diesel fuel is regulated by the standards EN 14214, ASTM D6751.

For obtaining JFs bio-additives we have proposed the method, developed by the Institute of bioorganic chemistry and petrochemistry of the National Academy of Sciences of Ukraine. The peculiarity of this method is special initial preparation of alcohol and strictly defined parameters that provide self-division of reacting mixture into ester and glycerine parts. The principal scheme and main stages of the esterification process are shown at Fig. 4.3.

At first stage the initial feedstock is prepared. For fatty acids esters production, plant oil has to be of high quality: it should be filtered, doesn't contain mechanical admixtures or pollutants, and posesses certain physical-chemical charcteristics, determined by specifications. Except that, alcohol is prepared as an agent of transesterfication. It means that its characteristics should satisfy requirements of technology.

At the second stage the solution of catalyst – alcoholate of basic metal (usually sodium or potassium) is prepared: usually the calculated and measured amount of alkali is dissolved in necessary amount of alcohol.

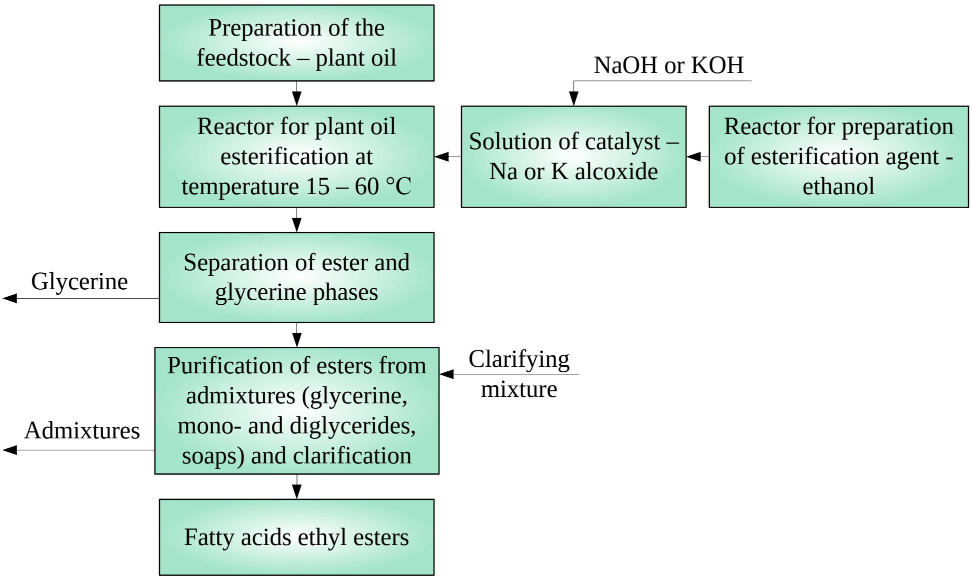


Fig. 4.3. Principal scheme and main stages of the esterification process

The next stage is oil alcoholysis itself. Oil is put into the reactor, where alcohol with dissolved catalyst is beilg added at constant mixing. Alcoholysis reaction runs at temperature 15÷60 ^{o}C. In a result of reaction esters and glycerin are formed.

After mixing finishing the reactive mixture goes for settling. During some time that depends on quality and properties of initial alcohol and oil, self-division of mixture on two phases happens – esters and glycerin phases.

The final stage if esters purification: extraction of excessive unconverted alcohol from esters' layer (if required) and utilization with secondary processing of glycerin phase.

Considering the advantages of this technology it is necessary to mention that it is quit simple for realization and allows manufacturing products of comparatively low prise. The equipment for enterprise on bio-additives production may be chosen depending on required quantity of end product. Existing equipment allows manufacturing 1÷10 ton of esters per day. Moreover, realization of technology requires only three main components, which cost is significantly lower comparing to conventiona crude oil feedstock. Glycerin as a by-product of this technology is widely used in medical, cosmetic, food, paint-coating and other branches of industry. So, the production process is almost wasteless. One more advantage is use of renewable feedstock – plant oil and alcohol (in case when ethanol is used); this provides sustainability of bio-additives production process.

4.2. Description of equipment and experiment realization

For developing the method of improving properties of esters we have used FAME and FAEE of rapeseed oil that were synthesized at the Institute of Bioorganic Chemistry and Petrochemistry NAS of Ukraine. Esters were obtained according to the technologies developed in this institute and their quality parameters were adjusted to requirements of standards on fuels for diesel engines.

For improving quality of bio-additives and making it typical for conventional JFs the method of vacuum distillation was applied. The complex of operations, which compose the developed method, is presented on Fig. 4.4.

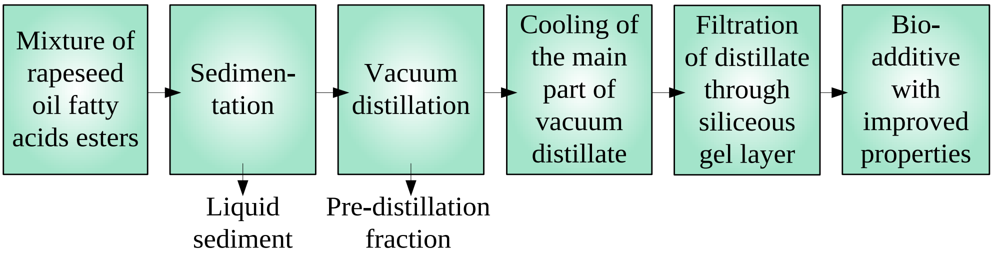


Fig. 4.4. Scheme of vacuum distillation

Vacuum distillation of esters was performed on a laboratory installation for vacuum distillation (Fig. 4.5) using an oil vacuum pump. This type of pump can provide stable operation of the vacuum system and stable residual pressure of 0.4÷0.6 kPa and quite easy in operation. The vacuum distillation installation was assembled according to the main safety rules.

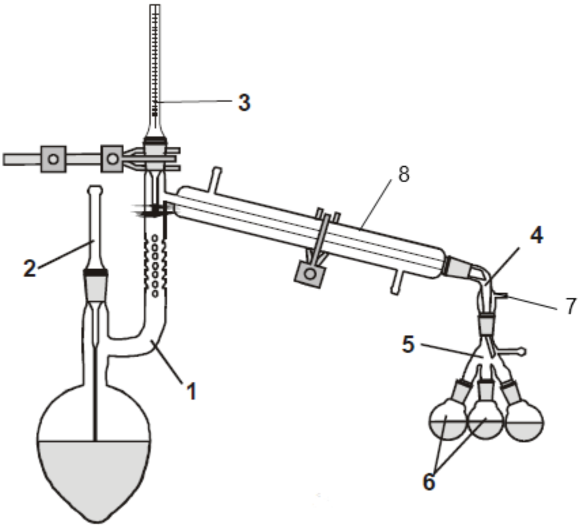


Fig. 4.5. Laboratory installation of vacuum distillation:
1 – Claisen flask with cap, *2* – capillary, *3* – thermometer, *4* – prolong, *5* – “spider”,
6 – receiving flask, *7* – bent pipe to vacuum system, *8* – condenser

For providing uniform boiling process during distillation under vacuum the glass capillary *2* was used for air penetration into the liquid. For separating fractions of pre-distillation and main distillate the so-called "spider" *5* was used. Using of spider allows separating several fractions of desired products. The rate of distillation under vacuum was adjusted by the intensity of the distillation flask *1* heating. The less rate the better quality of distillation. It is considered to be optimal when 1÷2 drops of distillate get into receiving flask *6* per second.

Experimental values of boiling points of RO esters were determined in the following way: residual pressure in the system was determined by the vacuum meter height, esters boiling points at low pressure – by the thermometer heights *3*. Later nomographic chart pressure – temperature (Fig. 4.6) was used: we connected points, related to obtained data by straight line and then get boiling point values at atmospheric pressure.

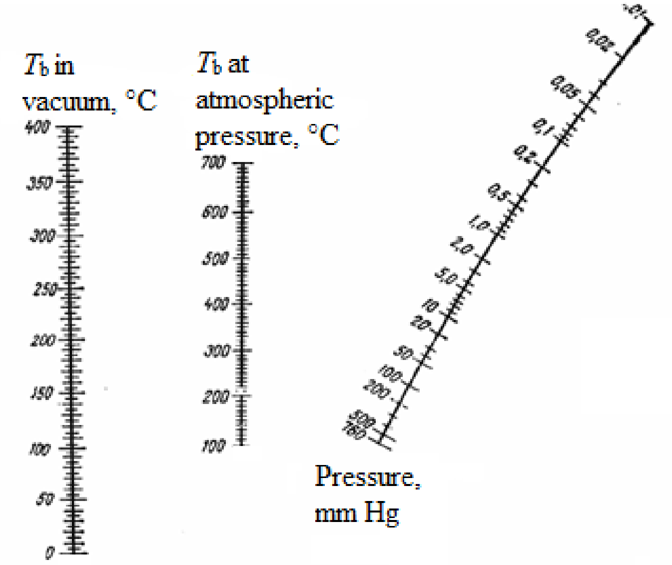


Fig. 4.6. Nomographic chart pressure – temperature

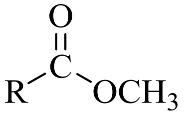
Mixture of fatty acids esters before vacuum distillation was settling during 1÷2 days for isolating mechanical admixture, mono- and diglycerides, soaps, etc. later the sediment was decanted. Before starting distillation the mass of the initial product was determined. After finishing the process mass of pre-distillation fraction, mass of the main distillate and mass of un-distilled residue were measured and losses from distillation were calculated. Later these data may be used for calculating material balance of the technological process.

Next vacuum distillate that was obtained after distillation was cooled to room temperature, filtering through the layer of silicious gel if necessary and immersed into glass vessel for storage.

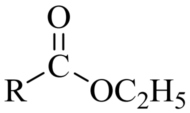
The chemical composition of bio-additives was determined on chromatograph Hewlett-Packard HP 5890 with mass selective detector HP 5971-NR1034B and computer database of mass spectra data. To separate the esters on the components was used silica capillary column 25 m long with a diameter of 0.2 mm with methylphenyl silicone as the stationary phase. Samples for analysis were injected at temperature of 170 °C, followed by heating to 280 °C at a speed 7 °C/min. During the chromatographic separation of samples mass spectra of substances were recorded. Obtained mass spectra were identified using computer database.

4.3. Molecular structure, composition and properties of products of plant oil processing

Bio-additives are the products of interaction of complete complex esters of glycerin and higher aliphatic (fatty) acids (triglycerides) and simple alcohol – methanol or ethanol. Molecular structure of bio-additives is complex esters, which contain residue of fatty acid and simple alcohol. Radicals of fatty acids are different according to the quantity of carbon atoms and of double bonds quantity. Common formulae of FAME and FAEE may be presented as following:



$$R-\overset{\overset{O}{\|}}{C}-OCH_3$$



$$R-\overset{\overset{O}{\|}}{C}-OC_2H_5$$

where R – radical of fatty acid.

Qualitative and quantitative composition of fatty acids residues usually depends on primary feedstock – plant oil. Fatty acid composition of oil quite different and may vary within one oil species up to several percents. This is stipulated by conditions of oil plant growing (climate, soil, presence of fertilizers, humidity, etc), specie and breed variety.

Literature sources contain only oriented or average data about fatty acid composition of oils and respectively esters, produced from these oils. In case, when exact data about composition of esters are needed, the chromatograph analysis should be done.

Using the method of chromatograph analysis it was found that bio-additives are mixtures of unsaturated and small amount of saturated fatty acids. The complete composition of studied esters is given in Tables 4.1, 4.2.

Analyzing the tables, we can make a conclusion that the products of RO transesterification contain esters of acids $C_{14}\div C_{23}$. Bio-additives are composed on about 80 % of three esters of unsaturated fatty acids:

- Octadecenic (oleic) acid – 52.6 %,
- Octadecadienic (linoleic) acid – 21.1 %,
- Octadecatrienic (linolenic) acid – 7.2 %.

Some portion – about 8 % is related to esters of saturated acids. The rest of compounds are unsaturated fatty acids esters, which content is not more than 1 %.

Qualitative and quantitative content of esters, other words, composition of bio-additive, directly determines its physical-chemical properties. Esters' properties depend on molecular structure of fatty acids radicals. According to unsaturated fatty acids are found in plant oils more often than saturated (about 4/5 of total content).

Table 4.1

Chemical and element composition of FAME

Name of compound	Chemical formula	Molecular mass	Content of esters, % (mas.)	Content of C, %	Content of H, %	Content of O, %
ME* tetradecanoic (miristic) acid	$C_{15}H_{30}O_2$	242	0.024	0.0432	0.00726	0.00768
ME hexadecenoic acid	$C_{17}H_{32}O_2$	268	0.200	0.408	0.0645	0.0639
ME hexadecanoic acid	$C_{17}H_{34}O_2$	270	6.00	12.659	2.125	1.983
ME heptadecenoic acid	$C_{18}H_{34}O_2$	282	0.047	0.096	0.017	0.0150
ME octadecenoic (oleic) acid	$C_{19}H_{36}O_2$	296	52.60	120.038	19.086	16.826
ME of octadecadienoic (linoleic) acid	$C_{19}H_{34}O_2$	294	21.110	48.175	7.234	6.573
ME of octadecatrienoic (linolenic) acid	$C_{19}H_{32}O_2$	292	7.200	16.431	2.322	2.3
ME of ectadecanoic (stearic) acid	$C_{19}H_{38}O_2$	298	1.900	4.336	0.689	0.607
ME of nonadecenoic acid	$C_{20}H_{38}O_2$	310	1.118	2.686	0.428	0.358
ME of nonadecanoic acid	$C_{20}H_{40}O_2$	312	0.245	0.589	0.099	0.078
ME of eicosenoic acid	$C_{21}H_{40}O_2$	324	1.251	3.155	0.504	0.400
ME of eicosanoic acid	$C_{21}H_{42}O_2$	326	0.454	1.145	0.192	0.145
ME of heneicosenoic acid	$C_{22}H_{42}O_2$	338	4.200	11.098	1.779	1.343
ME of heneicosanoic acid	$C_{22}H_{44}O_2$	340	0.124	0.328	0.055	0.036
ME of 13-docosenoic (erucic) acid	$C_{23}H_{44}O_2$	352	2.500	6.906	1.108	0.799
ME of docosanoic acid	$C_{23}H_{46}O_2$	354	0.216	0.598	0.096	0.069
ME of tetracosenoic acid	$C_{25}H_{48}O_2$	380	0.087	0.261	0.042	0.028
ME of tetracosanoic acid	$C_{25}H_{50}O_2$	382	0.087	0.261	0.043	0.028
Other ME			0.437	0.747	0.204	0.139
Total			100	230.305	36.095	34.679
Element content in FAME				76.493	11.988	11.519

* – ME – methyl esters;

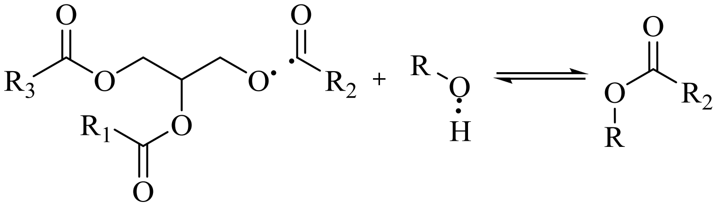
Table 4.2

Chemical and element composition of FAEE

Name of compound	Chemical formula	Molecular mass	Content of esters, % (mas.)	Content of C, %	Content of H, %	Content of O, %
EE* of tetradecanoic (miristic) acid	$C_{16}H_{32}O_2$	256	0.024	0.046	0.0077	0.00767
EE of hexadecenoic acid	$C_{18}H_{34}O_2$	282	0.200	0.432	0.0685	0.0639
EE of hexadecanoic acid	$C_{18}H_{36}O_2$	284	6.200	13.404	2.249	1.984
EE of heptadecenoic aci	$C_{18}H_{38}O_2$	296	0.047	0.102	0.018	0.0150
EE of octadecenoic (oleic) acid	$C_{20}H_{38}O_2$	310	52.60	126.345	20.146	16.826
EE of octadecadienoic (linoleic) acid	$C_{20}H_{36}O_2$	308	21.110	50.710	7.659	6.573
EE of octadecatrienic (linolenic) acid	$C_{20}H_{34}O2$	306	7.200	17.281	2.467	2.3
EE of ectadecanoic (stearic) acid	$C_{20}H_{38}O_2$	312	1.900	4.564	0.728	0.607
EE of nonadecenoic acid	$C_{22}H_{40}O_2$	324	1.118	2.6954	0.450	0.358
EE of nonadecanoic acid	$C_{22}H_{42}O_2$	326	0.245	0.647	0.104	0.078
EE of eicosenoic acid	$C_{22}H_{42}O_2$	338	1.251	3.306	0.529	0.400
EE of heneicosenoic acid	$C_{23}H_{44}O_2$	352	4.200	11.60	1.862	1.343
EE of heneicosanoic acid	$C_{23}H_{46}O_2$	354	0.124	0.343	0.055	0.036
EE 13-docosenic (erucic) acid	$C_{24}H_{46}O_2$	366	2.500	7.207	1.159	0.799
EE of docosanoic acid	$C_{24}H_{48}O_2$	368	0.216	0.622	0.100	0.069
EE of tetracosenoic acid	$C_{26}H_{50}O_2$	394	0.087	0.271	0.044	0.028
EE of tetracosanoic acid	$C_{26}H_{52}O_2$	396	0.087	0.271	0.045	0.028
Other EE			0.437	1.135	0.212	0.139
Total			100	242.18	38.095	34.679
Element content in FAEE				76.894	12.095	11.011

* – EE – ethyl esters.

Fatty acids esters are non-branched hydrocarbon chains with 14÷24 carbon atoms in acid radicals and molecular mass, varying in a range 240÷380. In a result of transesterification reaction of triglyceride with simple alcohol ester molecule contains fatty acid residue with carbonyl group –C=O (acyl or acid residue) and alcohol radical bonded with carbonyl group by oxygen atom. Other words, esters are derivatives of fatty acids, where hydroxyl –OH from carboxyl group is substituted by alcohol radical with hydroxyl oxygen atom:



where R_1, R_2, R_3 – radical of fatty acids;

R – radical of simple alcohol.

From the studies it is known that the angle of valent bond in acyl residue between carbon atoms is equal to 110° for saturated bonds (this relates to sp^3-hybridization of carbon atoms, which from σ-bonds only). Due to this saturated acyls have straight form (Fig. 4.7). It means that esters of saturated fatty acids displace in space in the form of straight uncurved chains.

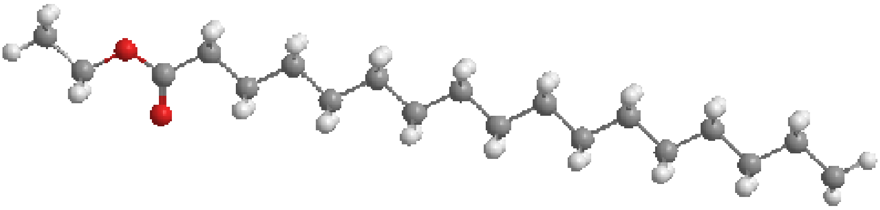


Fig. 4.7. 3-dimensional formula of saturated fatty acid ester

For unsaturated double bonds (that relates to sp^2-hybridization of carbon atoms, which form both σ-bonds and π-bonds) the angle of valent bond between carbon atoms is equal to 120°. The presence of double bond limits rotation of sp^2-hybridized carbon atoms relating each other. This stipulates existence of unsaturated fatty acids in a form of geometric isomers. Double bonds of almost all unsaturated fatty acids, which are found in plant oils, exist in *cis*-configuration. The presence of *cis*-double bonds influences on geometric form of fatty acid molecule, and thus, the form of esters molecule: it makes it curved and less compact (Fig. 4.8.).

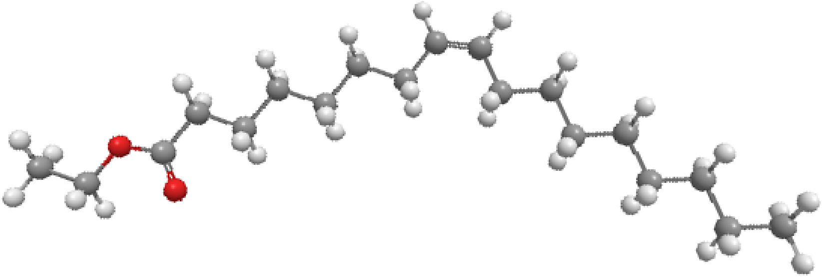


Fig. 4.8. 3-dimensional formula of unsaturated fatty acid ester in *cis*-configuration

Because of this *cis*-isomers of unsaturated acid esters occupy bigger volume and pack less compact during formation of crystals at low temperatures comparing to *trans*-isomers. Acyls of unsaturated fatty acids in *trans*-configuration (Fig.4.9) are very rare in plant oils.

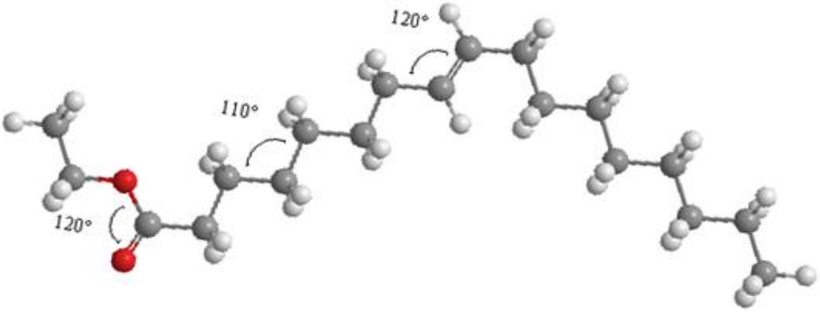


Fig. 4.9. 3-dimensional formula of unsaturated fatty acid ester in *trans*-configuration

In general, the structure of acyl radicals influence on physical and chemical properties of esters. With increasing length of hydrocarbon chain the compactness of molecules mutual disposition decreases and in a result density of esters also decreases. Rising of number of isolated double bonds in esters of unsaturated fatty acids with equal number of carbon atoms leads to increasing of its density. In general, the higher degree of unsaturation the higher is esters density.

Quantity of carbon atoms and presence of double bonds in molecules influences on esters' viscosity as well. Compounds with bigger number of double bonds possess smaller viscosity. Viscosity of esters is significantly lower comparing to fatty acids because of the absence of association in carboxyl group of esters.

Increasing number of carbon atoms in fatty acid radical and decreasing number of double bonds lead to rising of esters' melting point and pour point. Melting point of unsaturated fatty acids esters is lower comparing to esters of saturated fatty acids with equal number of carbon atoms in molecule. Melting point and pour point of unsaturated fatty acids esters with equal hydrocarbon chain length decrease with rising number of double bonds. In general pour point of esters decreases according to the dependence below:

esters of saturated fatty acids → esters of unsaturated fatty acids *trans* –isomers → esters of unsaturated fatty acids *cis* -isomers

Increasing length of hydrocarbon chain leads to rising of esters boiling point. Ethyl esters have slightly higher boiling points than methyl esters of the same fatty acids. This is stipulated by the presence of extra methyl group in the ethanol radical. Esters do not form azeotropic mixtures during boiling.

As it was previously mentioned the most widespread feedstock for production biofuels based on fatty acids esters on the territory of Poland is RO. That is why we have used rapeseed oil FAME and FAEE with defined properties (Table 4.3) for determination main physical-chemical properties of bio-additives.

Table 4.3

The main physical-chemical properties of FAME and FAEE of RO

No	Parameter	Mixture of FAME	Mixture of FAEE
1	Density at t = 20 ^{o}C, kg/m^3	873	887
2	Kinematic viscosity at t = 20 ^{o}C, mm^2/s	7.62	8.34
3	Pour point, ^{o}C	minus 16	minus 17
4	Flash point, ^{o}C	38	37.50

Chromatographic analysis of component composition of rapeseed oil FAME and FAEE has shown that products of RO esterification contain the following by-products: free alcohol, glycerin, products of incomplete transesterification (mon- and diglycerides), triglycerides and also sodium or potassium salts of fatty acids (Table 4.4). Presence of these substances makes using of studied bio-additives as components of JFs impossible.

Table 4.4

Component composition of FAME and FAEE before and after vacuum distillation

No	Components	Mixture of FAME	Mixture of FAEE
1	The total content of esters,%	82.3	83.8
2	Monoglycerides, %	1.84	1.1
3	Diglycerides, %	0.82	0.8
4	Triglycerides, %	1.13	0.73
5	Glycerin. alcohol and impurities, %	13.91	13.57

Significant quantity of glycerin indicates about incompleteness of transesterification reaction and incomplete transformation of fats into esters. Presence of free glycerin may cause clogging of filters in fuel system of aircrafts, its accumulation at the bottom of fuel tanks.

Presence of catalyst residue (sodium or potassium hydroxide or its salts) in fatty acids esters may lead to formation of sediments on JE details.

Ethanol (boiling point 78 °C) and methanol (boiling point 63 °C) cause decreasing of JFs' initial boiling point. This will negatively influence on processes of vapor-air mixture formation and fuel combustion during the exploitation of aircrafts.

Presence of water in fatty acids esters is inacceptable, because water may be the source of corrosion and medium for microbial organisms development. Except that water in JF causes its crystallization at low temperatures.

The obtained experimental data and theoretical analysis allows concluding that bio-additives produced by known technological scheme (Fig 4.3) and satisfying requirement of specifications for biodiesel fuel can't be used for direct blending with conventional JFs. This stipulated the need to develop method of high-quality bio-additives production.

Analyzing the experience of numerous scientists in production of biofuels from plant oils we have formulated the list of requirements to the process of bio-additives production:

- Complete transformation of triglycerides into esters;
- Complete removal of free glycerin that is produced during transesterification process;
- Complete removal of catalyst residues;
- Complete removal of alcohol that is used as an agent of transesterification;
- Absence of free fatty acids and products of incomplete transesterification.

Thus, the process that will satisfy the set requirements allows producing bio-additives, which may be used for blending with conventional JFs.

4.4. Model of technological process of bio-additives production

Considering the requirements, which were formulated to the quality of bio-additives we assumed that increasing cleanness of RO esters allows solving the question of biofuel compatibility with JF. To remove admixtures method of thermal distillation was proposed; it is widely used in modern chemical technology for separation and purification of various chemical substances. The process of substances separation is based on different boiling temperatures of certain substances, which are contained in processing mixture. The most affordable and easy to implement is atmospheric distillation. The use of modern equipment helps keeping temperature regime up to 400÷450 °C even in laboratory conditions.

However, from the works by, devoted to studies of fractional composition and thermal stability of esters it is known that the boiling temperature of the most of rapeseed oil esters exceeds their thermal decomposition temperature. This stipulates processes of isomerization, polymerization and pyrolisis of esters molecules during boiling with further formation of non-liquid residue and resins.

For eliminating processes of thermal destruction the following methods of thermal distillation became popular: distillation in vacuum, molecular distillation and distillation on thin films. Distillation in vacuum is the simpliest. The principle of the method is similar to atmospheric distillation but the difference is presence of equipment for pressure decrease in the system. For cleaning products of transesterification of RO vacuum distillation under reduced pressure was used.

In order to develop and substantiate the process of vacuum distillation, we appealed to the bases of chemical thermodynamics. The process of boiling is the process of liquid evaporation from its whole volume. When temperature rises, the speed of evaporation from surface also rises. The process of boiling starts when the saturated vapors pressure reaches normal atmospheric pressure of 101.3 kPa. Temperature when this condition is fulfilled is called normal boiling point. It means the following: changing the external pressure it is possible to change the boiling point of the liquid. The dependence of the saturated vapors pressure of a liquid on temperature and the dependence of boiling point on external pressure may be described by Clapeyron-Clausius equation. The equation in the following form

$$\frac{dP}{dT} = \frac{\Delta H_{ph.t.}}{T\Delta V_{ph.t.}}, \tag{4.1}$$

may be used for any kind of double-phase equilibrium transition in mono-component system. For the process of liquid – vapor transition the Clapeyron-Clausius equation may be presented as following:

$$\frac{dlnP}{dT} = \frac{\Delta H_{evap.}}{RT^2}, \tag{4.2}$$

and may be transformed into integral form as:

$$ln\frac{P_2}{P_1} = \frac{\Delta_v H}{R}\left(\frac{T_2-T_1}{T_1 \cdot T_2}\right) \tag{4.3}$$

For developing optimal conditions of vacuum distillation of esters we have built dependences of esters boiling points on external pressure. The equations (4.1–4.3) are adequate for mono-component systems only. That’s why the calculation of dependences was done for each individual ester that composes FAME mixture. Taking into account that all esters are compounds of similar structure, boiling point curves as functions of external pressure were calculated for esters, which make a comparatively high ratio in the mixture and take about 98.5 % of the total amount of FAME mixture. We didn’t do the calculations for esters, which content was less than 0.5 % of the total volume. In order to calculate the dependence using equation (4.3) the value T_1 was determined. The value T_2 is a boiling point of esters at normal atmospheric pressure P_2. Values of pressure P_1 were given for the range 0.001÷100 kPa. The values of heat of evaporation $\Delta H_{evap.}$ are individual for each substance and may be found in certain guides and research papers (Table 4.5).

Table 4.5

Thermodynamic properties of esters for the process of evaporation at normal pressure

Name of compound	$T_{boiling}$, °C	$\Delta_v H_.$, J/mole	Name of compound	$T_{boiling}$, °C	$\Delta_v H_.$, J/mole
ME hexadecenoic acid	341.4	58500	EE hexadecenoic acid	357.2	60300
ME palmitic acid	332.1	57500	EE palmitic acid	342.2	58600
ME oleic acid	351.4	59600	EE oleic acid	385.9	63500
ME linoleic acid	373.3	62100	EE linoleic acid	388.3	63700
ME linolenic acid	364.4	61100	EE linolenic acid	374.4	62200
ME stearic acid	355.5	60100	EE stearic acid	356	60100
ME nonadecenoic acid	383.7	63200	EE nonadecenoic acid	388.4	63800
ME nonadecanoic acid	362.8	60900	EE nonadecanoic acid	359.1	60500
ME eicosenoic acid	402.2	65300	EE eicosenoic acid	416.5	67000
ME heneicosenoic acid	416.8	67000	EE heneicosenoic acid	-	-
ME erucic acid	422.9	67700	EE erucic acid	436.8	69300
ME docosanoic acid	398.0	64900	EE docosanoic acid	387.8	63700

In general we can make a conclusion that esters heats of evaporation have comparatively narrow range: 57500÷67700 J/mol for FAME and 58600÷69300 J/mol for FAEE. Analogously we have calculates boiling point curves of individual esters, which are contained in FAEE mixture.

The diagrams of phase equilibrium of FAME (Fig. 4.10) and FAEE (Fig. 4.11) were built basing on the results of calculation.

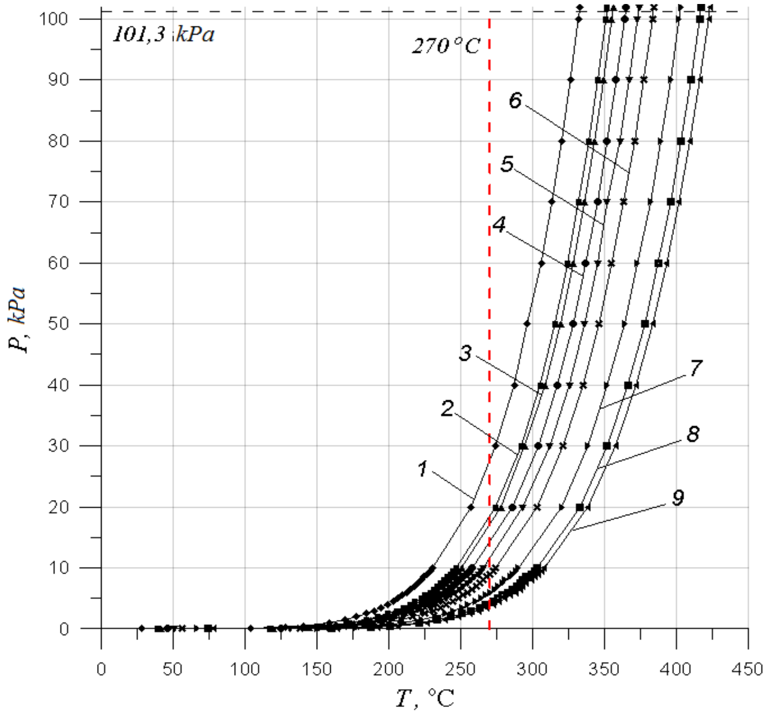


Fig. 4.10. The diagram of the liquid – vapor phase equilibrium for methyl esters of acids: *1* – palmitic, *2* – oleic, *3* – stearic, *4* – linolenic, *5* – linoleic, *6* – nonadecenic, *7* – eicosenoic, *8* – heneicosenic, *9* – erucic

We can see that FAME boiling points have quite narrow range of 332÷423 °C. it is known that FAME keeps thermal stability at temperatures below 270 °C. Processes of *cis-trans*-isomerization of double bonds in esters acyl radicals take place in the temperature range from 270÷275 °C to 400 °C. Temperature range 300÷375 °C is favorable for processes of esters polymerization by Diels-Adler reaction with further formation of hexane rings. At temperatures 360÷400 °C esters are subjected to pyrolisis with further formation of saturated esters of smaller molecular mass (C_5–C_{14}) and *n*-alkanes (C_8–C_{15}). In general kinetics of FAME thermal decomposition is affected not only by temperature but also by duration of high temperature influence.

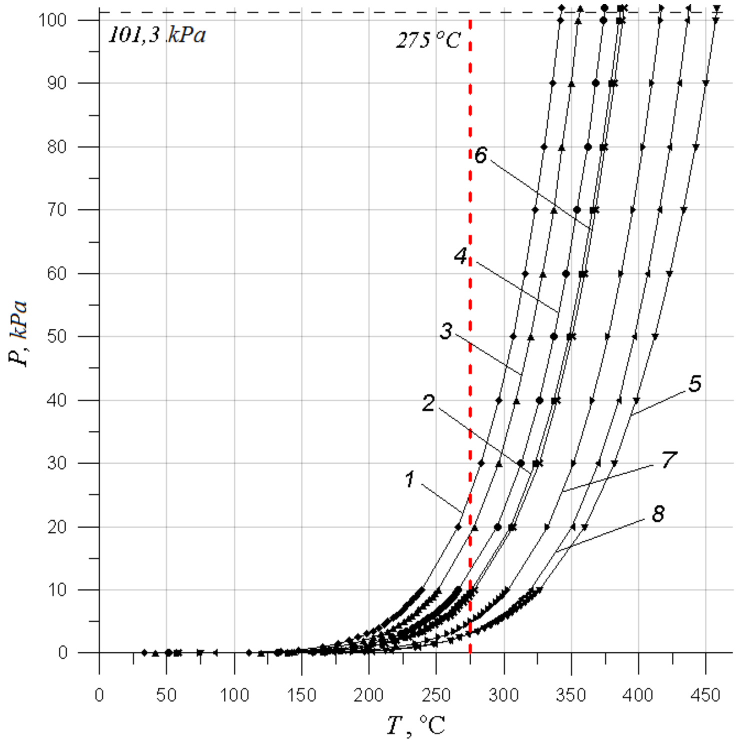


Fig. 4.11. The diagram of the liquid – vapor phase equilibrium for ethyl esters of acids:
1 – palmitic, *2* – oleic, *3* – stearic, *4* – linolenic, *5* – linoleic, *6* – nonadecenic,
7 – eicosenoic, *8* – erucic

Boiling points of FAEE are slightly higher and lay in a range 343÷458 °C (Fig. 4.11). This may be explained by the presence of an extra methyl group in alcohol radicals of esters that results in higher molecular mass. Due to the influence of high temperatures FAEE are subjected to the similar processes as FAME: *cis-trans*-isomerization at temperatures 275÷400 °C, polymerization at temperatures 300÷425 °C and pyrolisis at temperature higher than 350 °C.

The diagrams above show that boiling points of esters at atmospheric pressure are above the conditional line of its thermal decomposition (red lines on diagrams). According to the data about esters' thermal decomposition, the pressure inside the system should be decreased till the value that can provide FAME distillation below 270 °C and FAEE distillation below 275 °C. Moreover, the less pressure the less time of esters heating till boiling point and, thus, the less impact of high temperature.

Taking into account technical characteristics of laboratory installation we have proposed to organize vacuum distillation at pressure 0.4÷0.7 kPa. Organizing the process in the mentioned above pressure range allows reaching significant decrease of esters boiling points. Calculated range of FAME boiling points is: start of boiling within 135÷149 °C, end of boiling within 195÷211 °C (Fig. 4.12).

Calculated range of FAEE boiling points is: start of boiling within 142÷156 °C, end of boiling within 210÷226 °C (Fig. 4.13). These conditions of the process allows distilling esters and eliminate their thermal decomposition.

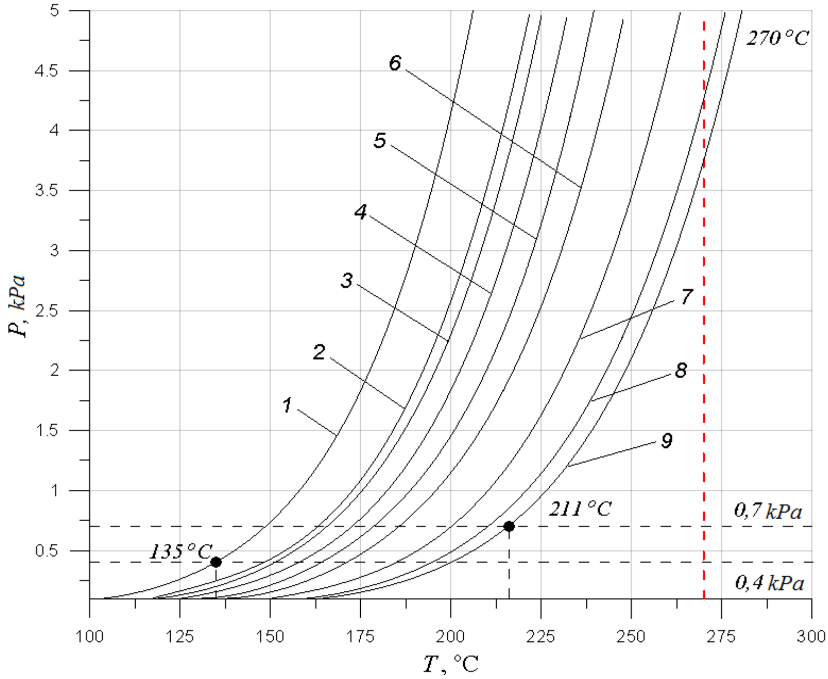


Fig. 4.12. The diagram of the liquid – vapor phase equilibrium in the range 0,001 – 5 kPa for methyl esters of acids: *1* – palmitic, *2* – oleic, *3* – stearic, *4* – linolenic, *5* – linoleic, *6* – nonadecenic, *7* – eicosenoic, *8* – heneicosenic, *9* – erucic

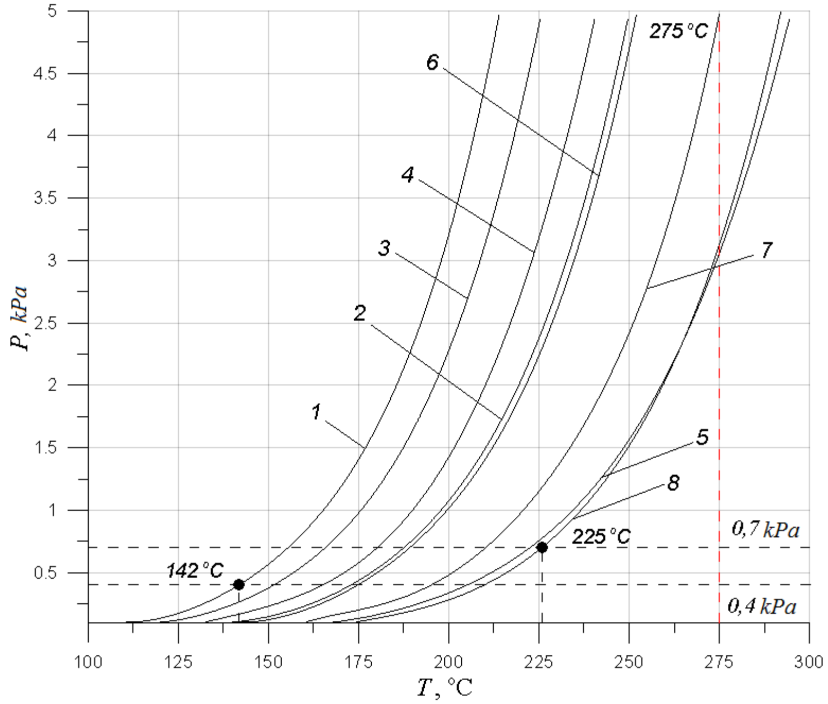


Fig. 4.13. The diagram of the liquid – vapor phase equilibrium in the range 0,001 – 5 kPa for ethyl esters of acids: *1* – palmitic, *2* – oleic, *3* – stearic, *4* – linolenic, *5* – linoleic, *6* – nonadecenic, *7* – eicosenoic, *8* – erucic

In general it is possible to define three main stages of the vacuum distillation process:

- Extraction of alcohol (methanol or ethanol),
- Distillation of esters,
- Removing of non-liquid residue that stays after distillation process finish.

The main product, obtained in a result of vacuum distillation may be additionally filtered. This is the last stage of bio-additives production. Detailed description of the laboratory equipment for vacuum distillation and stages of bio-additives production method are described in chapter 4.2. The improved scheme of bio-additives production is presented on Fig. 4.14.

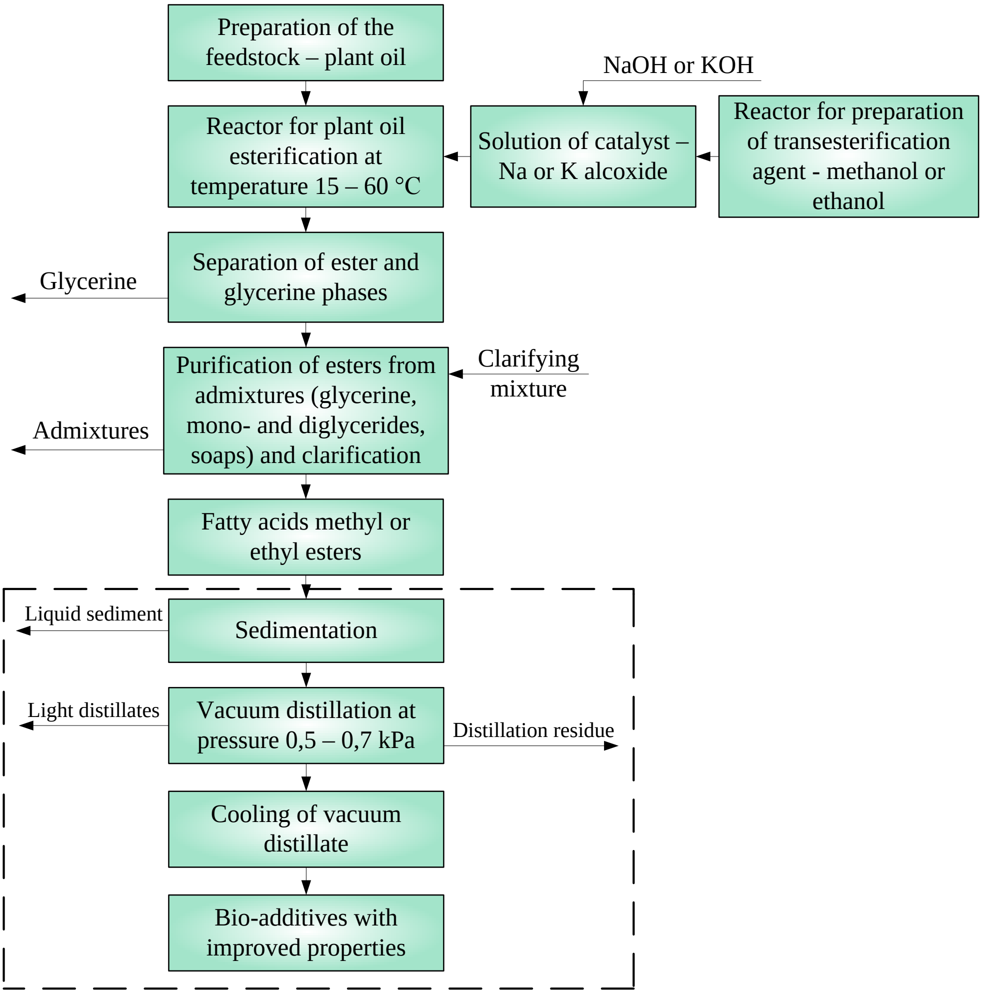


Fig. 4.14. The improved scheme of bio-additives production by vacuum distillation

The effectiveness of the proposed method of improving rapeseed oil esters properties is illustrated in Tables 4.6÷4.8. Table 4.6 presents component composition of FAME and FAEE before and after distillation. Table 4.7 and 4.8 describe physical-chemical properties of the mentioned above substances.

As we can see from the table above, mixtures of FAME and FAEE after vacuum distillation almost do not contain undesirable components, such as alcohol, glycerin, mono-, diglycerides, free fatty acids and other by-products. It means that the quality of final products – modified bio-additives has been significantly improved.

Table 4.6

Component composition of FAME and FAEE before and after vacuum distillation

No	Components	Mixture of FAME	Mixture of FAME after vacuum distillation	Mixture of FAEE	Mixture of FAEE after vacuum distillation
1	The total content of esters,%	82.30	< 99 %	83.8	< 99 %
2	Monoglycerides, %	1.84	–	1.1	–
3	Diglycerides, %	0.82	–	0.8	–
4	Triglycerides, %	1.13	–	0.73	–
5	Glycerol, alcohol and impurities, %	13.91	> 1 %	13.57	> 1 %

Table 4.7

Physical and chemical properties of FAME of rape oil before and after vacuum distillation

No	Parameter	Mixture of FAME	Mixture of FAME after vacuum distillation	Change of parameters, %
1	Density at t = 20 ^{o}C, kg/m^3	873	867	- 0.69
2	Kinematic viscosity at t = 20 ^{o}C, mm^2/s	7.62	7.35	- 3.54
3	Pour point, ^{o}C	minus 16	minus 18.50	- 15.60
4	Flash point, ^{o}C	38	170	+ 347.40

Table 4.8

Physical and chemical properties of FAEE of rape oil before and after vacuum distillation

No	Parameter	Mixture of FAEE	Mixture of FAEE after vacuum distillation	Change of parameters, %
1	Density at t = 20 ^{o}C, kg/m^3	887	879	- 0.90
2	Kinematic viscosity at t = 20 ^{o}C, mm^2/s	8.34	6.73	- 19.3
3	Pour point, ^{o}C	minus 17	minus 19	- 11.76
4	Flash point, ^{o}C	37.50	167	+ 345.30

From the Tables 4.7 and 4.8 we can see that applying vacuum distillation allows improving some physical-chemical properties of FAME and FAEE: the density of FAME and FAEE has decreased by 0.69 % and 0.90 %, the kinematic viscosity has decreased by 3.54 % and 19.30 %, and the pour point has decreased by 15.60 % and 11.76 % respectively. Due to alcohols removing, a flashpoint of FAME and FAEE is dramatically increased and reached values typical for esters of fatty acids.

Improvement of the process of bio-additives production by the stage of vacuum distillation allowed eliminating thermal destruction of esters and providing high level of purification from by-products of oil transesterification process and products of esters thermal decomposition. Thus, we may predict that obtained bio-additives may be used as components for blending with JFs.

4.5. Study of intermolecular interaction within the system „hydrocarbon fuel – fatty acids esters”

In order to study and determine the behavior of the influence of plant oil bio-additives on physical-chemical properties of conventional JF, it was necessary to fulfill the profound analysis of blending (mixing) mechanisms of JF and bio-additives. Also, it was necessary to determine the nature of intermolecular interaction within the system „hydrocarbon fuel – fatty acids esters”. This need is explained by the fact that this question is not enough considered in the domestic and foreign scientific literature. For example, the studies give information about the solubility of triglycerides of plant oils in some polar solvents. The sudies by foreign scientists describe the solubility of biodiesel and diesele fuels in various organic solvents. However, the information about mutual solubility of fatty acids esters and hydrocarbons of kerosene-gasoil fraction of crude-oil refining (JF) is absent in modern literature. Thus, this question requires deep studying and systematization.

Samples of blended JFs may be considered at macrolevel as a two-component system, where each of the components (JF and bio-additive) is in liquid state at normal conditions. At the same time at the micolevel blended JF is a multi-component system, which include paraffinic, naphthenic and aromatic hydrocarbons, saturated and unsaturated fatty acids esters.

In order to study and analyze processes of compounding (blending) of hudrocarbon fuel and fatty acids esters we applied fundamentals of physical chemistry: processees of intermoleacular interaction, colloidal chemistry and theory of solutions.

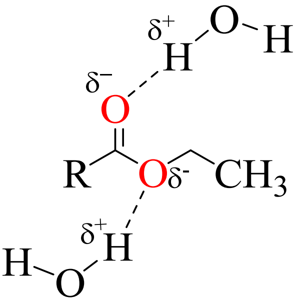
Solving is a complex physical-chemical process. Followers of the physical theory of solutions consider that dissolving is a uniform distribution of particles of dissolved substance within a whole volume of solvent. According to the chemical theory, solutions are the systems, formed by the particles of solvent, dissolved substance and unstable chemical compounds, which are formed between them due to the hydrogen bond or forces of electrostatic interaction. The modern theory of solutions considers the process of solving as a interaction between particles of various polarity.

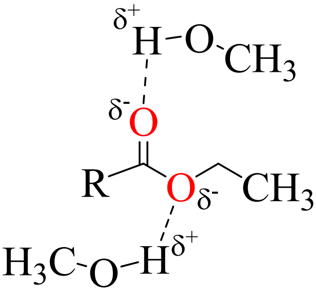
From the studies it is known that basis of dissolving (mixing) processes is the process of salvation – interaction of solvent particles with particles of dissolved substance. During the process of dissolving some portion of energy is discharged in a result of breaking bonds between molecules of dissolved substance. Another portion of the energy is absorbed duting formation of new bonds between molecules of solvent and dissolved substance. Otherwords, the process of dissolving is an intermolecular interaction between components of the system. Intermolecular interaction includes Van-der-Waals forces of interaction and hydrogen.

In order to analyze the process of fatty acids esters dissolving in hydrocarbon fuel it is necessary to determine the presence and role of mentioned above forces between the molecules of fatty acids esters. As it was already mentioned, ester molecule is a radical of fatty acid with crbonyl group –C=O that is connected by hydroxyl oxygen atom with alcohol radical.

Presence of oxygen atoms speaks about ability of molecules to form hydrogen bonds. It means that they can be acceptors of hydroegn bonds. At the same time hydrogen atoms in esters' molecules are connected by strong covalent bonds with carbon atoms in acid and alcohol radicals and they are not able to be recievers of hydrogen bond. It means that hydrogen bonds between fatty acids esters' molecules are not formed and molecules are not able to mutual association via hydrogen bonds.

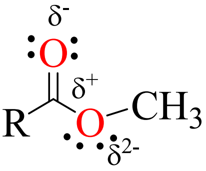
Esters molecules can form hydrogen bonds only with other molecules, being acceptors of such bond. This explains solubility of esters with number of carbon atoms in acyl radicals up to 5 in water and alcohols. In these mediums hydrogen atoms of their molecules contact with electronegative oxygen atoms. However, rising the length of hydrocarbon chain causes decreasing of esters solubility in polar solvents.

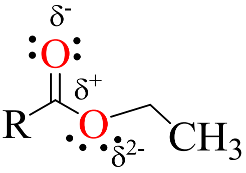




Hydrogen bonding is a certain type of dipol-dipol or orientation Van-der-Waals interaction. The base of of orientation interaction (Keesom force) is ability of one molecules to orient respecting to other by opposite charges.

Electronegativity of Oxygen atoms (3.5) in molecule is more than electronegativity of Carbon (2.5). Unshared pairs of Oxygen electrons shift electronic density of neighbor Carbon atoms and partially achieve negative charge (induction effect). In its turn carbonyl atom of Carbon achieves partially positive charge.





As a result, ester molecule is polar and has stable electric dipole moment. Such peculiarity of fatty acid ester molecule structure explains its ability for orientation interaction.

Ester molecule consists of two parts: polar – hydrophylic and non-polar – hydrophobic. Consequently, hydrophylic part is able to orientation interaction. At the same time acyl radicals are non-polar (hydrophobic) and are not able to oriebtation interaction. Forces of dispersion interaction (London forces) appear between them. These forces are stipulated by the appearances of instant dipoles in a result of shift of electronic density of electronic shell, which are at the state of constant movement respecting to nucleus. Constant movement of electrons couses unsymmetricity of redistribution of charges in molecules and instant dipoles appear in them. Thus, non-polar molecules can become polar for a very short moment. In general dispersion interaction depends on ability of molecules to deformation and distance between them.

3-D electrostatic model of fatty acid ester molecule (Fig. 4.15) presents its polar part, where accumulation of negative charge is colored in red and positive charge, colored respectively in blue. Non-polar acyl radical is colored in green.

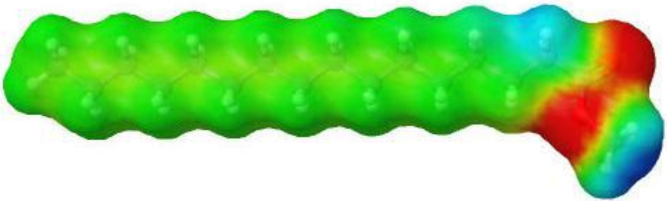


Fig. 4.15. 3-D electrostatic model of fatty acid ester

While arranging in a space, esters molecules orient by the oppposite charges. Dipole-dipole bonds form between polar parts of the molecules. Forces of dispersion interaction appear between hydrophobic acyl radicals. At the same time longer radicals provide greater area of its contact ans respectively area for dispersion forces formation. It means that increasing of hydrocarbon length causes rising of intermolecular interaction force. It is important that with increasing of hydrocarbon length forces of dispersion interaction become prevaling over orientation and ester molecule recieves hydrophobic properties (it becomes insoluble in polar solvents).

Presence of double bonds in acyl radicals of fatty acids esters causes significant influence on its intermolecular interaction and respectively on physical chemical properties of esters. The angle of valent double bond between carbon atoms is equal to 120 ° on the contrary to single bond (110 °); this makes esters molecule more curved. The distance between “curved”acyl radicals is greater than in case of straight (saturated) ones. This makes forces of disperion interaction between molecules weaker.

Except orientation and dispersion forces the induction force can also appear between between esters molecules – when non-polar parts of molecules become polarized under the influence of electromagnetic field of polar part of the molecule and obtain induced dipole moment.

It was found that forces of dispersion interaction between molecules of esters are prevalent. The energy of of dispersion interaction may be expressed by the London’s formulae:

$$E_{disp} = -\frac{3I}{4}\frac{\alpha^2}{d^6}, \quad (4.4)$$

where

I – ionizing energy of the molecule,

α – coefficient that describe the ability of the molecule to polarization,

d – distance between instant dipoles.

It arises from the formulae (4.4) that increasing molecules' ability to polarization α (otherwords, increasing of its' size) causes increasing of interaction energy. At the same time the ionizing energy *I* of esters molecules changes insignificantly with a rise of its linear size and does not influence on the value of energy of dispersion.

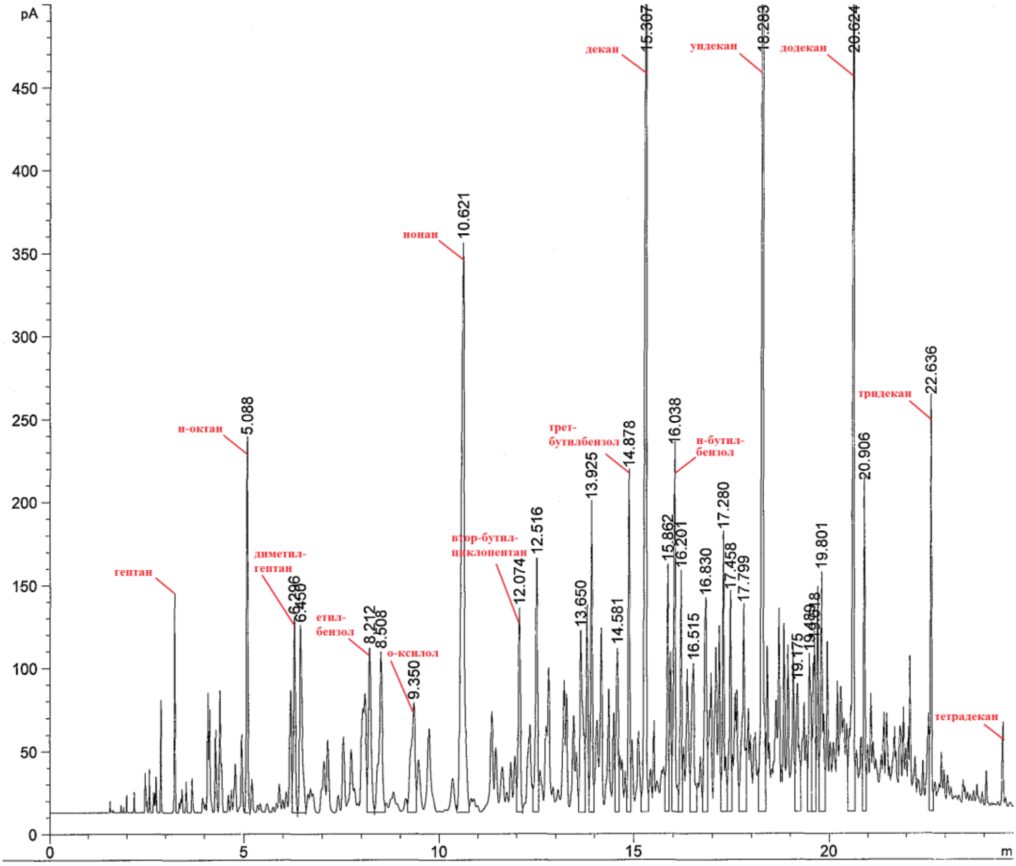
$$\xrightarrow{\text{Ability to polarization, } \alpha}$$

Methyl	$C_{16}H_{31}OOCH_3$	$C_{18}H_{35}OOCH_3$	$C_{19}H_{35}OOCH_3$	$C_{20}H_{37}OOCH_3$	$C_{22}H_{41}OOCH_3$
esters	$32.7\cdot10^{-24}$ sm^3	$36.4\cdot10^{-24}$ sm^3	$38.3\cdot10^{-24}$ sm^3	$40.1\cdot10^{-24}$ sm^3	$43.8\cdot10^{-24}$ sm^3
Ethyl	$C_{16}H_{31}OOC_2H_5$	$C_{18}H_{35}OOC_2H_5$	$C_{19}H_{35}OOC_2H_5$	$C_{20}H_{37}OOC_2H_5$	$C_{22}H_{41}OOC_2H_5$
esters	$34.6\cdot10^{-24}$ sm^3	$38.2\cdot10^{-24}$ sm^3	$40.0\cdot10^{-24}$ sm^3	$41.9\cdot10^{-24}$ sm^3	$45.6\cdot10^{-24}$ sm^3

From the studies it is known that JFs are kerosene-gasoil fraction of crude-oil distillation that contains mainly paraffinic, naphthenic and aromatic hydrocarbons $C_5 \div C_{16}$. In order to study the mechanism of of interaction between molecules of kerosene-gasoil fraction and fatty acids esters the chromatograph analysis of JF was done. It allowed us determining its component compositon and defining hydrocarbons, which are the most typical for this kind of fuel (Fig. 4.16). The obtained experimental data fully corresponds to theoretical data in literature sources.

Jet fuel hydrocarbons may be conditionally divided into two groups; non-polar and non-polar but able to polarization – paraffinic-naphthenic and aromatic hydrocarbons. Some paraffins and naphthens can provide small reduced dopole moment.

3-D electrostatic models of typical molecules of hydrocarbon fuel and fatty acids esters of RO are given in Table 4.9. hydrocarbon molecules have smaller dimensions comparing to esters' molecules, thus smaller ability to polarization and energy of dispersion interaction.



4.16. Chromatogram of JF of grade Jet A-1

It is found that during blending hydrocarbon JF with fatty acids esters mutual mixing takes place due to the induction and dispersion Van-der-Waals forces of interaction. The dispersion force component is prevaling. Increasing the portion of fatty acids esters in the system “hydrocarbon fuel – fatty acids esters” causes rising of intermolecular interaction. This effect is indicated by the increasing of heat of evaporation of its components.

Heat of evaporation, Δ*H*

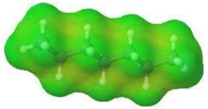
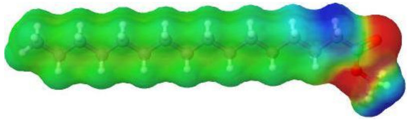
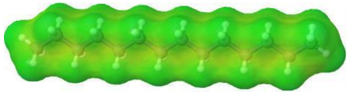
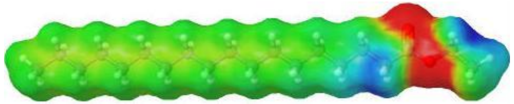
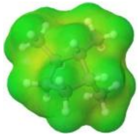
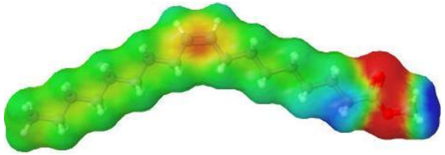
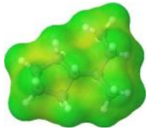
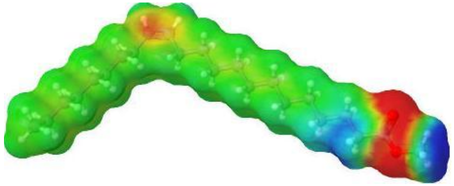
$$\longrightarrow$$

Hydrocarbons of JF	Methyl esters	Ethyl esters
31–47 kJ/mol	57.5–67.7 kJ/mol	58.6–69.3 kJ/mol

This effect can be explained by the increasing of share of disperion force component into the total intermolecular interaction in a result of enlarged polarity of molecules within the system. Induction interaction within the system takes place due to the polarization of naphthenic and aromatic hydrocarbons of JF with carboxylic groups of esters’ molecules.

Table 4.9

Comparison of the 3-D electrostatic models of JF’s molecules and fatty acids esters’ molecules

Hydrocarbon JF		Bio-additives	
1	*2*	*3*	*4*
Compound	3D electrostatic model of compound	Compound	3D electrostatic model of compound
Parrafinic hydrocarbons		Saturated esters	
Heptane		Methyl-palmitate	
Tetradecane		Ethylstearate	
Naphtenic hydrocarbons		Unsaturated esters with one double bond	
Tri-methyl-cyclopentane		Methyloleate	
Secondary buthyl-cyclopentane		Methyl-erucate	

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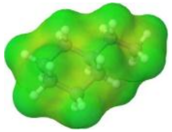
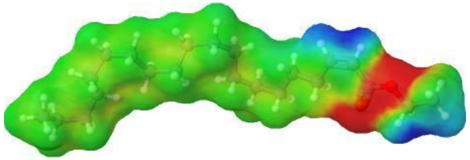
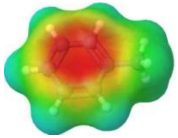
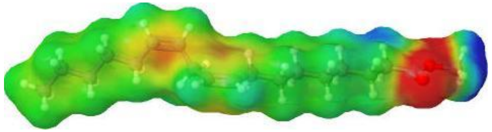
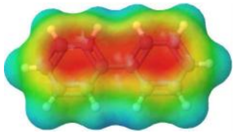
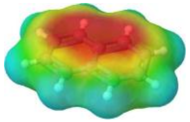
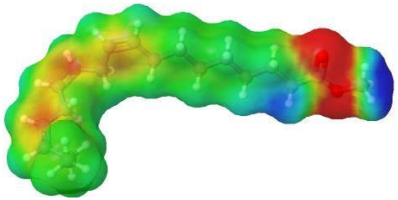
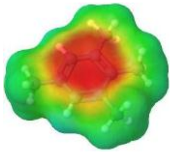
<tr><td>Ethyl-cyclohexane</td><td></td><td>Ethyl-eicosenoate</td><td></td></tr>
<tr><td colspan="2">Aromatic hydrocarbons</td><td colspan="2">Unsaturated esters with two double bonds</td></tr>
<tr><td>Toluene</td><td></td><td rowspan="2">Methyl-linoleate</td><td rowspan="2"></td></tr>
<tr><td rowspan="2">Biphenyl</td><td rowspan="2"></td></tr>
<tr><td colspan="2">Unsaturated esters with three double bonds</td></tr>
<tr><td>Naphthalene</td><td></td><td rowspan="2">Methyl-linolenate</td><td rowspan="2"></td></tr>
<tr><td>Tetra-methyl-benzene</td><td></td></tr>
</table>

With increasing portion of fatty acids esters in the system “hydrocarbon fuel – fatty acids esters” the energy of the system decrease on 31÷69.3 kJ/mol. Reduction of total system’s energy explains the influence of fatty acids esters on physical-chemical properties of blended JFs.

The fulfilled analysis of the character of intermolecular interaction of fatty acids esters, JF’s hydrocarbons and teir mixture gives us ground to state that process of JF and fatty acid esters comppounding (blending) results in formation of homogeneous system, where each of the components is reduced to the size of molecules. Interaction between components of the system takes place due to the action of electrostatic forces of intermolecular interaction (Van-der-Waals forces). At the same time there is no chemical interaction between components of the system.

During preparation of samples of blended JFs it was found that blending of hydrocarbon JF with bio-additives is unlimited in any ratios. During samples storage there were no demixing, settling of components was not observed. Otherwords, samples are characterized by aggregative stability.

Chapter 5

COMPLEX CHARACTERISTICS OF PHYSICAL-CHEMICAL AND EXPLOITATION PROPERTIES OF JET FUELS BLENDED WITH BIO-ADDITIVES

It is well-known that leading role in providing reliability and efficiency of JE and aircraft itself is played by quality of fuels and lubricating materials. Modern JFs must meet requirements, connected to efficiency, environmental safety reliability and durability of air transport.

Physical-chemical and thus exploitation properties are those objective properties of JFs, which are revealed during its application in the process of engines, mechanisms and systems exploitation. All the exploitation properties are connected in a certain way to the complex of physical-chemical properties and quality parameters of JFs.

5.1. Aim and scope of the study

Laboratory tests of physical-chemical and exploitation properties of newly developed JFs blended with bio-additives were done with the aim of studying quality of new JFs and checking the hypothesis that quality parameters of alternative JFs do not exceed the values of current standard requirements with reference to conventional jet fuel. In order to reach the set aim it was necessary to study properties of conventional JF, four samples of bio-additives and JFs blends, which contain 10 %, 20 %, 30 %, 40 % and 50 % of bio-additives. The quality of fuel samples was determined according to the following physical-chemical and exploitation properties: density, fractional composition, heat of combustion and energy value, kinematic viscosity, low-temperature properties, anti-wear properties, fire safety and corrosiveness. The mentioned properties are considered to be identifying for quality control of conventional and blended JFs.

5.2. Characteristic of fuel samples

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

For obtaining blended JFs four types of bio-additives were used:

- FAME of RO that were produced by Polski Koncern Naftowy «ORLEN» (Plok, Poland), and its quality parameters meet requirements of specifications EN 14214, and ASTM D6751,
- FAME of RO that were produced in the Institute of bioorganic chemistry and petrochemistry of the National Academy of Sciences of Ukraine and were specially modified by vacuum distillation according to the method described in chapter 4,

- FAEE of RO that were produced in the Institute of bioorganic chemistry and petrochemistry of the National Academy of Sciences of Ukraine and were specially modified by vacuum distillation according to the method described in chapter 4,
- FAEE of CamO that were produced in the Institute of bioorganic chemistry and petrochemistry of the National Academy of Sciences of Ukraine.

Within the scope of the study we have studied physical-chemical and exploitation properties of pure JF, pure samples of bio-additives and JF blends, which contained 10 %, 20 %, 30 %, 40 % and 50 % of each type of bio-additives. All together 25 fuel samples were studied during this work. The list of studied fuel samples and its designations are presented in Table 5.1.

Table 5.1

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

No	Sample description	Sample designation
1	Jet fuel of grade Jet A-1	JF
2	Bio-additive – fatty acids methyl esters of rape oil	FAME
3	Jet fuel blended with 10% of bio-additive	JF+10% FAME
4	Jet fuel blended with 20% of bio-additive	JF+20% FAME
5	Jet fuel blended with 30% of bio-additive	JF+30% FAME
6	Jet fuel blended with 40% of bio-additive	JF+40% FAME
7	Jet fuel blended with 50% of bio-additive	JF+50% FAME
8	Bio-additive – modified fatty acids methyl esters of rape	Modified FAME
9	Jet fuel blended with 10% of modified bio-additive	JF+10% modified FAME
10	Jet fuel blended with 20% of modified bio-additive	JF+20% modified FAME
11	Jet fuel blended with 30% of modified bio-additive	JF+30% modified FAME
12	Jet fuel blended with 40% of modified bio-additive	JF+40% modified FAME
13	Jet fuel blended with 50% of modified bio-additive	JF+50% modified FAME
14	Bio-additive – modified fatty acids ethyl esters of rape oil	Modified FAEE
15	Jet fuel blended with 10% of modified bio-additive	JF+10% modified FAEE
16	Jet fuel blended with 20% of modified bio-additive	JF+20% modified FAEE
17	Jet fuel blended with 30% of modified bio-additive	JF+30% modified FAEE
18	Jet fuel blended with 40% of modified bio-additive	JF+40% modified FAEE
19	Jet fuel blended with 50% of modified bio-additive	JF+50% modified FAEE
20	Bio-additive – fatty acids ethyl esters of camelina oil	CamO FAEE
21	Jet fuel blended with 10% of bio-additive	JF+10% CamO FAEE
22	Jet fuel blended with 20% of bio-additive	JF+20% CamO FAEE
23	Jet fuel blended with 30% of bio-additive	JF+30% CamO FAEE
24	Jet fuel blended with 40% of bio-additive	JF+40% CamO FAEE
25	Jet fuel blended with 50% of bio-additive	JF+50% CamO FAEE

5.3. Description of equipment and experiment realization

Physical-chemical and exploitation properties of JF, bio-additives and JFs blended with bio-additives were studied using standard methods and standard equipment based in the Laboratory of Exploitation Materials at the Department of Internal Combustion Engines and Transport of Rzeszow University of technology.

1) Density of fuel samples was determined according to ASTM D4052. Measurements were done using Accurate Density Meter DMA 4500M (Fig. 5.1) produced by Anton Paar GmbH (Austria) with the following technical parameters:

- measuring range: density 0÷3 g/cm^3, temperature 0÷90 °C,
- accuracy: $5\cdot10^{-5}$ g/cm^3, 0.03 °C,
- minimal sample volume 1 ml.

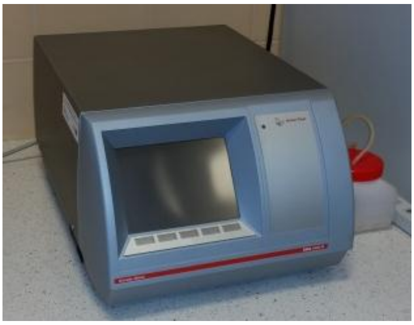


Fig. 5.1. Accurate Density Meter DMA 4500M for density measurement

2) Fractional composition of fuel samples was determined according to ASTM D86. Measurements were done using Automated Distillation Analyzer for Refining, Petrochemical Industries “OPTIDIST” (Fig. 5.2) produced by Walter Herzog (Germany) & ISL (France) with the following technical parameters:
    - measuring temperature range: 0÷450 °C,
    - resolution: 0.03 ml,
    - accuracy: ±0.1 ml.

Fig. 5.2. Automated Distillation Analyzer for Refining “OPTIDIST”

3) Kinematic viscosity of fuel samples was determined according to ASTM D445. Measurements were done using Automated Ubbelohde Viscometer HVU 482 (Fig. 5.3) produced by Walter Herzog (Germany) with the following technical parameters:
   - measuring temperature range: -40÷ +100 °C,
   - measuring range according to capillary used: 1÷50 000 mm^2/s,
   - accuracy of temperature stabilization: ±0.01°C.

Fig. 5.3. Automated Ubbelohde Viscometer HVU 482

4) Heat of combustion of fuel samples was determined according to ASTM D4809. Measurements were done using Automated Bomb Calorimeter IKA C 200 (Fig. 5.4) produced by IKA Werke GmbH & Co. KG (Germany) with the following technical parameters:

- measuring range: max. 40 000 J/g,
- accuracy of temperature measurement: ± 0,0001 K,
- measuring time by isoperibolic method – 17 min.

Fig. 5.4. Automated Bomb Calorimeter IKA C 200

5) Flash point of fuel samples was determined according to ASTM D93. Measurements were done using Pensky-Martens Flash Point Analyzer HFP 339 (Fig. 5.5) produced by Walter Herzog (Germany) with the following technical parameters:
   - measuring range: 0÷400 °C,
   - accuracy: 0.1°C,
   - speed of heating: 0.5÷14 °C/min depending on the program used,
   - igniter: electric; frequency of igniter deeping into cup – 0.5÷5 °C.

Fig. 5.5. Pensky-Martens Flash Point Analyzer HFP 339

6) Corrosiveness of fuel samples was determined according to ASTM D130. Measurements were done using Analyzer for Corrosion Testing of Fuel (also LPG) To Copper (Fig. 5.6) produced by ANKO (Poland).

Fig. 5.6. Analyzer for Corrosion Testing of Fuel (also LPG) To Copper

7) Freezing point of fuel samples was determined according to ГОСТ 5066-91 (ИСО 3013-74). Measurements were done using Petroleum products low-temperature properties analyzer UTF 70 (Fig. 5.7) produced by Crioholod (Ukraine) with the following technical parameters:

- measuring range: -70÷+30 °C,
- sample volume: 30 ml.

The tests were fulfilled at the laboratory “Aviatest” of the Scientific-Research Center of Chemmotology and Certification of Fuels, Lubricants and Technical Liquids of the National aviation university (Kyiv, Ukraine).

Fig. 5.7. Petroleum products low-temperature properties analyzer UTF 70

8) Pour point of fuel samples was determined according to ASTM D 6371. Measurements were done using Automated Cold Filter Plugging Point Analyzer FPP 5Gs (Fig. 5.8) produced by ISL – France.

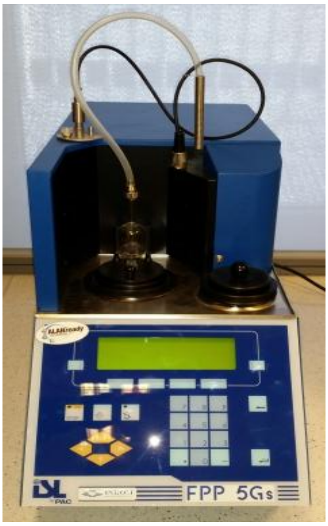


Fig. 5.8. Automated Cold Filter Plugging Point Analyzer FPP 5Gs

9) Content of sulfur in fuel samples was determined according to ГОСТ 19121-73. Measurements were done using glass device for sulfur content in oil products determination (Fig. 5.9) The tests were fulfilled at the laboratory “Avitest” of the Scientific-Research Center of Chemmotology and Certification of Fuels, Lubricants and Technical Liquids of the National aviation university (Kyiv, Ukraine).

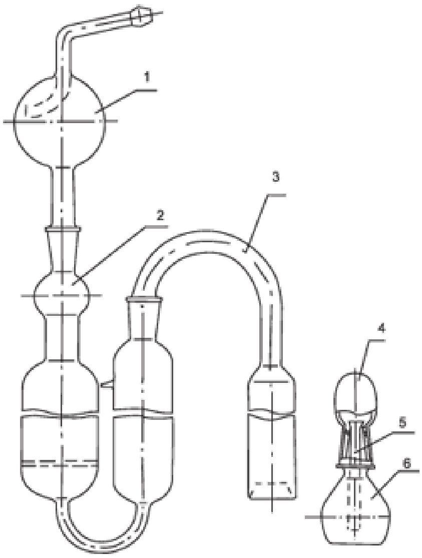


Fig. 5.9. Device for sulfur content in oil products determination:
1 – drop collector, *2* – absorber, *3* – lamp glass, *4* – lamp cap, *5* – wick, *6* – lamp

10) Antiwear properties of fuel samples were investigated using a T-02U four-ball tester that consists of the testing device and a metering-control system. The mechanical part (testing device), shown of Fig. 5.10 includes body, power train, friction pair load bearing drive, ball cup assembly and a base.

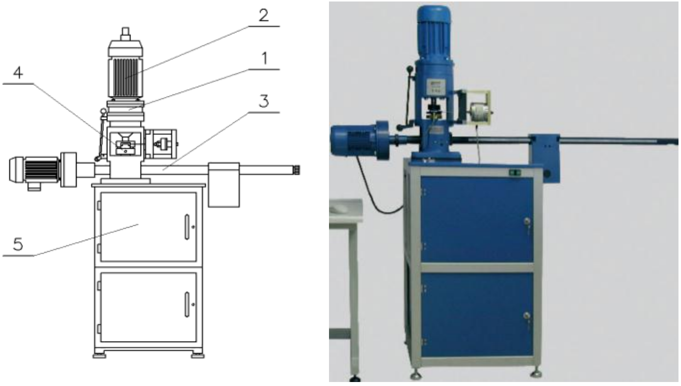


Fig. 5.10. Four ball tester T-02U:
1 – body, *2* – power train, *3* – friction pair load bearing drive, *4* – ball cup assembly, *5* – base

The friction pair (Fig. 5.11) consists of three lower balls fixed in a clamp and loaded with appropriate force applied by the top ball mounted on a spindle rotating with a determined speed. The typical ball bearings of 1/2” diameter were used for the tests. The bearings are made of GCR15 bearing steel with hardness of 60÷65 HRC. The mechanical system allows linear increasing of the load applied to the friction pair during a test. The metering-control system consists of a dedicated microprocessor based controller, asynchronous motor controller and a computer with special control software.

The tests were conducted under conditions of gradual load increase. The rotation speed during tests was 500 rpm, with the load increase rate of 409 N/s. The initial temperature of the fuel sample at the start of the test run was 60 ± 1.0 °C. Within the scope of this test, by definition a friction pair seizure is said to have occurred once the boundary friction torque M_T, of 10 Nm is exceeded. This value is determined by the durability of the top ball shank in the friction pair. The friction torque M_T and the linearly increasing friction pair load P were recorded during testing.

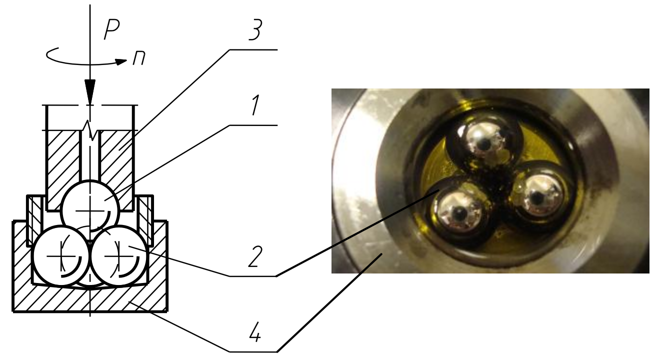


Fig. 5.11. Four ball tester friction pair:
1 – top ball, *2* – bottom balls, *3* – spring clamp, *4* – balls cup

The principle of the method is determining of the scuffing load applied to the friction pair (Fig. 5.12). Load *P* in point *1* where the friction torque value starts to increase rapidly is called the scuffing load and denoted as P_S. The values of P_S were reading from files recorded during test run. The reading errors of P_S have been estimated to be ±20 N. The point 2 is a point of scuffing. At this moment the maximal friction torque M_T that is equal to 10 Nm, is reached. The load *P* in point *2* is called boundary scuffing load $P_{b.l.}$.

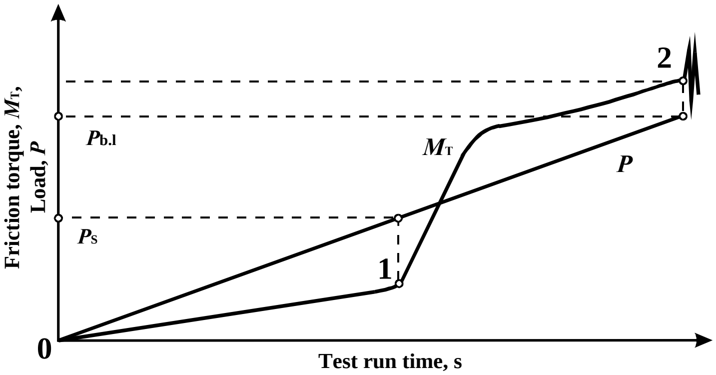


Fig. 5.12. The method for determining the scuffing load P_S:
1 – the point of scuffing initialization; *2* – point of scuffing

Thus, the fuel sample with the highest value of applied scuffing load is considered to have the best antiwear properties. Other words, it means that the boundary film of this fuel sample demonstrated the highest durability to breaking.

11) Thermal stability of JF, bio-additives and blended JFs, otherwords, thermal analysis was done at the derivatograph Q-1500D of the system “Paulik–Paulik–Erday” with computer registration of analytic signal of mass loss and thermal effects. The samples were analyzed in dynamic regime with heating speed of 8 °C/min in air atmosphere; mass of samples was 0.2 g. The reference substance was aluminum oxide. Analysis of curves of the thermal gravimetry (TG) and the

differential thermal gravimetry (DTG) allows determining and studying the mass loss of samples during its heating. The curves of the differential thermal analysis (DTA) allow determining temperature intervals of thermal effects, which take place during samples heating. The analysis allows concluding about thermal resistance of fuels, which is important characteristic of combustion process and termal stability.

Graphical data were built with the help of computer programs Mathcad 15, Grapher 8, ChemDraw Ultra 11.0, Chem3D Pro 11.0, Avogadro, Jmol and MS Visio.

5.4. Results and discussion

5.4.1. Density

The density ρ of JFs is one of its main physical characteristics and defined as the ratio of fuel mass *m* to volume *V* that it occupies:

$$\rho = \frac{m}{V}, \text{ kg/m}^3. \tag{5.1}$$

Density influence directly on the flammability of fuel: the processes of evaporation, fuel-air mixture (FAM) formation, completeness of combustion and fuel flow (FF). The required density of JFs ensures reliable operation of fuel system of JE.

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

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

The density of the JFs depends on its chemical and fractional composition. Bio-additives – FAME and FAEE of RO and FAEE of CamO – possess much higher density values comparing to the density of conventional JF (Table 5.2). It can be explained by its chemical structure. Unlike hydrocarbons of conventional JFs, which contain 5÷16 carbon atoms, acyl radicals of ester molecules contain on average 15÷26 carbon atoms. This is the reason of a strong dispersion interaction forces between them and, consequently, higher density compared to JFs. According to the data in Table 5.2 density of both RO and CamO FAEE is slightly lower than of FAME bio-additives. This can be explained by the presence of additional CH_2 group in radical of ethanol, which decreases compactness of mutual displacement of ester molecules.

Table 5.2

Density of studied fuel samples

No	Designation of fuel sample	Density, kg/m^3
1	Jet fuel of grade Jet A-1	794.03
2	FAME of rapeseed oil	882.92
3	Modified FAME of rapeseed oil	883.68
4	Modified FAEE of rapeseed oil	876.58
5	FAEE of camelina oil	874.49

According to the research of bio-additives samples impact on JFs' density (Fig. 5.13, 5.14), it was found that density dependence is additive in nature and may be depicted as a straight line.

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

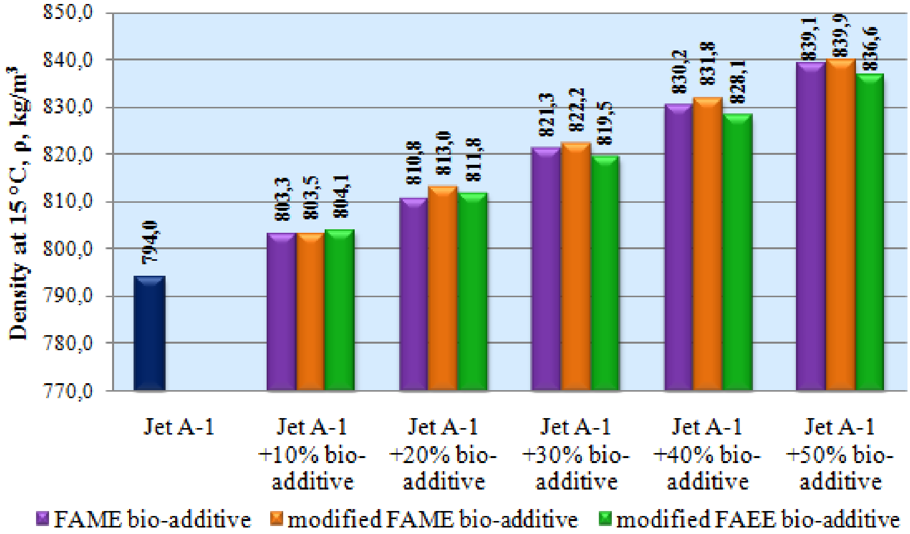


Fig. 5.13. Density of tested fuel samples with RO bio-additives at *t* 15 °C

It was found that JFs blended with RO FAEE has slightly lower density values. Modified FAEE have a lower density comparing to FAME, which affects the density of blended JFs respectively. The similar results are observed for JF blends with CamO FAEE, which have lower density comparing to RO FAEE.

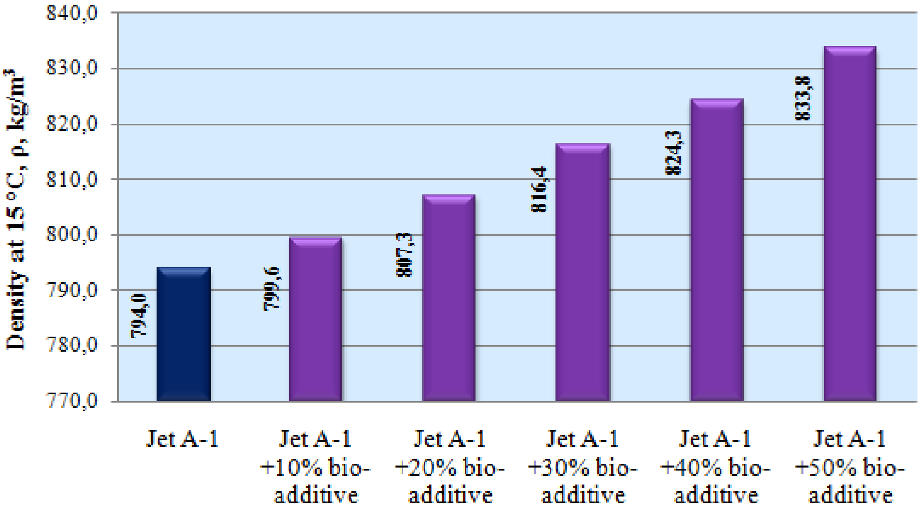


Fig. 5.14. Density of tested fuel samples with CamO bio-additives at *t* 15 °C

The results of mathematical processing of the experimental data allowed deriving the regression equations, which describe the dependence of the density ρ of blended JFs on the concentration of bioadditives *c*:

For FAME bio-additive:

$$\rho_1 = 794.04 + 0.872c + 6.482 \cdot 10^{-4} c^2,$$

For modified FAME bio-additive:

$$\rho_2 = 793.92 + 0.983c - 1.159 \cdot 10^{-3} c^2,$$

For modified FAEE bio-additive:

$$\rho_3 = 794.542 + 0.874c - 7.821 \cdot 10^{-4} c^2.$$

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

5.4.2. Fractional composition

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

Since bio-additives are also a mixture of organic compounds, a range of boiling points is also typical for it. They belong to another class of organic compounds, which differ from petroleum hydrocarbons and from each other by structure, molecular weight and boiling points. Within the scope of the work fractional composition of bio-additives: RO FAME, RO modified FAME and RO modified FAEE was studied (Fig. 5.15).

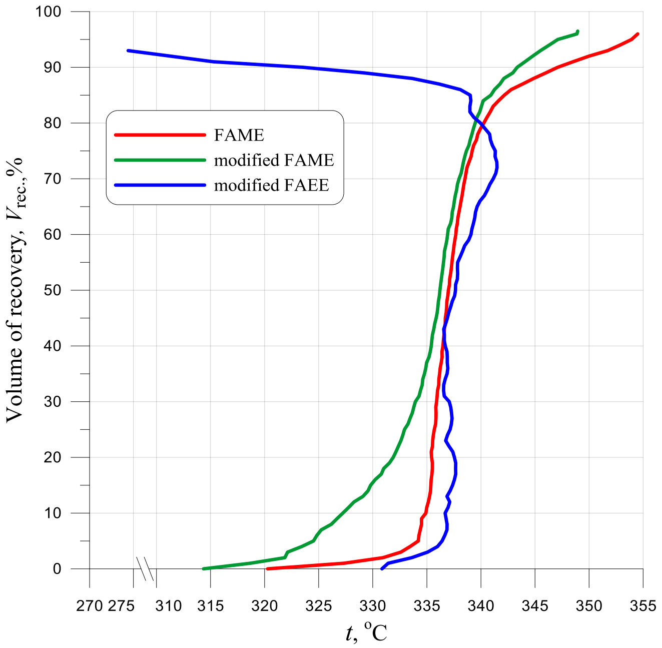


Fig. 5.15. Fractional composition of bio-additives

The received data indicate homogeneous composition of bio-additives, which differ from the fractional composition of JFs (150÷300 °C). The curves show that the main part of fatty acid esters (about 75÷80 %) boils at narrow temperature range (~20÷25 °C): FAME ~334÷343 °C, modified FAME ~320÷345 °C. This is due to the fact that bio-additives are on ~80 % composed of esters of oleic, linoleic and linolenic acids.

The differences in boiling curve of modified FAEE and boiling curves of FAME and modified FAME were marked. Methyl esters are characterized by a steady gradual increase of the boiling temperatures. Boiling of ethyl esters is not uniform and accompanied by periodic decrease of boiling temperature.

Initial boiling point of modified FAEE is higher (331 °C) comparing to FAME (320 °C) and modified FAME (314 °C), which is explained by the presence of additional CH_2 group in the alcohol radicals of ethyl esters and, consequently, higher heat of evaporation compared to methyl esters. Maximal boiling point of modified FAEE was 342 °C. Temperature drop till 274 °C may be caused by modified FAEE thermal decomposition that occurs with the formation of lighter products, with lower boiling points. Additional CH_2 group in ethyl ester molecules causes an increase of boiling temperature that exceeds the temperature of molecules thermal decomposition.

Next, the influence of bio-additives on fractional composition of JFs was studied (Fig. 5.16÷5.19). Fuel samples containing RO FAME, RO modified FAME, RO modified FAEE and CamO FAEE in JF of grade Jet A-1 in quantities of 10 %, 20 %, 30 %, 40 % and 50 % (v/v) were studied.

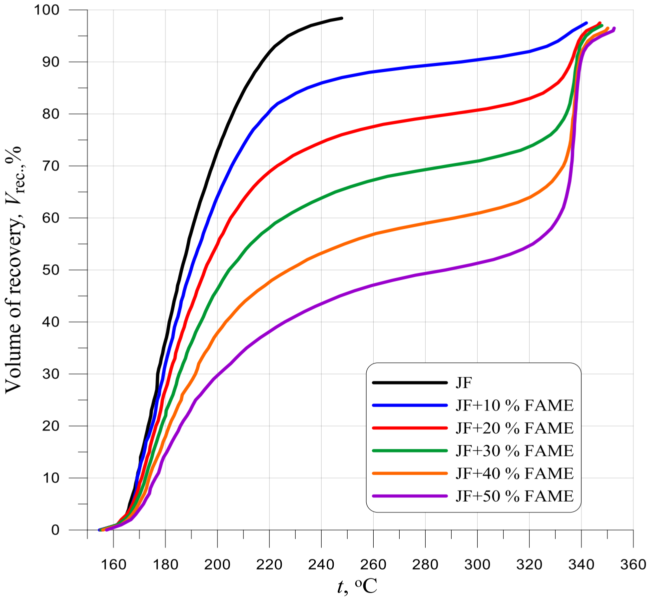


Fig. 5.16. Fractional composition of JF of grade Jet A-1 blended with RO FAME

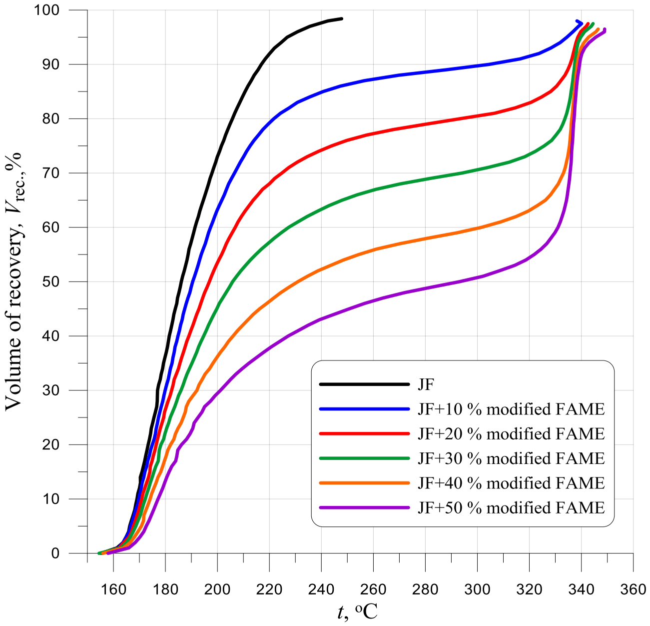


Fig. 5.17. Fractional composition of JF of grade Jet A-1 blended with RO modified FAME

The graphs show that blending JF with bio-additives affect its fractional composition, extending toward the final boiling point. Increasing of boiling points of blended JFs is explained by much stronger intermolecular bonds between esters molecules and higher heat of evaporation values of ester consequently: 57.5÷67.7 kJ/mol for FAME; 58.6÷69.3 kJ/mol for FAEE comparing to JF's hydrocarbon 31÷47 kJ/mol.

However, quite different results were obtained for fractinal composition of JF samples blended with CamO bio-additives. From the graph on Fig. 5.19 it may be seen that boiling of fuel samples starts at about 76÷77 °C. This means that CamO bio-additive contains some amount of ethanol that left in esters mixture after production process. Analyzing the data on the graph it may be concluded that the content of ethanol is up to 5÷7 % The final boiling points of fuel sample are about 347÷350 °C, which are similar to samples with RO bio-additives.

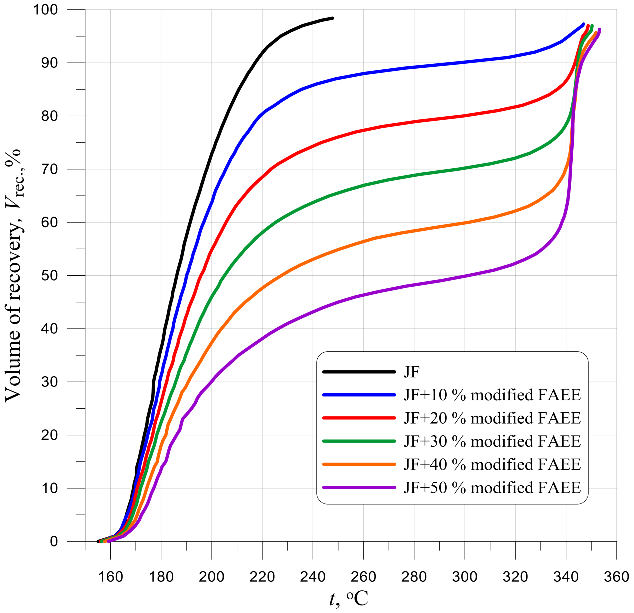


Fig. 5.18. Fractional composition of JF of grade Jet A-1 blended with RO modified FAEE

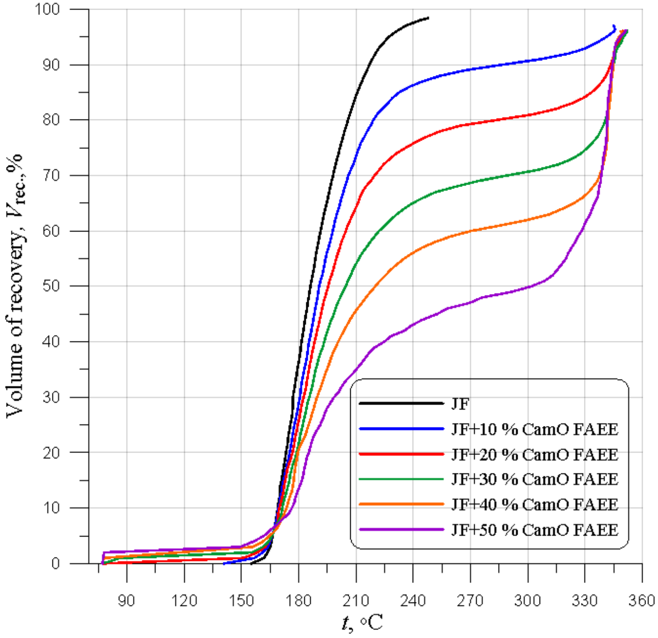


Fig. 5.19. Fractional composition of JF of grade Jet A-1 blended with CamO FAEE

Evaporability of JFs has an ambiguous effect on the exploitation properties of aircrafts. During high-altitude flights evaporability affects the fuel losses from evaporation in the fuel tanks, due to a decrease of atmospheric pressure. In addition, the evaporability of fuel increases during the climbing with increasing temperature due to aerodynamic heating. Increased evaporability negatively affects the operation of fuel pumps during high-altitude flights and causes formation of vapor locks in fuel system of JE. Increasing content of light fractions in JFs leads to increasing of vapor pressure. Other words, the lighter fractional composition of fuel, the greater is evaporability and vice versa. During the exploitation of JFs it was observed that the increase in evaporability negatively affects their fire safety.

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

However, the lighter fraction composition and higher vapor pressure, the better starting properties of JFs. Thus, fuels with high evaporability are able to provide JE launch with poor FAM comparing to fuels with lower evaporability. In addition, increased volatility of fuels contributes to the increase of completeness of combustion and reduction of carbon formation in combustion chambers. Studies of blended JFs showed that initial boiling point and temperature of 10 % (vol.) of recovery, which characterize evaporability and starting properties of JFs are within the values, which are set by specifications for JF of grade Jet A-1 (Table 3.1). Thus, the use of blended fuels should not have a negative impact on the launch of JEs. The final boiling point of blended JFs (up to 355 °C) significantly exceeds the norms established by specifications (up to 300 °C). This heavy fractional composition due to increased density of blended JFs will increase their energy value. Moreover, analyzing the requirements of specification for JFs of grades T6, T8-B, Jp-5, Jp-8, which are characterized by increased final boiling points, it can be concluded that bio-additives can be used also for blending with conventional JFs of heavy fractional composition.

5.4.3. Energy properties

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

Usually the flammability or energy properties of JF are estimated in two ways:

1. per unit mass – (net) heat of combustion Q_m, kJ/kg,
2. per unit volume – energy value (energy content) Q_v, kJ/l.

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

Data about the elemental composition of JF allows calculating its heat of combustion. *Higher heat of combustion* Q_h takes into account the heat of condensation of water vapors, which are formed during combustion. During the process of water condensation 2500 kJ/kg of energy is released. It is known that heat of vapors condensation is not used during engine operation, so the *lower heat of combustion* Q_l is used to characterize the fuel. Its value is less than higher heat of combustion on heat of water vapors condensation. So, knowing that combustion of 1 kg of fuel produces 9 kg of water it can be easily calculated:

$$Q_{\mathrm{l}} = Q_{\mathrm{h}} - 2500 \cdot 9[H] = Q_{\mathrm{h}} - 22500[H] \tag{5.2}$$

The method ASTM D4809 [127] allows experimental determination of Q_h of fuel samples. Later Q_l values were calculated according to the formula:

$$Q_{\mathrm{l}} = Q_{\mathrm{h}} - 25(9\mathrm{H} + \mathrm{W}), \tag{5.3}$$

where Q_l – lower heat of combustion, kJ/kg;
Q_h – higher heat of combustion, kJ/kg;
H – mass ration of hydrogen in fuel sample, % (mas.).

Statistical data about the hydrogen content in JFs were used for calculation Ql. The content of hydrogen in bio-additives was calculated according to the data in Table 4.1. The content of sulfur was determined according to the method, described in chapter 5.3. The elemental composition of JFs and bio-additives is given in Table. 5.3.

Table 5.3

Elemental composition of JF and bio-additives samples

No	Designation of fuel sample	Content of chemical elements in fuel,%			
		C	H	S	O
1	Jet fuel of grade Jet A-1	84.975	14.0	0.025	-
2	FAME of rapeseed oil	76.564	12.013	0.0071	11.423
3	Modified FAME of rapeseed oil	76.490	11.988	0.0066	11.5157
4	Modified FAEE of rapeseed oil	76.889	12.095	0.0085	11.0075

The results of measurements and calculations of heat of combustion of JF and bio-additives samples are presented in Table 5.4.

Table 5.4

Heat of combustion of JF and bio-additives samples

No	Designation of fuel sample	Higher net heat of combustion, kJ/kg	Lower net heat of combustion, kJ/kg
1	Jet fuel of grade Jet A-1	46368	43218
2	FAME of rapeseed oil	40018	37315
3	Modified FAME of rapeseed oil	39828	37131
4	Modified FAEE of rapeseed oil	40271	37550
5	FAEE of camelina oil	39842	-

From the data above we see that heat of combustion of JF meets the requirements established by specification (not less than 42800 kJ/kg). The heat of combustion of bio-additives is lower on 5700÷6000 kJ/kg, that is explained by differences in elemental composition of bio-additives: esters contain ~12 % of hydrogen, while JF – 14 %. Esters contain 11÷11.5 % of oxygen, which almost absent in conventional JF. Modified FAEE has the highest heat of combustion among bio-additives. FAEE molecules contain one more CH_2 group comparing to FAME. Due to this mass ratio of hydrogen is greater, and oxygen – is lower.

Later the lower heat of combustion Ql of JFs blended with bio-additives was investigated. It was found that blending of conventional JF with bio-additives reduces its net heat of combustion (Fig. 5.20).

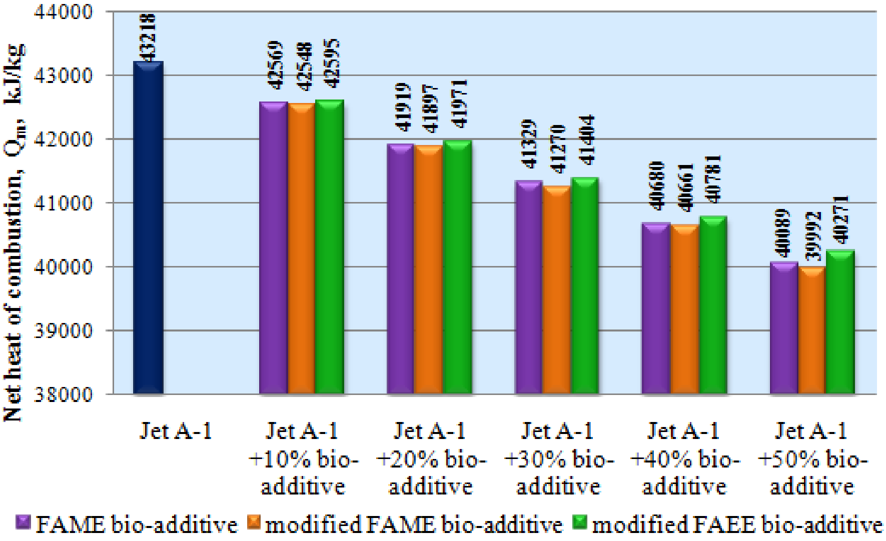


Fig. 5.20. Net heat of combustion of tested fuel samples with RO bio-additives

The results of mathematical processing of the experimental data allowed deriving the regression equations, which describe the dependence of the net heat of combustion Q_l of blended JFs on the concentration of bioadditives c:

For FAME bio-additive:

$$Q_{\mathrm{l}\,1} = 4.322\cdot 10^4 - 65.202c + 0.053c^2,$$

For modified FAME bio-additive:

$$Q_{\mathrm{l}\,2} = 4.322\cdot 10^4 - 65.596c + 0.031c^2,$$

For modified FAEE bio-additive:

$$Q_{\mathrm{l}\,3} = 4.322\cdot 10^4 - 65.349c + 0.102c^2.$$

Later the higher heat of combustion Q_h of JFs modified with bio-additives was investigated. It was found that blending of conventional JF with bio-additives reduces its higher heat of combustion (Fig. 5.21).

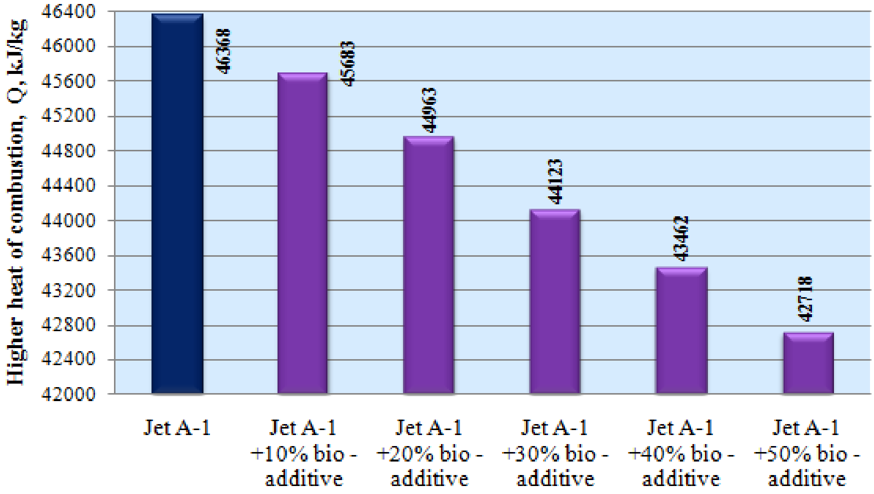


Fig. 5.21. Higher heat of combustion of JF of grade Jet A-1 blended with CamO FAEE

An additional energy characteristic of JFs is energy value Q_v that influences on flight range. It increases the amount of energy on aircraft board and therefore the flight range. The relationship of mass heat of combustion and energy value may be represented by this expression:

$$Q_{\mathrm{v}} = Q_{\mathrm{m}} \cdot \rho. \tag{5.4}$$

where:

Q_v – energy value, kJ/kg,
Q_m – net heat of combustion, kJ/kg,
ρ – density, kg/m^3.

Taking into account that the density of blended JFs increases it is necessary to study how this affects its energy value. The calculation results are shown at Fig. 5.22. The energy value of esters is also lower comparing to the JF. However, due to the greater density of bio-additives the difference in energy values of bio-additives and JF is not significant and makes about 1370÷1500 kJ/l.

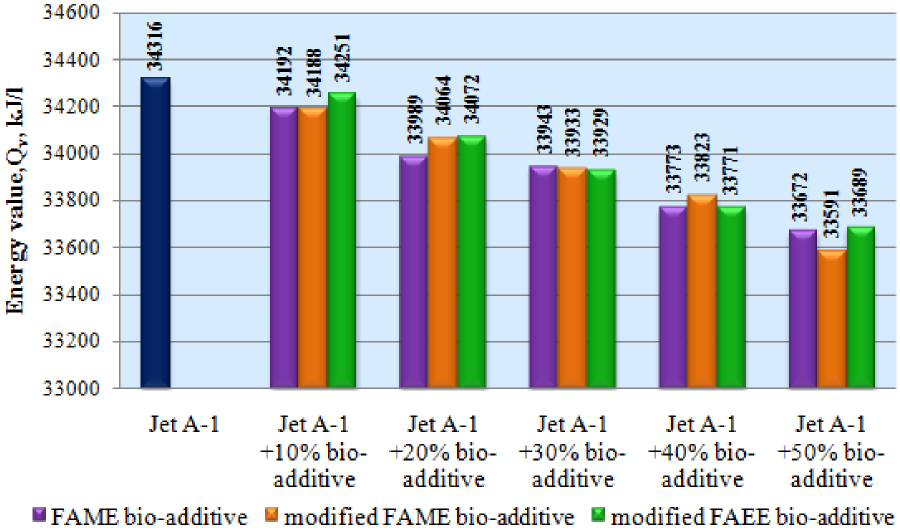


Fig. 5.22. Energy value of tested fuel samples

The results have shown that the blending JFs with bio-additives decreases its heat of combustion. Due to the fact that esters and blended JFs have higher density, it is reasonable to analyze the changes in heat of combustion and energy value with increasing content of esters in JF (Fig. 5.23÷5.25).

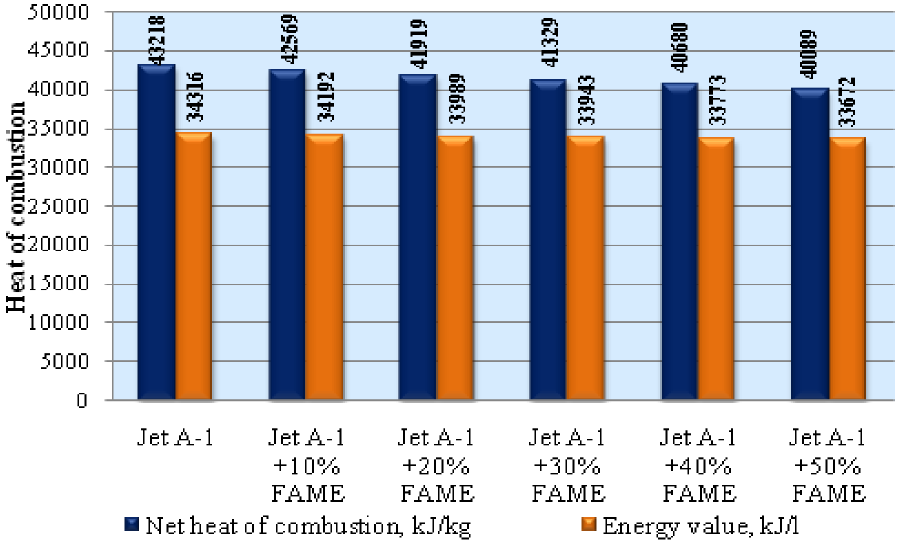


Fig. 5.23. The dependence of heat of combustion and energy value of JF when blending with RO FAME bio-additive

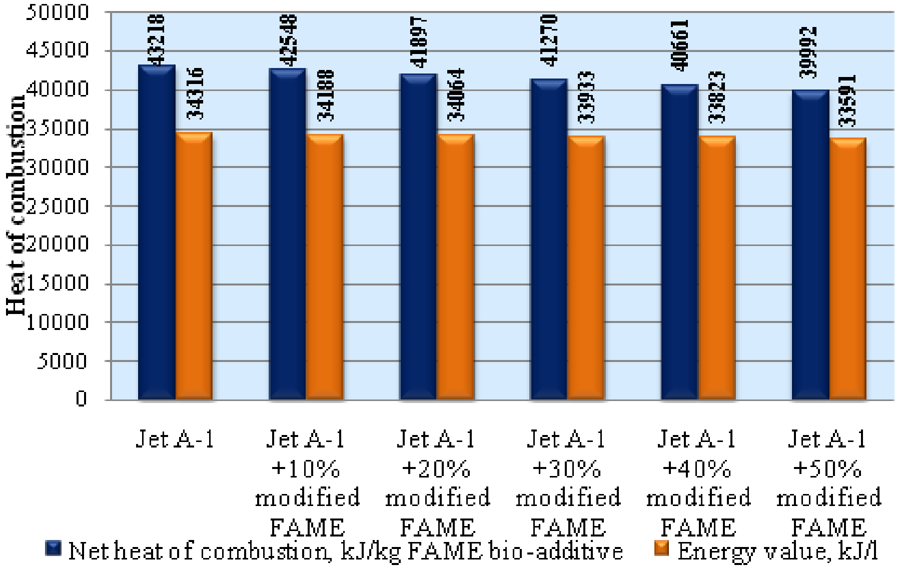


Fig. 5.24. The dependence of heat of combustion and energy value of JF when blending with RO modified FAME bio-additive

The diagrams above show that due to increased density of esters, the reduction of energy value of blended JFs is negligibly small and within 1.8÷2.1% when adding bio-components in quantity 50 %. Increasing of blended JFs density compensates its heat of combustion. The energy value of blended JFs is at the level, typical for conventional JFs.

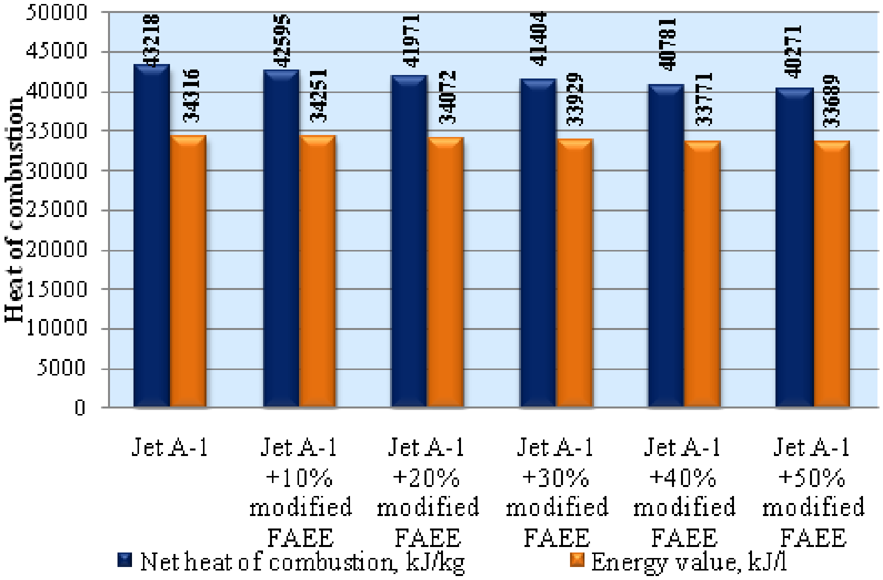


Fig. 5.25. The dependence of heat of combustion and energy value of JF when blending with RO modified FAEE bio-additive

5.4.4. Kinematic viscosity

Stable operation of JE’s fuel system at low temperatures largely depends on the fluidity of JFs that is measured by viscosity – a property of liquids to resist deformation of its volume by external forces. Viscosity decreases with increasing temperature and slightly increases with increasing external pressure. According to specifications for JF the standard value for describing viscosity is kinematic viscosity ν, mm^2/s.

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

Bio-additives based on FAME and FAEE of RO and FAEE of CamO are characterized by much higher viscosity values comparing to petroleum-derived JFs (Table. 5.5).

The reason for this is chemical structure of bio-additives. Chain length determines the large size of the compounds, which leads to higher energy of intermolecular interaction. Viscosity characterizes the strength of intermolecular interaction within the fuel. The greater energy of intermolecular interaction, the greater is viscosity. It explains stronger dependence of esters’ viscosity on temperature (Fig. 5.25).

Table 5.5

Kinematic viscosity of JF and bio-additives samples

No	Designation of fuel sample	Kinematic viscosity at *t*=20 °C, mm^2/s
1	Jet fuel of grade Jet A-1	1.5004
2	FAME of rapeseed oil	7.2017
3	Modified FAME of rapeseed oil	6.7341
4	Modified FAEE of rapeseed oil	7.2710
5	FAEE of camelina oil	6.4218

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

Modified RO FAEE has higher viscosity values due to the presence of additional CH_2 group. The highest viscosity values are typical for RO FAME; the reason is presence of esters of high molecular weight and hydrocarbon chain length, which were not separated during vacuum distillation. The lowest viscosity values are typical for CamO FAEE bioaditive. Probably, this may be explained by the presence in bio-additive of small quantity of ethanol that possesses much smaller viscosity.

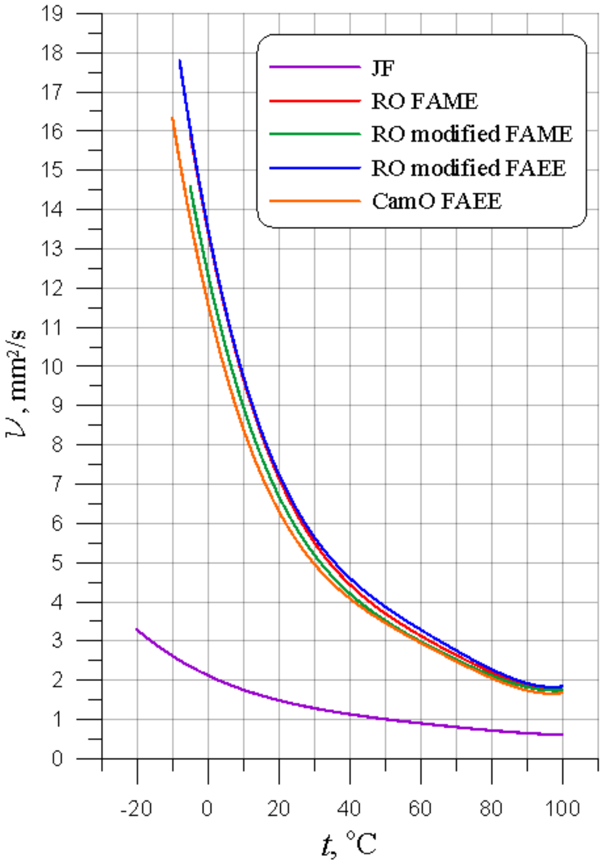


Fig. 5.25. Fuel samples viscosity as a function of temperature

Later the influence of RO and CamO bio-additives on kinematic viscosity of blended JFs at 20 °C was studied (Fig. 5.26, 5.27).

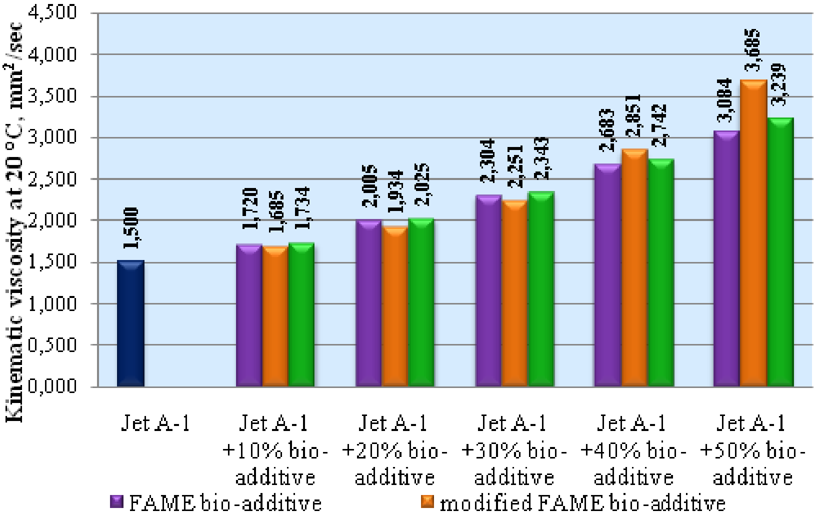


Fig. 5.26. Kinematic viscosity of tested fuel samples with RO bio-additives at 20 °C

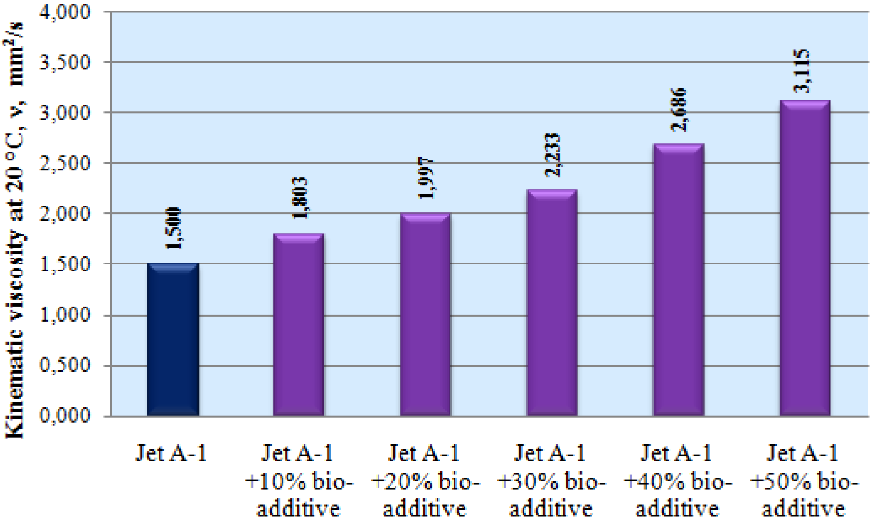


Fig. 5.27. Kinematic viscosity of tested fuel samples with CamO bio-additive at 20 °C

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

The results of mathematical processing of the experimental data allowed deriving the regression equations, which describe the dependence of kinematic viscosity ν of blended JFs on the concentration of bioadditives *c*:

For FAME bio-additive:

$$\nu_1 = 1.542 + 5.759 \cdot 10^{-4} c + 8.308 \cdot 10^{-4} c^2,$$

For modified FAME bio-additive:

$$\nu_2 = 1.499 + 0.02c + 2.295 \cdot 10^{-3} c^2,$$

For modified FAEE bio-additive:

$$\nu_3 = 1.508 + 0.019c + 3.119 \cdot 10^{-4} c^2.$$

5.4.5. Low-temperature properties

Low-temperature fuel properties of JFs are characterized by its behavior at low temperatures and are strictly controlled by specifications. During exploitation JEs usually have to work at very low temperatures, especially in winter. In summer period fuel also can be cooled during high-altitude flights of subsonic jet aircrafts. The reason for this is that the ambient temperature at an altitude of 9–12 km reaches minus 50÷70 °C.

Cooling of JFs may be accompanied with clogging of fuel filters that may be associated with aircrafts accidents and disasters. Cooling of fuel also affects reduction of spraying efficiency by fuel nozzles and worsening fuel pumps operation.

In general, low-temperature properties of fuels are characterized by complex of physical and chemical phenomena, which occur in fuels at temperatures below 0 °C. Low temperature is a condition for occuring insoluble organic precipitates that affect operation of the fuel system. The main reasons for its occurrence are the sharp decrease of solubility of some components in fuel at low temperatures and phase transitions. These precipitates are a composition of amorphous and crystalline compounds. Amorphous parts include heterorganic compounds and salts of organic acids, crystalline parts include hydrocarbons with a high freezing point (FP).

The main source of low-temperature precipitate in JFs is the crystallization of fuel's hydrocarbons when freezing point is reached. Decreasing of temperature causes crystallization of hydrocarbons, rise of crystals concentration and fuel gradually loses its fluidity and then freezes. When reaching pour point (PP) the complete turbidity of fuel is observed. A deeper cooling results in complete solidification of fuel that looks similar to wax.

According to specifications for JFs low-temperature properties are regulated by FP and content of naphthenic acids soaps. In addition, low-temperature properties are estimated by fuel kinematic viscosity at low temperatures. Within the scope of study, low-temperature properties of JFs blended with bio-additives were estimated by PP, FP and kinematic viscosity at low temperatures.

Bio-additives based on FAME and FAEE of RO and FAEE of CamO are characterized by significantly higher values of PP comparing to JF (Table 5.6). High values of bio-additives PP are stipulated by chemical structure of molecules and by Van der Waals interactions between them. The length of the hydrocarbons chain (C_{15}÷C_{25}) defines the large size of the compounds. Due to this binding energy between molecules is higher comparing to conventional JFs.

Table 5.6

PP of JF and bio-additives samples

No	Designation of fuel sample	Pour point, ^oC
1	Jet fuel of grade Jet A-1	minus 59.0
2	FAME of rapeseed oil	minus 15.0
3	Modified FAME of rapeseed oil	minus 19.0
4	Modified FAEE of rapeseed oil	minus 18.5
5	FAEE of camelina oil	minus 11.0

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

The experimental results have shown that blending JFs with bio-additives increased its PP (Fig. 5.28, 5.29). When concentrations of bio-additives are small (less than 30 % (v/v), they are uniformly distributed in the volume of JF and distances between esters' molecules are not enough for interaction appearance. Further increase of esters content causes rise of PP that gradually approaches to values typical for pure esters.

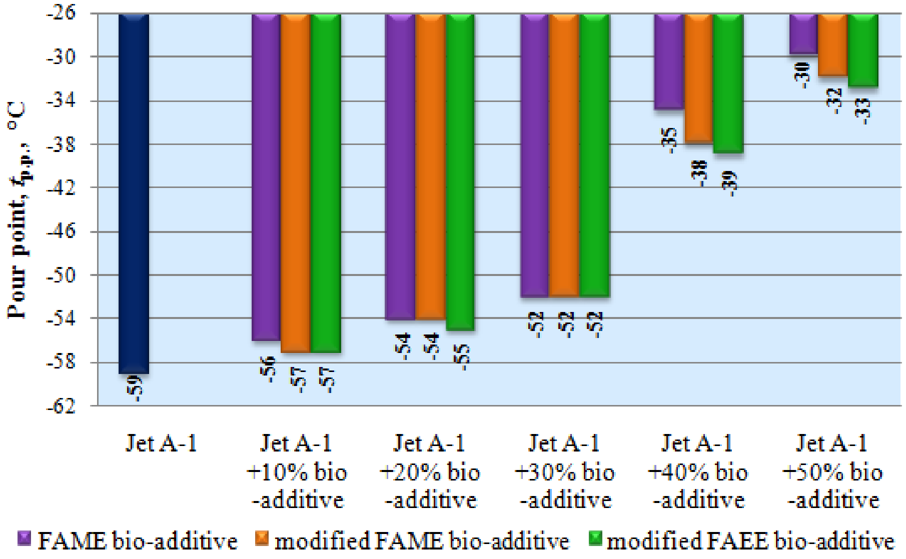


Fig. 5.28. PP of tested fuel samples with RO bio-additives

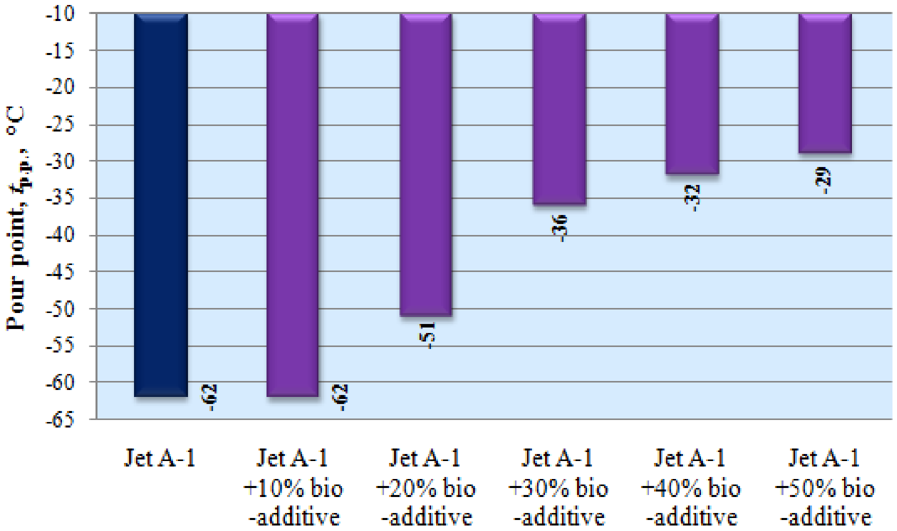


Fig. 5.29. PP of tested fuel samples with CamO bio-additive

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

Basing on the results of experiments we can make the conclusion that sample of blended JFs, which contain up to 30 % of RO FAME, RO modified FAME and RO modified FAEE, satisfy requirements of specifications concerning PP of JFs.

The results of mathematical processing of the experimental data allowed deriving the regression equations, which describe the dependence of PP t_{pp} of blended JFs on the concentration of bioadditives c:

For FAME bio-additive:

$$t_{\text{pp }1} = -58.5 - 0.025c + 0.013c^2,$$

For modified FAME bio-additive:

$$t_{\text{pp }2} = -58.714 - 0.017c + 0.011c^2,$$

For modified FAEE bio-additive:

$$t_{\text{pp }3} = -58.714 - 0.037c + 0.011c^2.$$

Another parameter that was used for characterizing low-temperature properties of blended JFs is colfilte plugging point (CFPP). CFPP is understood as the lowest temperature, at which a given volume of fuel still passes through a standardized filtration device in a specified time when cooled under certain conditions. This test gives an estimate for the lowest temperature that a fuel will give trouble free flow in certain fuel systems. This parameter is typical for describing low-temperaute properties of diesel fuels. However, taking into account that fractional compositions of JF and diesel fuel partially coinsides, CFPP was taken as an additional test for characterizing JFs low-temperature properties.

Similarly to previous tests bio-additives based on FAME and FAEE of RO and FAEE of CamO are characterized by significantly higher values of CFPP comparing to JF (Table 5.7).

Table 5.7

CFPP of JF and bio-additives samples

No	Designation of fuel sample	Pour point, ^{o}C
1	Jet fuel of grade Jet A-1	minus 63.0
2	FAME of rapeseed oil	minus 13.0
3	Modified FAME of rapeseed oil	minus 7.0
4	Modified FAEE of rapeseed oil	minus 10.0
5	FAEE of camelina oil	minus 11.0

Analagously, the experimental results have shown that blending JFs with RO FAME, RO modified FAME, RO modified FAEE and CamO FAEE bio-additives increased its CFPP (Fig. 5.30, 5.31). It may be seen from the graphs that the lowest values of CFPP were obtained for blended JFs with RO modified bio-additive.

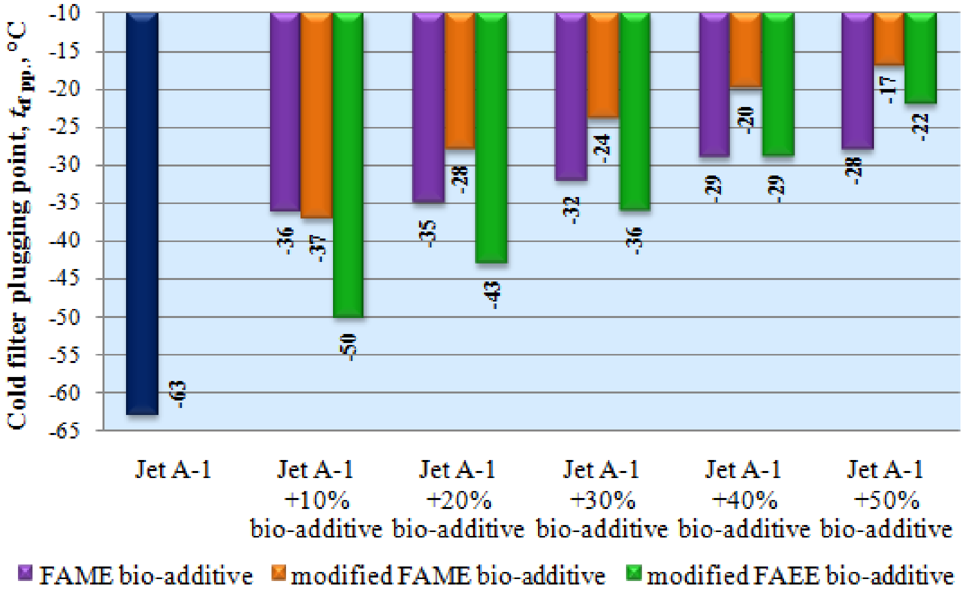


Fig. 5.30. CFPP of tested fuel samples with RO bio-additives

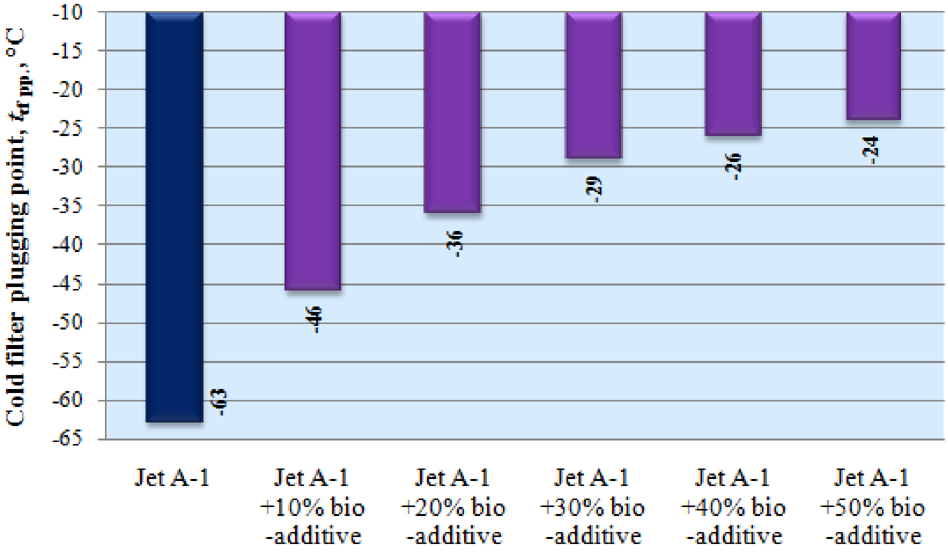


Fig. 5.31. CFPP of tested fuel samples with CamO bio-additive

From the studies [99, 138, 139] it is known that the reason for the decreasing of fuel pumpability at low temperatures is a significant increase in fuels' viscosity. In order to evaluate viscosity of blended JFs at low temperatures we have studied the mutual influence of temperature and concentration of bio-additives on the above mentioned property (Fig. 5.32÷5.35).

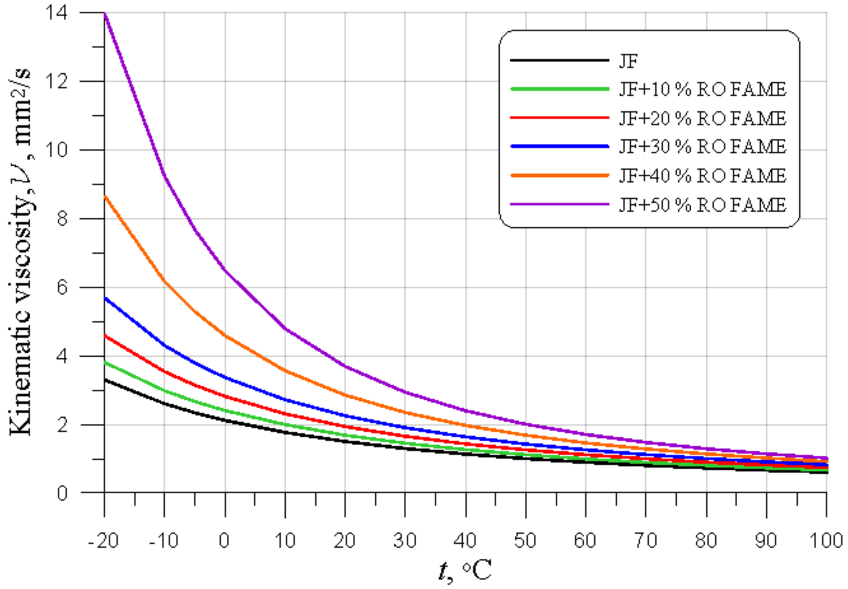


Fig. 5.32. Kinematic viscosity of tested fuel samples with RO FAME bio-additive as a function of temperature

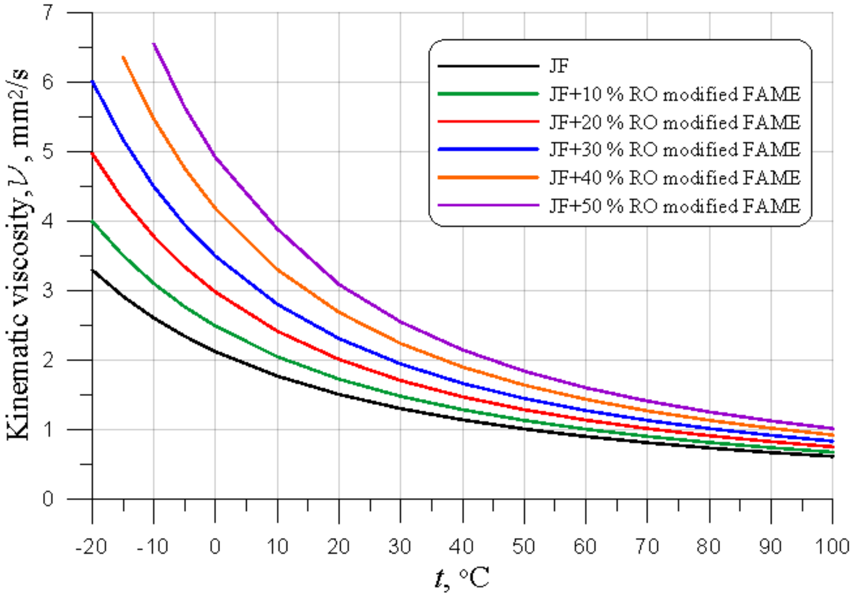


Fig. 5.33. Kinematic viscosity of tested fuel samples with RO modified FAME bio-additive as a function of temperature

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

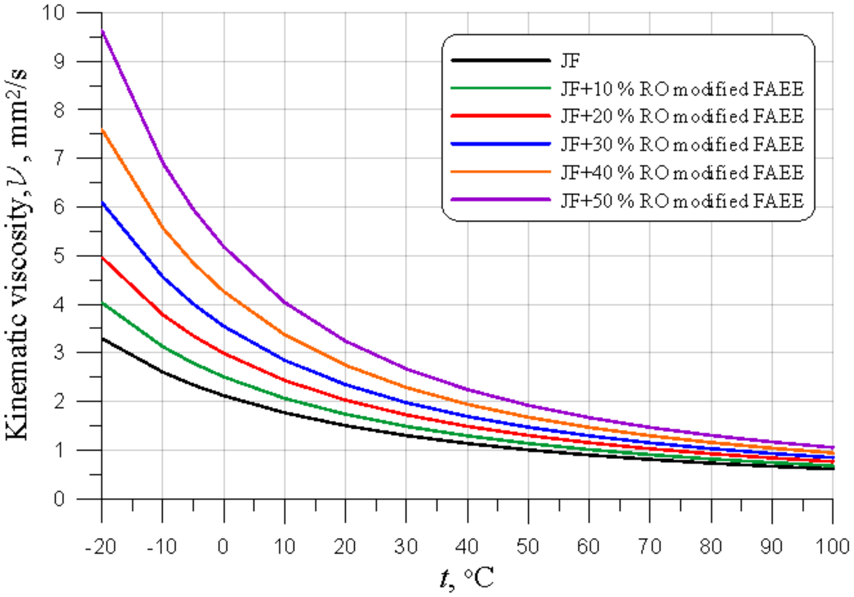


Fig. 5.34. Kinematic viscosity of tested fuel samples with RO modified FAEE bio-additive as a function of temperature

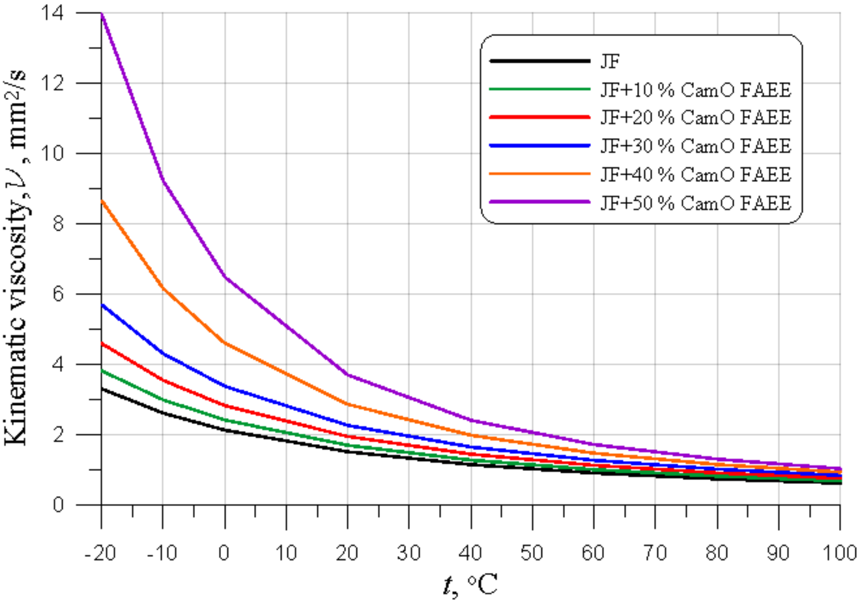


Fig. 5.35. Kinematic viscosity of tested fuel samples with CamO FAEE bio-additive as a function of temperature

For better understanding the mutual influence of temperature and concentration of bio-additives on the viscosity the method of linear regression analysis was applied and 3D models for JF samples blended with RO FAME, RO modified FAME and RO modified FAEE were built (Fig. 5.37÷5.39).

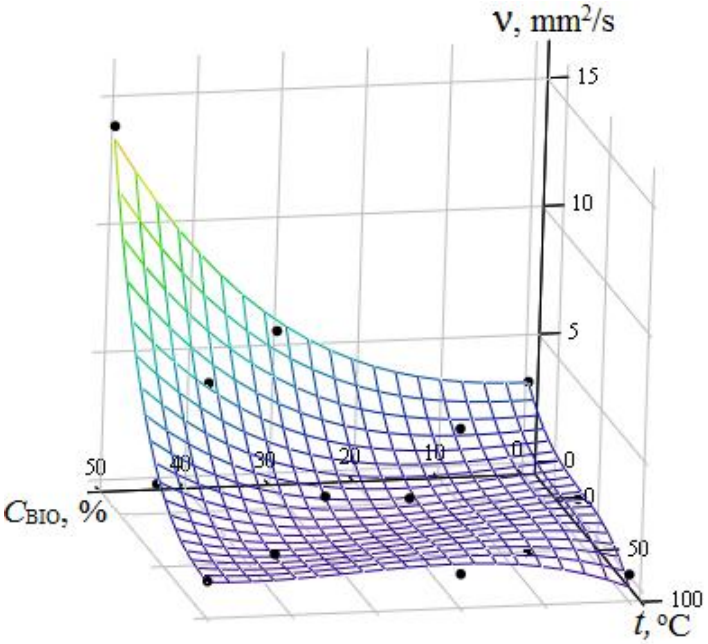


Fig. 5.37. 3D-model of kinematic viscosity of JF of grade Jet A-1 as a function of RO FAME bio-additive content and external temperature

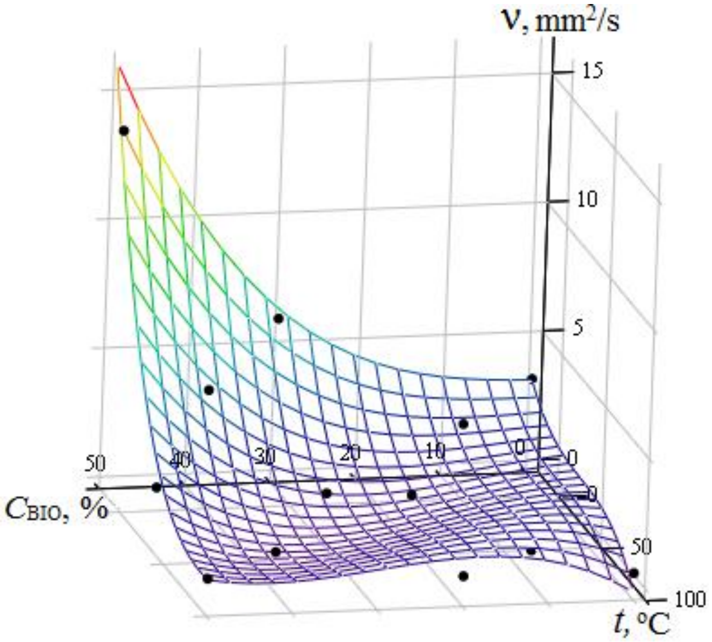


Fig. 5.38. 3D-model of kinematic viscosity of JF of grade Jet A-1 as a function of RO modified FAME bio-additive content and external temperature

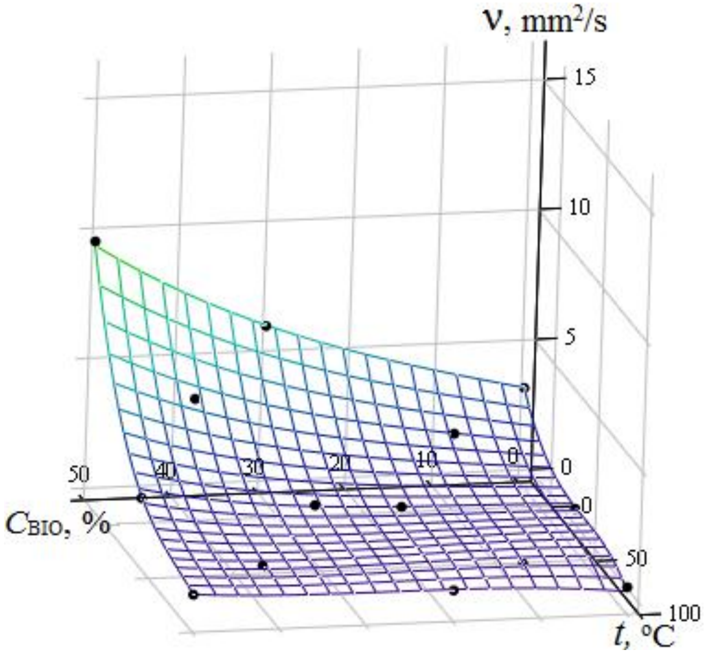


Fig. 5.39. 3D-model of kinematic viscosity of JF of grade Jet A-1 as a function of RO modified FAEE bio-additive content and external temperature

The results of mathematical processing of the experimental data allowed deriving the regression equations of the 3rd order, which describe the mutual influence of temperature t and concentration of bio-additives c on kinematic viscosity ν of blended JFs:

For RO FAME bio-additive:

$$\nu_1 = 2.361 \cdot 10^{-5} - 6.095 \cdot 10^{-6} t + 7.708 \cdot 10^{-4} c - 0.037\, t\, c - 7.784 \cdot 10^{-4} t^2 - 5.334 \cdot 10^{-5} c^2 + 2.179\, t^2 c^2 - 0.024 t^3 + 5.85 \cdot 10^{-4} c^3 + 4.817 \cdot 10^{-5} t^3 c^3,$$

For RO modified FAME bio-additive:

$$\nu_2 = 3.178 \cdot 10^{-5} - 7.146 \cdot 10^{-6} t + 8.053 \cdot 10^{-4} c - 0.033\, t\, c - 8.835 \cdot 10^{-4} t^2 - 7.269 \cdot 10^{-5} c^2 + 2.228\, t^2 c^2 - 0.021 t^3 - 1.031 \cdot 10^{3} c^3 + 9.149 \cdot 10^{-5} t^3 c^3,$$

For RO modified FAEE bio-additive:

$$\nu_3 = 1.252 \cdot 10^{-5} - 6.075 \cdot 10^{-6} t + 9.171 \cdot 10^{-4} c - 0.046\, t\, c - 1.312 \cdot 10^{-3} t^2 - 1.24 \cdot 10^{-5} c^2 + 1.967\, t^2 c^2 + 0.044 t^3 - 1.272 \cdot 10^{-4} c^3 + 1.662 \cdot 10^{-5} t^3 c^3.$$

The coefficients of the derived equations show the presence of both individual impact of factors and their mutual influence.

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

5.4.6. Anti-wear properties

It is known that antiwear properties of jet fuels determine reliability and operational life of aircrafts' fuel system equipment and friction pairs in particular. These pairs usually work in regimes of rolling friction, sliding friction and combined friction at various loads, temperatures, pressure, speed of relative movement. In the conditions of semi-liquid friction the antiwear properties of jet fuels are determined by:

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

As it is noted in works using of fatty acids esters positively influences on lubricating properties of fuels. The following figures 5.36÷5.60 depict the friction torque M_T, friction pair load P and friction coefficient μ that were recorded during tests. The scuffing load P_S describing the criteria for lubricity assessment is marked.

The presented results show that the conventional JF of grade Jet A-1 has demonstrated the lowest value of scuffing load – 511 N. At the same the highest values of scuffing load were observed for two types of bio-additives: 961 N – for FAME and 1150 N – for modified FAME. In general obtained results indicate that increasing portion of bio-additives in blended JFs improves its antiwear properties.

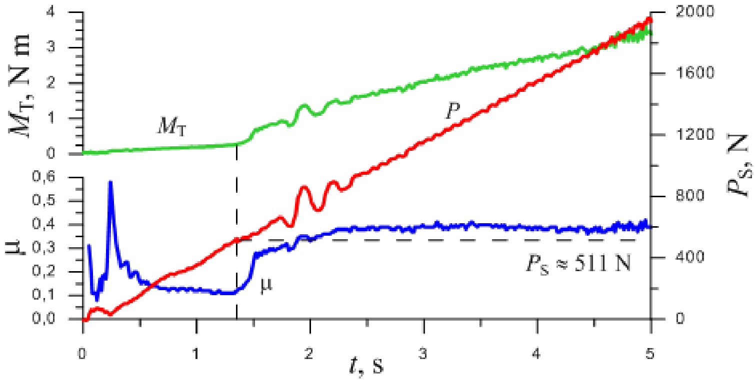


Fig. 5.36. Friction pair load P, friction torque M_T and friction coefficient μ as a function of testing run time t for conventional JF of grade Jet A1; P_S – scuffing load

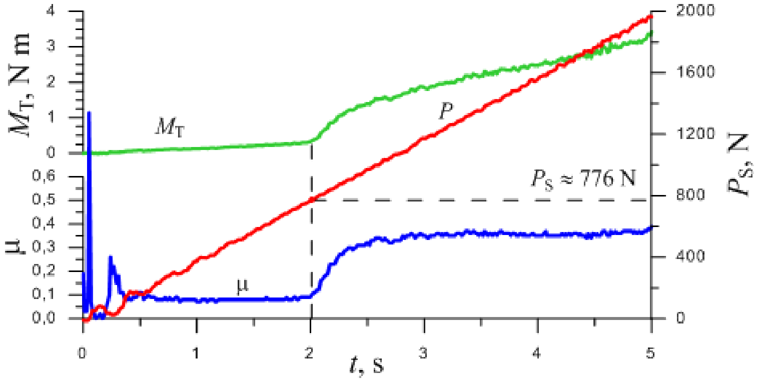


Fig. 5.37. Friction pair load P, friction torque M_T and friction coefficient μ as a function of testing run time t for JF of grade Jet A-1+10% RO FAME; P_S – scuffing load

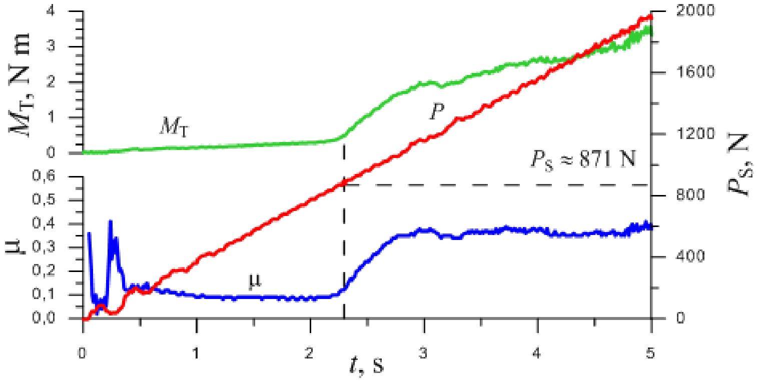


Fig. 5.38. Friction pair load P, friction torque M_T and friction coefficient μ as a function of testing run time t for JF of grade Jet A-1+20% RO FAME; P_S – scuffing load

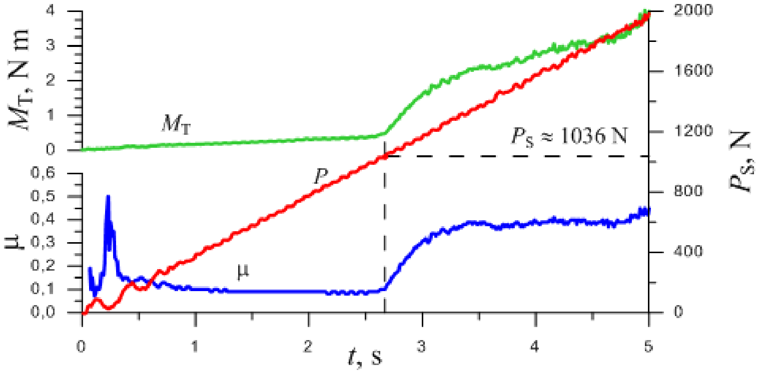


Fig. 5.39. Friction pair load P, friction torque M_T and friction coefficient μ as a function of testing run time t for JF of grade Jet A-1+30% RO FAME; P_S – scuffing load

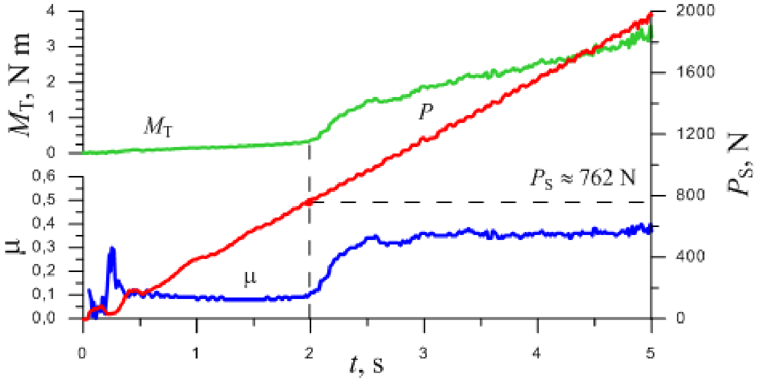


Fig. 5.40. Friction pair load P, friction torque M_T and friction coefficient μ as a function of testing run time t for JF of grade Jet A-1+40% RO FAME; P_S – scuffing load

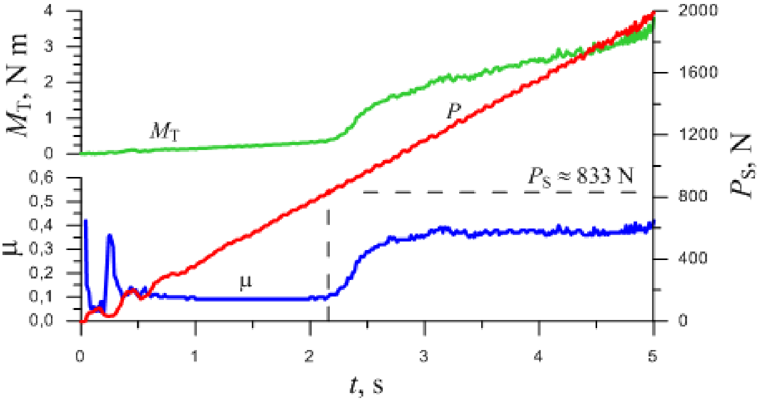


Fig. 5.41. Friction pair load P, friction torque M_T and friction coefficient μ as a function of testing run time t for JF of grade Jet A-1+50% RO FAME; P_S – scuffing load

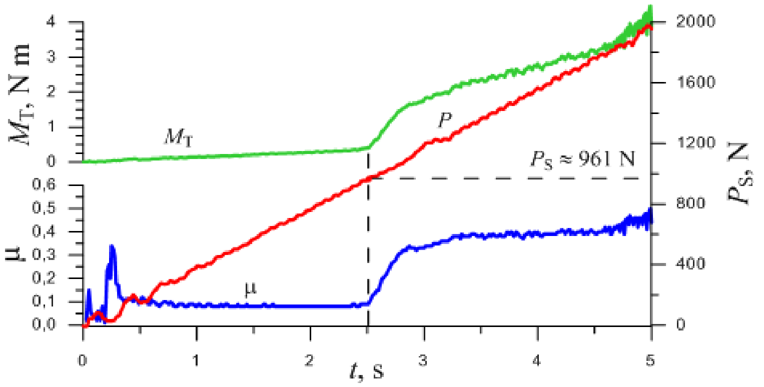


Fig. 5.42. Friction pair load P, friction torque M_T and friction coefficient μ as a function of testing run time t for RO FAME bio-additiv; P_S – scuffing load

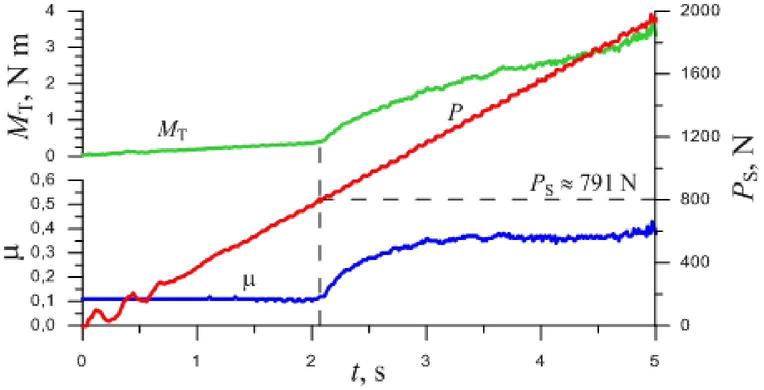


Fig. 5.43. Friction pair load P, friction torque M_T and friction coefficient μ as a function of testing run time t for JF of grade Jet A-1+10% RO modified FAME; P_S – scuffing load

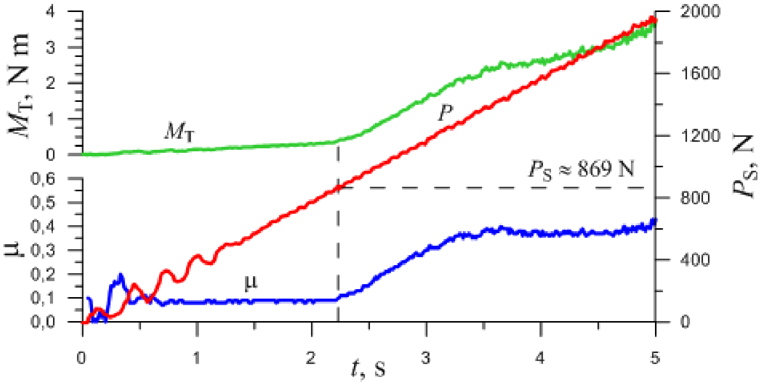


Fig. 5.44. Friction pair load P, friction torque M_T and friction coefficient μ as a function of testing run time t for JF of grade Jet A-1+20% RO modified FAME; P_S – scuffing load

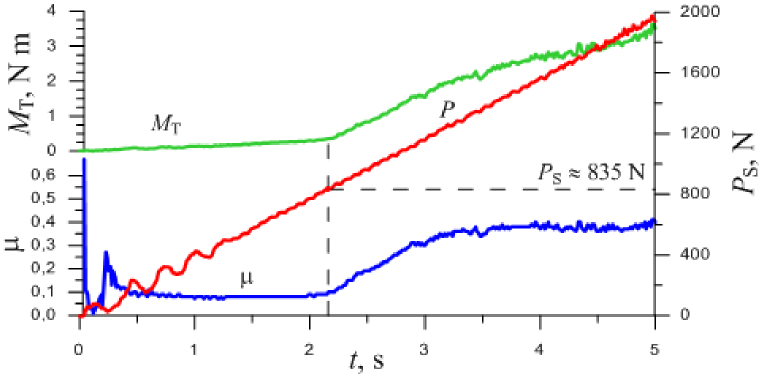


Fig. 5.45. Friction pair load P, friction torque MT and friction coefficient μ as a function of testing run time t for JF of grade Jet A-1+30% RO modified FAME; P_S – scuffing load

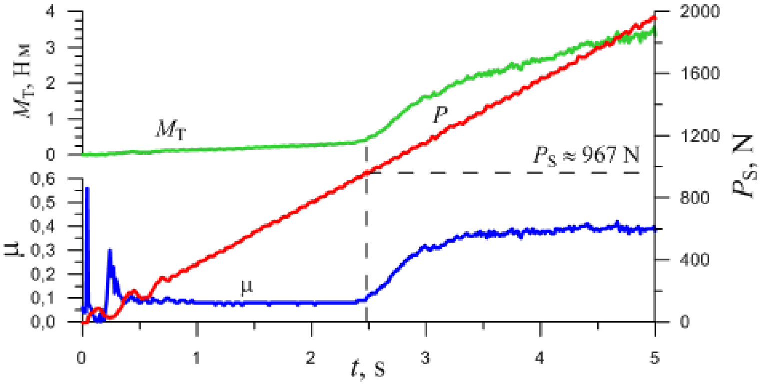


Fig. 5.46. Friction pair load P, friction torque M_T and friction coefficient μ as a function of testing run time t for JF of grade Jet A-1+40% RO modified FAME; P_S – scuffing load

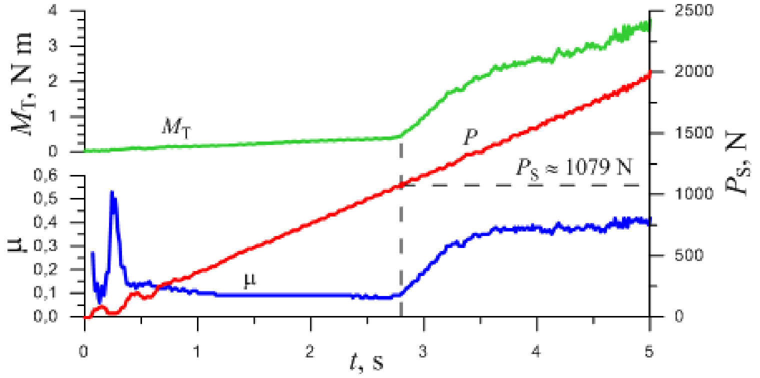


Fig. 5.47. Friction pair load P, friction torque M_T and friction coefficient μ as a function of testing run time t for JF of grade Jet A-1+50% RO modified FAME; P_S – scuffing load

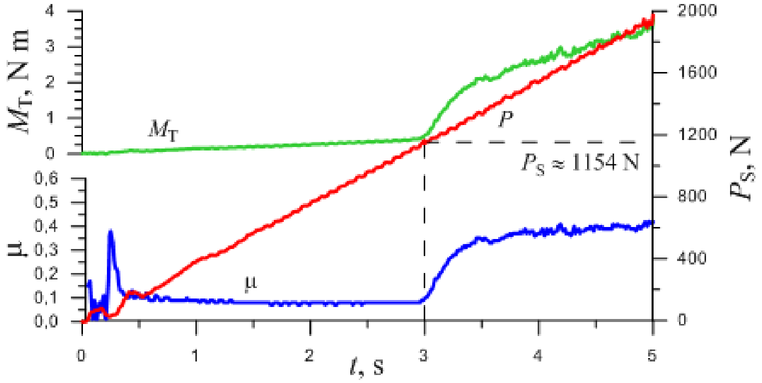


Fig. 5.48. Friction pair load P, friction torque M_T and friction coefficient μ as a function of testing run time t for RO modified FAME; P_S – scuffing load

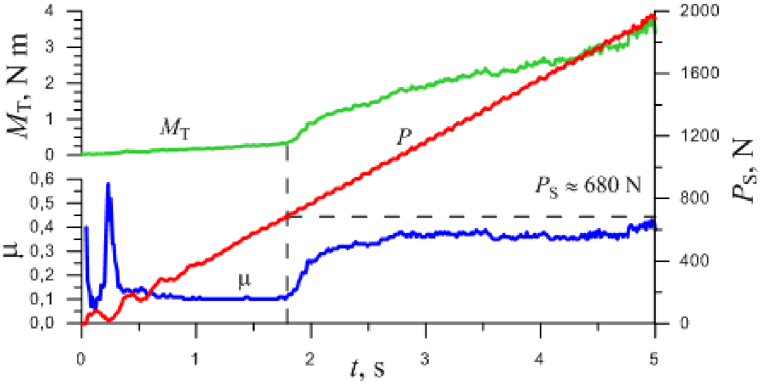


Fig. 5.49. Friction pair load P, friction torque M_T and friction coefficient μ as a function of testing run time t for JF of grade Jet A-1+10% RO modified FAEE; P_S – scuffing load

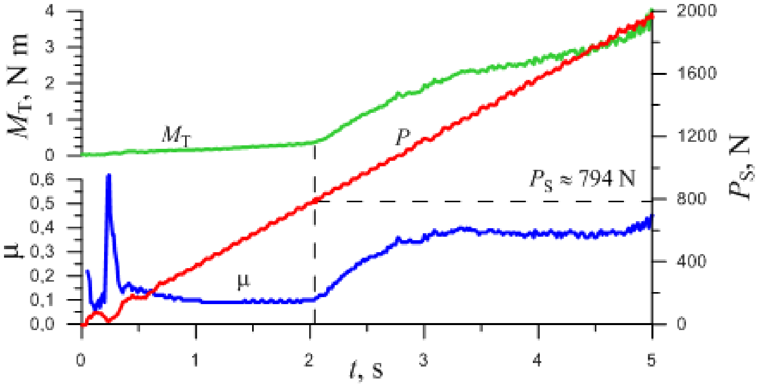


Fig. 5.50. Friction pair load P, friction torque M_T and friction coefficient μ as a function of testing run time t for JF of grade Jet A-1+20% RO modified FAEE; P_S – scuffing load

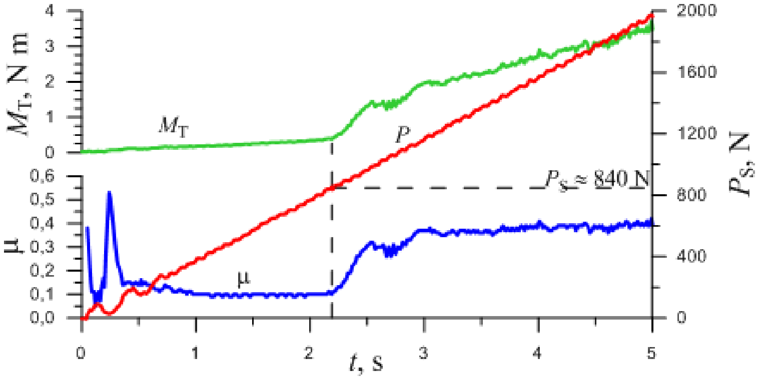


Fig. 5.51. Friction pair load P, friction torque M_T and friction coefficient μ as a function of testing run time t for JF of grade Jet A-1+30% RO modified FAEE; P_S – scuffing load

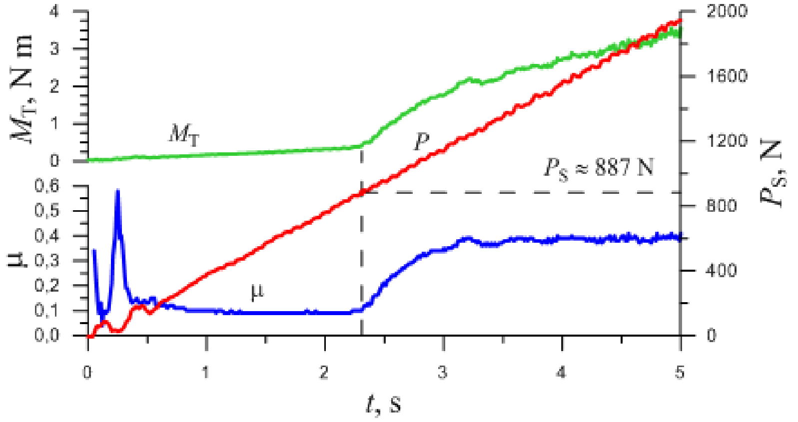


Fig. 5.52. Friction pair load P, friction torque M_T and friction coefficient μ as a function of testing run time t for JF of grade Jet A-1+40% RO modified FAEE; P_S – scuffing load

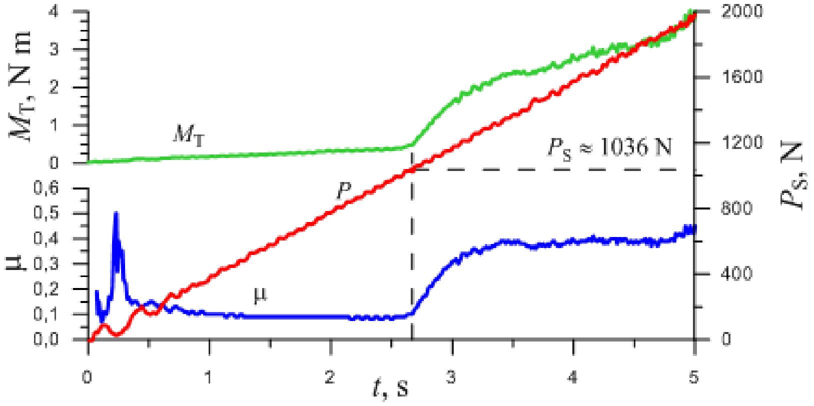


Fig. 5.53. Friction pair load P, friction torque M_T and friction coefficient μ as a function of testing run time t for JF of grade Jet A-1+50% RO modified FAEE; P_S – scuffing load

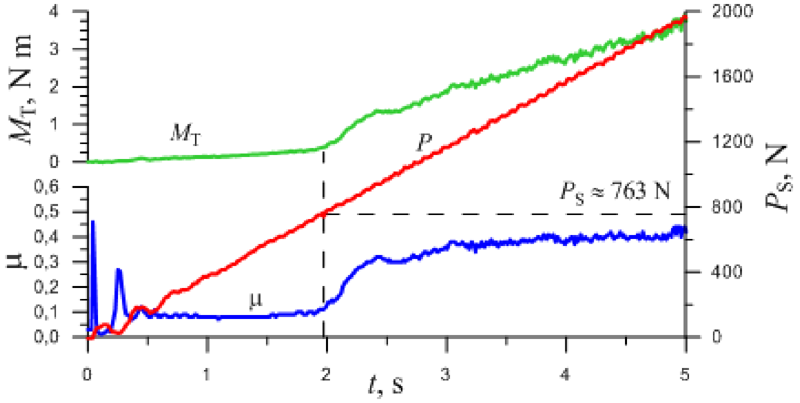


Fig. 5.54. Friction pair load P, friction torque M_T and friction coefficient μ as a function of testing run time t for RO modified FAEE; P_S – scuffing load

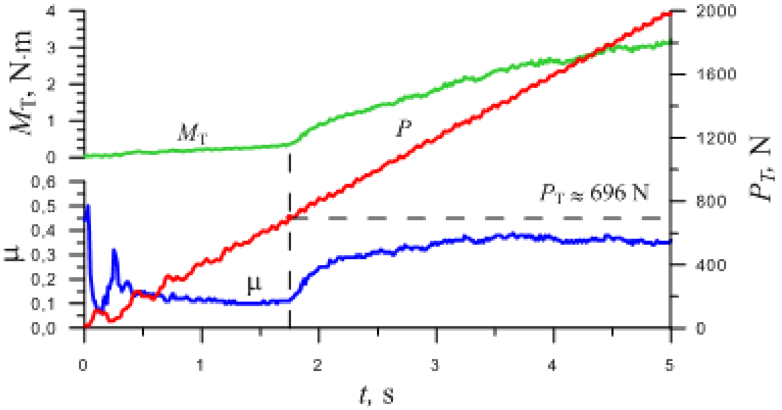


Fig. 5.55. Friction pair load P, friction torque M_T and friction coefficient μ as a function of testing run time t for JF of grade Jet A-1+10% CamO FAEE; P_S – scuffing load

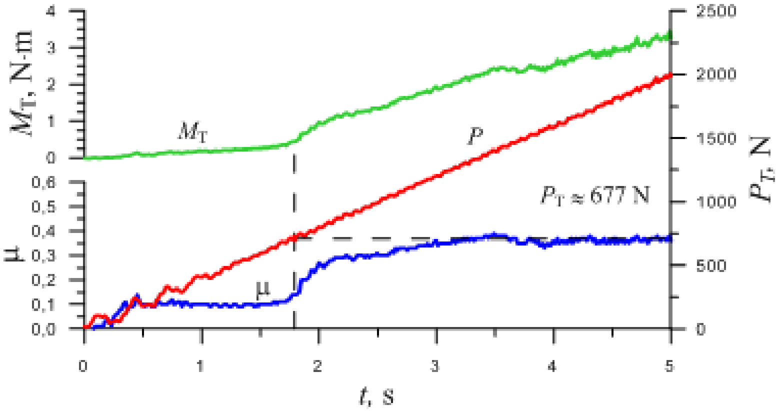


Fig. 5.56. Friction pair load P, friction torque M_T and friction coefficient μ as a function of testing run time t for JF of grade Jet A-1+20% CamO FAEE; P_S – scuffing load

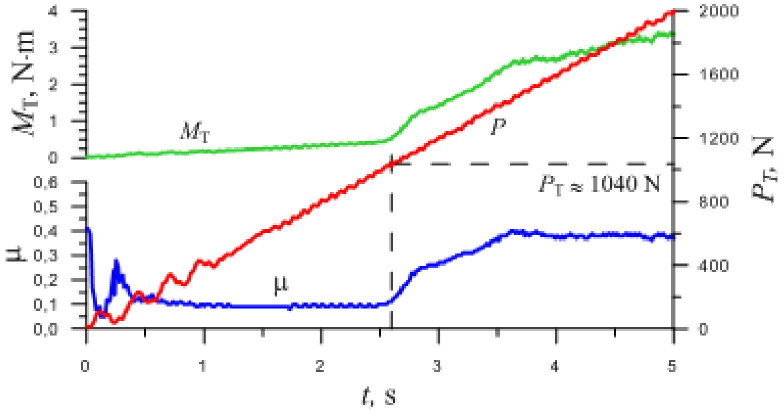


Fig. 5.57. Friction pair load P, friction torque M_T and friction coefficient μ as a function of testing run time t for JF of grade Jet A-1+30% CamO FAEE; P_S – scuffing load

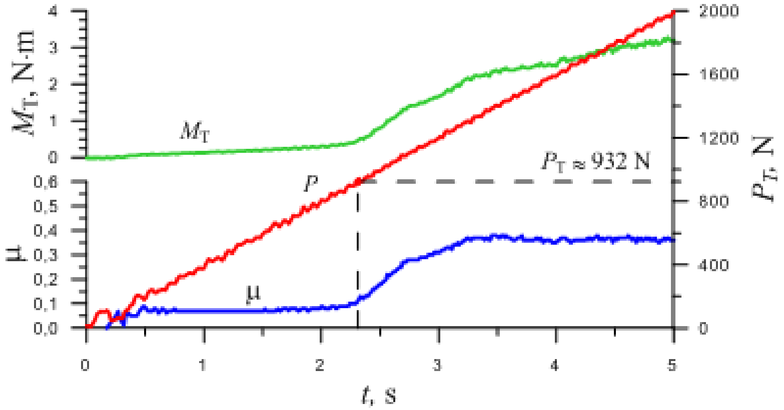


Fig. 5.58. Friction pair load P, friction torque M_T and friction coefficient μ as a function of testing run time t for JF of grade Jet A-1+40% CamO FAEE; P_S – scuffing load

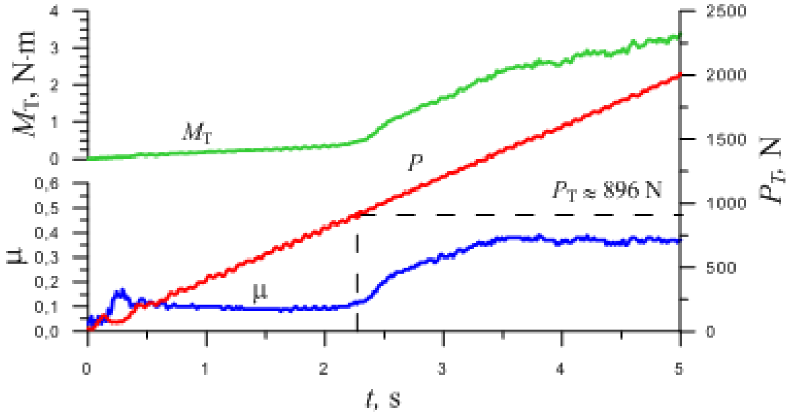


Fig. 5.59. Friction pair load P, friction torque M_T and friction coefficient μ as a function of testing run time t for JF of grade Jet A-1+50% CamO FAEE; P_S – scuffing load

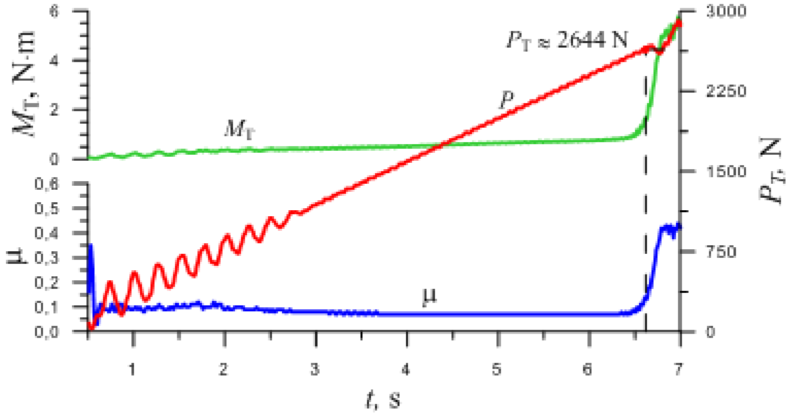


Fig. 5.60. Friction pair load P, friction torque M_T and friction coefficient μ as a function of testing run time t for CamO FAEE; P_S – scuffing load

Surfactants in fuel cause its surface activity – ability of fuel or its components to absorb at the surface of metal, form the boundary film and thus prevent dry friction of details. Fuel hydrocarbons almost do not protect friction pairs from wear. Substances, which are considered to be surface active, are gums, oxygen-, sulfur- and nitrogen-organic compounds. But presence of these substances is undesired, because of thermal stability and corrosion properties of fuel. Fatty acids esters are natural surfactants. Presence of oxygen atom in carboxyl group in molecules stipulates strong polarity of esters. Such structure provides ability to absorb on surfaces of solid bodies and thus, ability to form polymolecular film – boundary layer. In a result of experimental data processing the dependence of scuffing load P_S of the friction load in the medium of studied blended JFs on the content of bio-additives (Fig. 5.61, 5.62) was obtained.

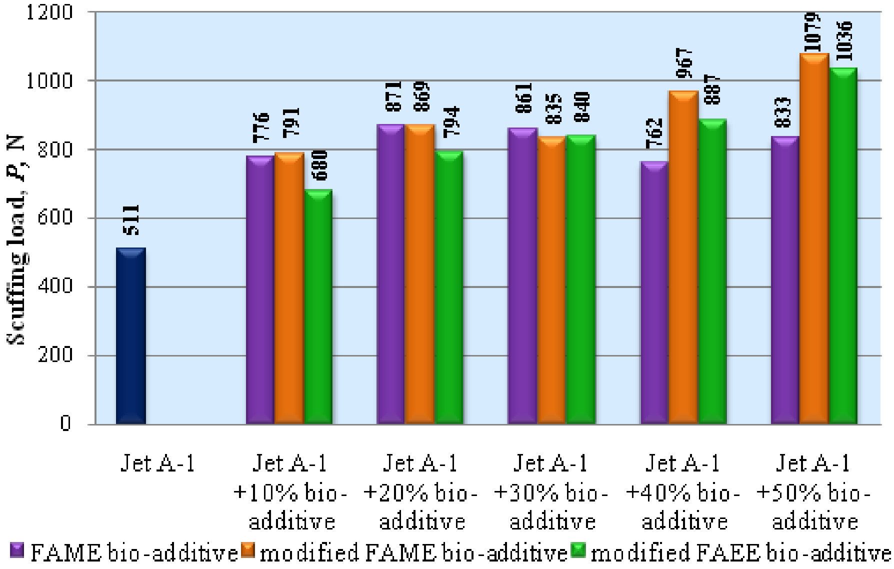


Fig. 5.61. Friction pair load in medium of tested fuel samples as a function of RO bio-additives content

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

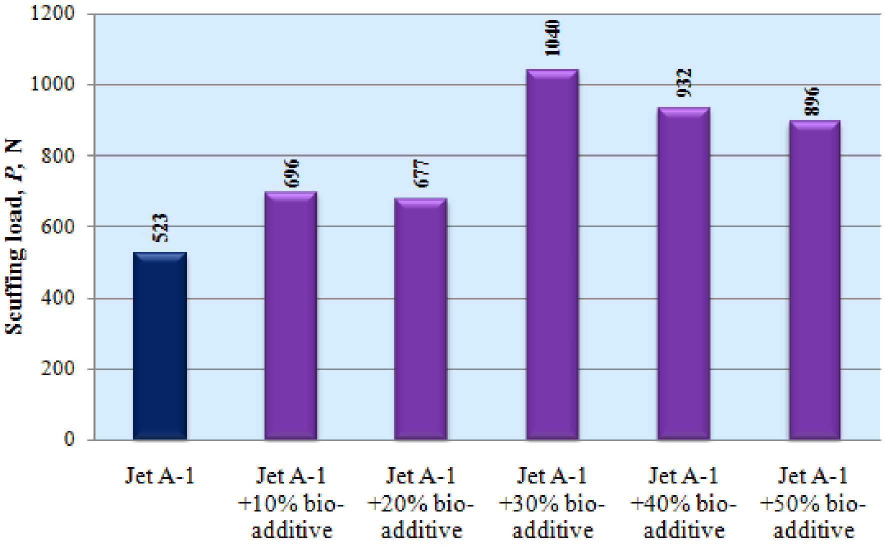


Fig. 5.62. Friction pair load in medium of tested fuel samples as a function of CamO bio-additives content

5.4.7. Fire safety

According to modern international specifications one of the dominant operational properties of JFs is its fire safety. JFs belong to flammable liquids. They are characterized by high volatility, easy form a flammable mixture with air, during combustion form a large number of products of combustion and are good insulators. According to its fire safety JFs belong to hazardous liquids at high temperatures.

Traditionally fire safety of JFs is characterized by its flash point (FlP) t_{fl}. This parameter shows the conditions under which the fuel becomes fire dangerous. FlP of a monocomponent substance can be expressed by the formula:

$$t_{\text{fl}} = -73.14 + 0.659 \cdot t_{\text{b}} \cdot \sum_{j=1}^{j} 2\alpha_j \, l_j \tag{5.5}$$

where:

t_{b} – boiling point of studied substance, °C,

α_j – empirical coefficient that is determined for certain structural groups of molecules using data from literature sources [73],

l_j – number of bond of *j*-type in the molecule of studied substance.

Taking into account that fact that most fuels are multicomponent liquids, the following equation is applied to calculate its FlP [97, 117]:

$$\sum_{i=1}^{k} x_i \cdot exp\left[\frac{\Delta H_{ii}}{R(t_{\text{fl}\,i}+273)} - \frac{\Delta H_{ii}}{R(t_{\text{fl}}+273)}\right] = 1 \tag{5.6}$$

where:

x_{i} – mole ration of *i*-component in the liquid phase of fuel,

ΔH_{ii} – mole heat of evaporation of *i*-component of fuel, kJ/mol,

R – universal gas constant,

$t_{\text{fl i}}$ – FlP of *i*-component of fuel, ^{o}C.

Specifications for JFs regulate the lower limit of this parameter. Thus, the fuels of grades TS-1, RT and Jet A-1 should have FlP values, which are not lower than 28, 30 and 38 °C respectively. According to experimental results of fire safety researches it was found that FAME, modified FAME and modified FAEE of RO are characterized by much higher values of FlP comparing to conventional JFs (Table 5.7). Low FlP value of CamO FAEE is explained by the presence of ethanol in bio-additive, left after the production process.

Table 5.7

FlP of JF and bio-additives samples

No	Designation of fuel sample	Flash point, °C
1	Jet fuel of grade Jet A-1	43
2	FAME of rapeseed oil	130
3	Modified FAME of rapeseed oil	167
4	Modified FAEE of rapeseed oil	170
5	FAEE of camelina oil	35

Such difference between FlP values of JF and bio-additives can be explained by differences in chemical structure of esters and JF. Applying formula (5.5), we can see that FlP increases with the length of the hydrocarbon chain in molecules l_j and with increase of its boiling point t_b (Table 5.8). In addition, high values of esters FlP are stipulated by the presence of C–O and C=O groups in its molecules that is expressed by factor α_j.

Table 5.8

Coefficient l_j for different type of chemical bonds

Structural group	C–C	C=C	C–H	C–O	C=O
α_j	- 2.03	11.72	1.105	2.47	11.60

It was found that blending JFs with bio-additives leads to increase of its FlP (Fig. 5.63). Equation (5.6) shows that increase of the ratio of components with higher heat of evaporation (which is typical for esters) causes rising of FlP of blended JF. For the formation of FAM above the fuel, which is sufficient for flashing it is necessary to apply greater amount of heat, otherwords, heat to a higher temperature.

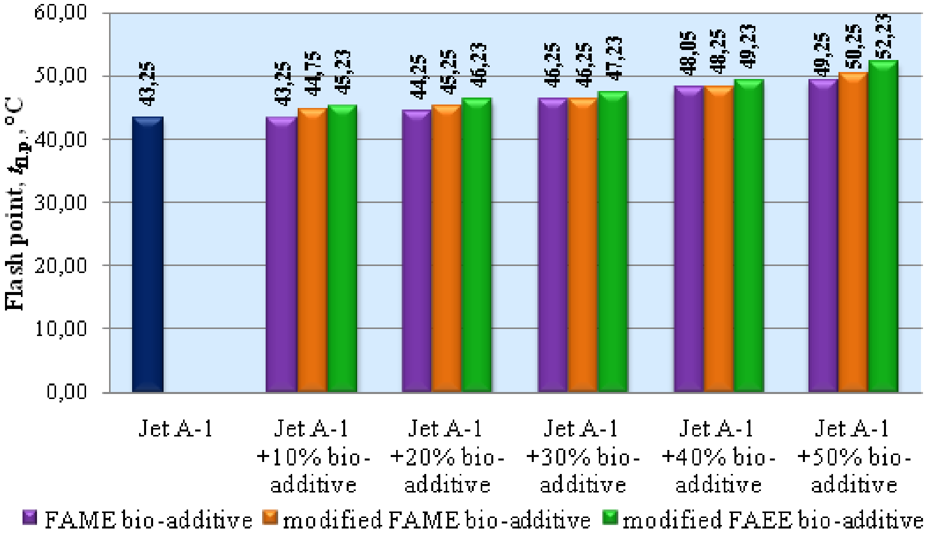


Fig. 5.63. FlP of tested fuel samples

JFs blended with bio-additives are characterized by increased FlP. Thus, the results have shown that blending with bio-additives allows improving fire safety of JFs.

The results of mathematical processing of the experimental data allowed deriving the regression equations, which describe the dependence of FlP t_{fl} of blended JFs on the concentration of bioadditives c:

For FAME bio-additive:

$$t_{\text{fl}\,1} = 42.679 + 0.054c + 1.607 \cdot 10^{-3}c^2,$$

For modified FAME bio-additive:

$$t_{\text{fl}\,2} = 43.268 + 0.057c + 1.518 \cdot 10^{-3}c^2,$$

For modified FAEE bio-additive:

$$t_{\text{fl}\,3} = 43.304 + 0.056c + 2.054 \cdot 10^{-3}c^2.$$

5.4.8. Corrosiveness

It is known that corrosiveness is one of the most important exploitation properties of JFs. It influences on durability, and reliability of JEs. During exploitation details of fuel system equipment are the most subjected to corrosive influence of fuel; details of the JE's jet pipe are subjected to corrosive influence of fuel combustion products. Corrosiveness is characterized by the presence of corrosively aggressive components in fuel. These components include sulfur and sulfur containing compounds, where the most aggressive are hydrogen sulfide and mercaptanes (thiols). Except that, the reasons of JFs corrosiveness are oxygen-containing heterogenic compounds, water-soluble alkalis and acids, dissolved oxygen and insoluble moisture.

Authors of studies, devoted to researches of JFs corrosive activity, determine three main types of corrosion processes that fuel equipment is subjected to:

1) Chemical,
2) Electrochemical,
3) Biochemical.

The process of chemical corrosion takes place during chemical interaction of corrosively-active substances, which are present in fuel, with color metals or their alloys that are used for producing details of aircrafts' fuel systems. The processes of corrosion are especially intensive when the water is present. The highest activity among sulfur compounds is typical for mercaptanes, elemental sulfur and hydrogen sulfide. Sulfides, disulfides, thiophenes and thiophanes are related to neutral sulfur compounds (Fig. 5.64). However, at temperatures more than 120 °C these compounds decompose and form mercaptanes and hydrogen sulfide. Other words, they become corrosively active. Copper (bronze) alloys and steel details with coating (usually cadmium) are subjected to most intensive corrosion during exploitation.

Mercaptane (thiol) Hydrogen sulfide Thiophene Thiophane

R_1-S-R_2 $R_1-S-S-R_2$

Sulfide Disulfide

Fig. 5.64. Typical sulfur compounds found in conventional JF

Among JFs the highest corrosive activity is typical for fuels, which are produced from sulfur oils. Hydrogen sulfide is removed from fuels completely during crude oil processing.

However, because of the technological reasons elemental sulfur and mercaptanes are still present in JFs is small quantities. The content of sulfur and sulfur compounds in JFs is regulated by specifications (Table 5.9).

Corrosive action of JFs is revealed at first in destruction of copper surface; later significant corrosive sediments of black color appear on copper details. With time these sediments cut from surface and accumulate in fuel in the form of black insoluble particles, which cause clogging of filtering equipment. Corrosion of fuelling equipment, which are made of copper alloys, also depends on products of JF oxidation that are contained in fuel.

Table 5.9

Permissible content of sulfur and sulfur compound s in some grades of JFs

No	Parameter	JF grade		
		Jet A-1	TS-1	RT
1	Total sulfur content, % (m/m)	<0.3	0.25	0.1
2	Mercaptane sulfur content, % (m/m) or Doctor test	<0.003 negative	0.003 -	0.,001 -
3	Hydrogen sulfide content	-	absence	absence

The most widespread method for JFs corrosiveness control is copper strip test. The degree of copper strip corrosion is estimated comparing to etalon sample (Fig. 5.65).

Fig. 5.65. The standard samples for determination copper strip corrosion

The results of tests of JF, bio-additives and samples of JFs blended with bio-additives on copper strip are presented in Table 5.10.

Table 5.10

The result of copper strip test of fuel samples

Bio-additive	JF of grade Jet A-1	100% bio-additive	JF + 10% of bio-additive	JF + 20% of bio-additive	JF + 30% of bio-additive	JF + 40% of bio-additive	JF + 50% of bio-additive
RO FAME	1a	1a	1a	1a	1b	1b	1a
RO modified FAME	1a	1a	1a	1a	1b	1b	1b
RO modified FAEE	1a	1a	1a	1a	1a	1a	1b
CamO FAEE	1a	1b	1a	1a	1a	1b	1b

According to the requirements of ASTM and Def Stan specifications for JF of grade Jet A-1 the degree of copper strip corrosion have to be not more than 1 according to the scale on Fig. 5.65. As we can see from the data in Table 5.10 the degree of corrosiveness of JFs blended with bio-additives completely satisfies requirements of existing specification.

5.4.9. Thermal stability and combustion characteristics

In order to study and compare the thermal stability and combustion characteristics of blended JFs we havee fulfill the thermogravimetric analysis of conventional JF, RO modified FAEE and samples of JF blended with RO modified FAEE. Thermogravimetric curves (TG), which are presented at Fig. 5.66÷5.72 show the loss ofsamples mass during its heating. Differential thermogravimetric curves (DTG) relate to dependance of mass loss speed on temperature. Differential termal analysis curves (DTA) relate to temperature difference between the tested sample and the reference one at certain temperature. Comparison of DTA and TG curves is presented at Fig 5.73, 5.74.

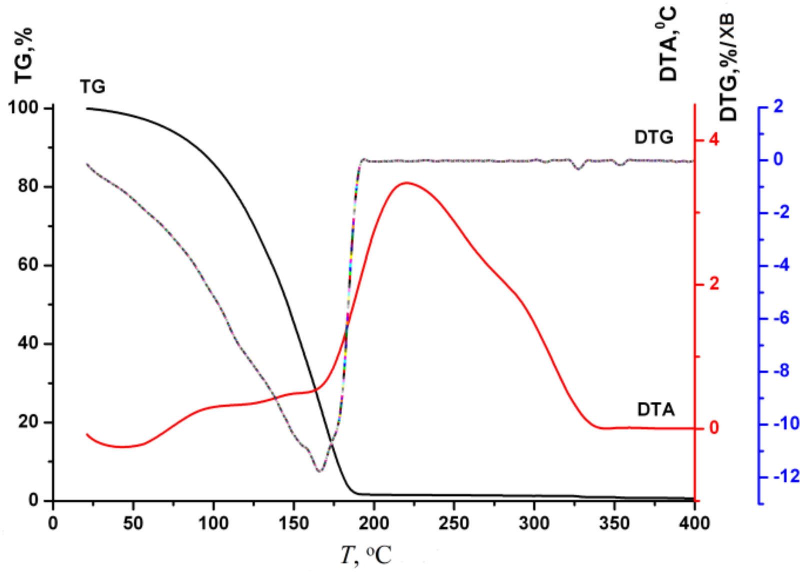


Fig. 5.66. Thermogram of JF of grade Jet A-1

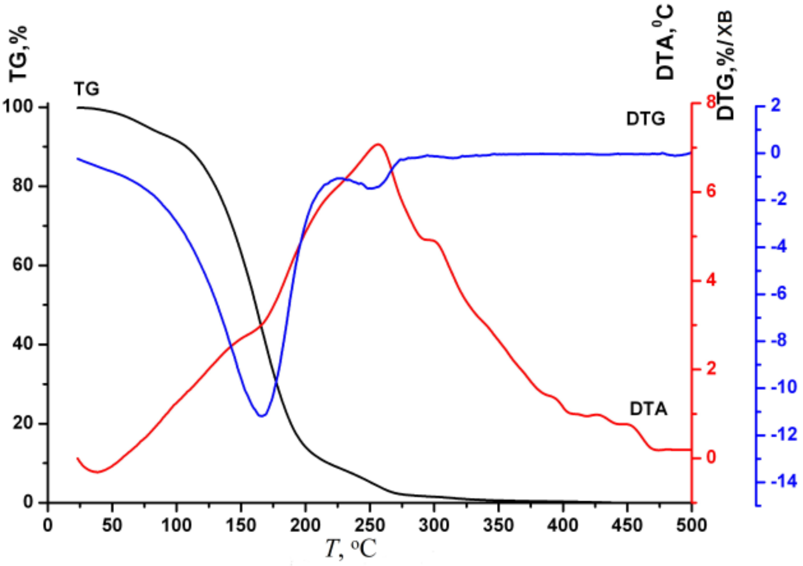


Fig. 5.67. Thermogram of JF of grade Jet A-1+10% of RO modified FAEE bio-additive

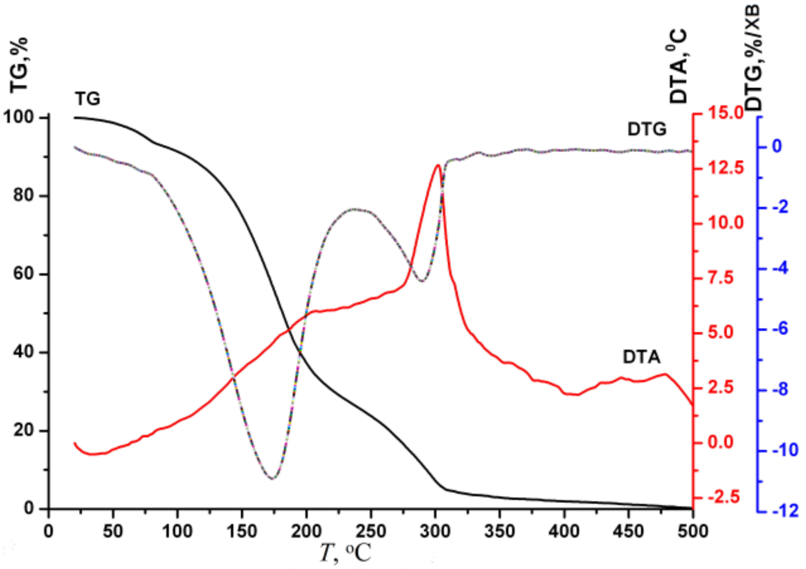


Fig. 5.68. Thermogram of JF of grade Jet A-1+20% of RO modified FAEE bio-additive

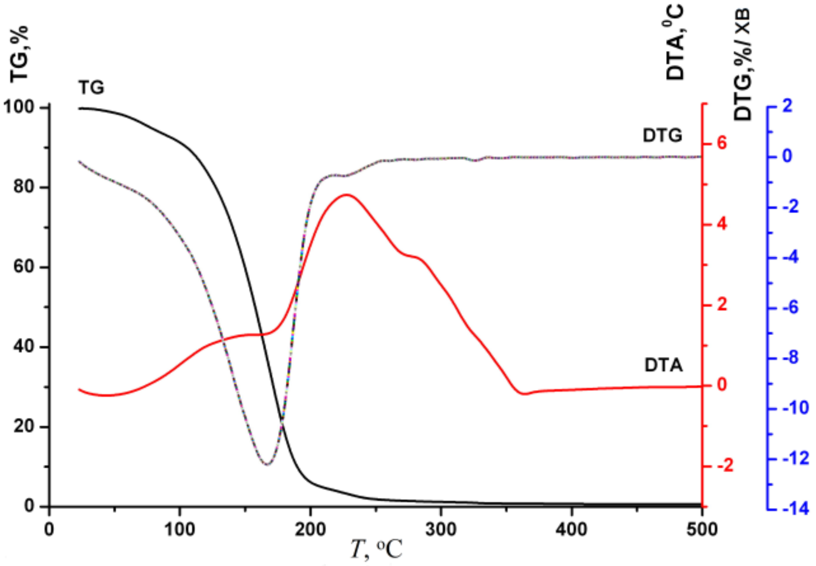


Fig. 5.69. Thermogram of JF of grade Jet A-1+30% of RO modified FAEE bio-additive

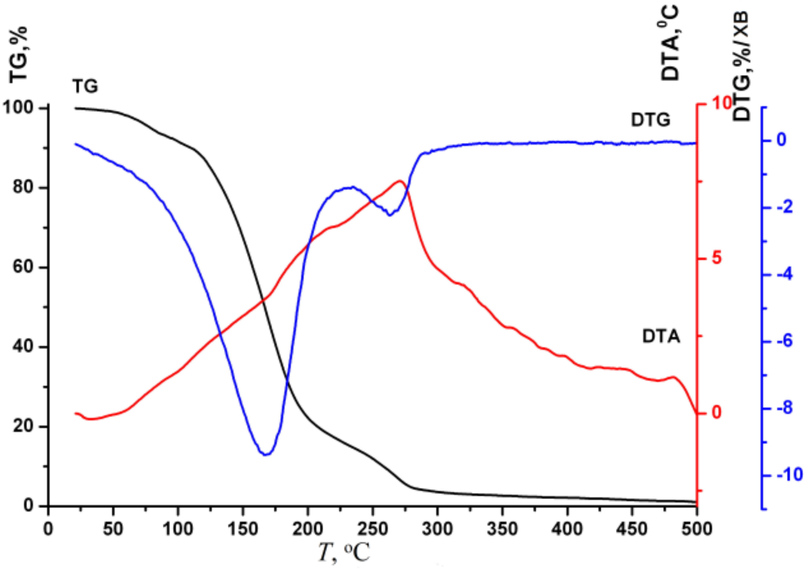


Fig. 5.70. Thermogram of JF of grade Jet A-1+40% of RO modified FAEE bio-additive

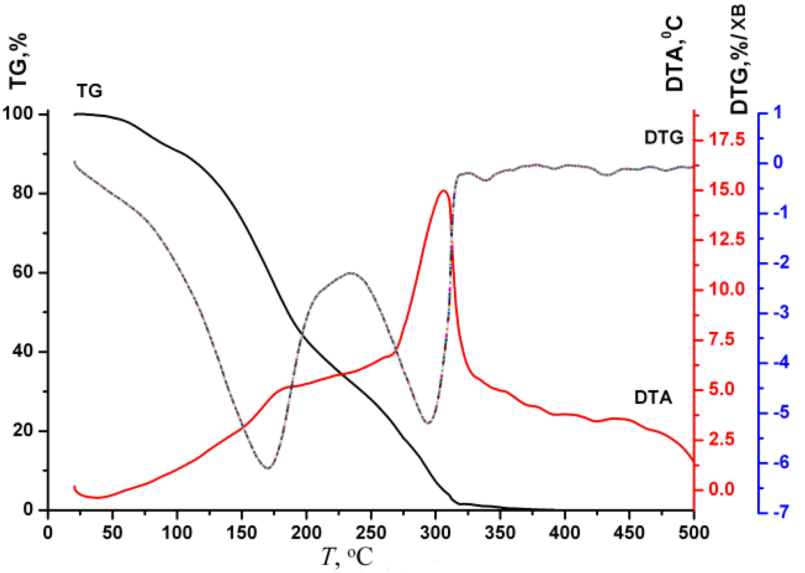


Fig. 5.71. Thermogram of JF of grade Jet A-1+50% of RO modified FAEE bio-additive

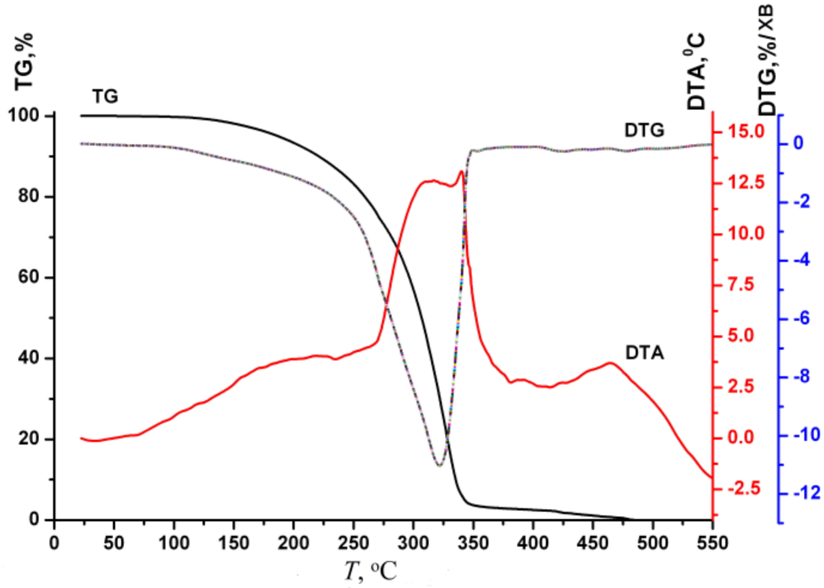


Fig. 5.72. Thermogram of RO modified FAEE bio-additive

The mass loss in a temperature range 20÷260 °C, which is accompanied with appearence of light endothermal effect at the DTA curves on Fig. 5.70÷5.75, corresponds to discharge of volatile comppounds, which are the components of JF.

Intensive mass loss of samples on Fig. 5.70÷5.76, in a temperature range 20÷260 °C can correspond to partial evaporation of compponents, its thermal and thermal-oxidative destruction.

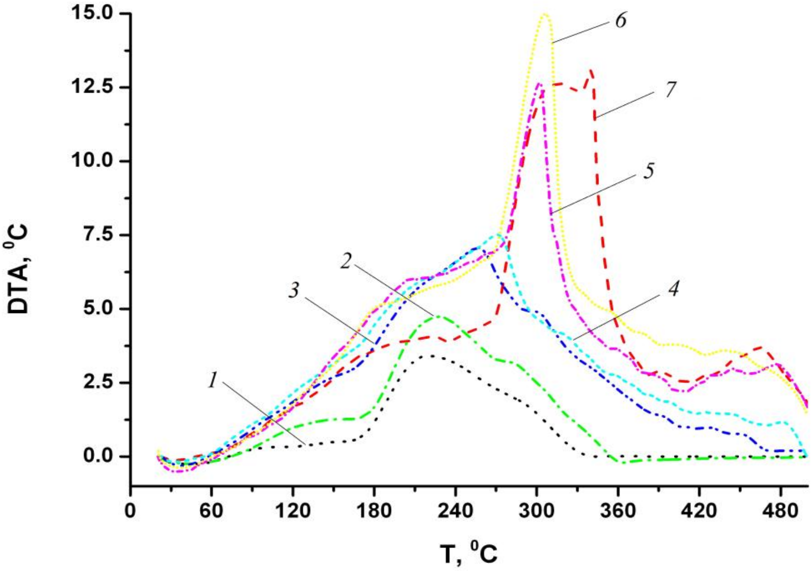


Fig. 5.73. DTA curves of fuel samples: *1* – JF of grade Jet A-1; *2* – JF+10% modified FAEE; *3* – JF+20% modified FAEE; *4* – JF+30% modified FAEE; *5* – JF+40% modified FAEE; *6* – JF+50% modified FAEE; *7* – modified FAEE

In this temperature interval exothermal effect appears at DTA curves. With the increase of RO FAEE bio-additive content in samples the value of exothermal effect rises, its maximum shifts to the area of higher temperatures, which demonstrate the rise of thermal stability of fuel samples (Fig. 5.77).

The appearance of exothermal effect at DTA curves at temperatures higher than 266 ^{o}C corresponds to combustion of organic part of samples. It should be metioned that increasing the content of RO FAEE bio-additives in blended JF samples corresponds to rising of the value of combustion heat effect.

Comparing the TG curves is shown at Fig. 5.78. The least thermally stable is hydrocarbon JF. During heating it is characterized by the most intesive mass loss. The highest thermal stability was detected for RO FAEE bio-aditive, which is characterized by the least intesive mass loss.

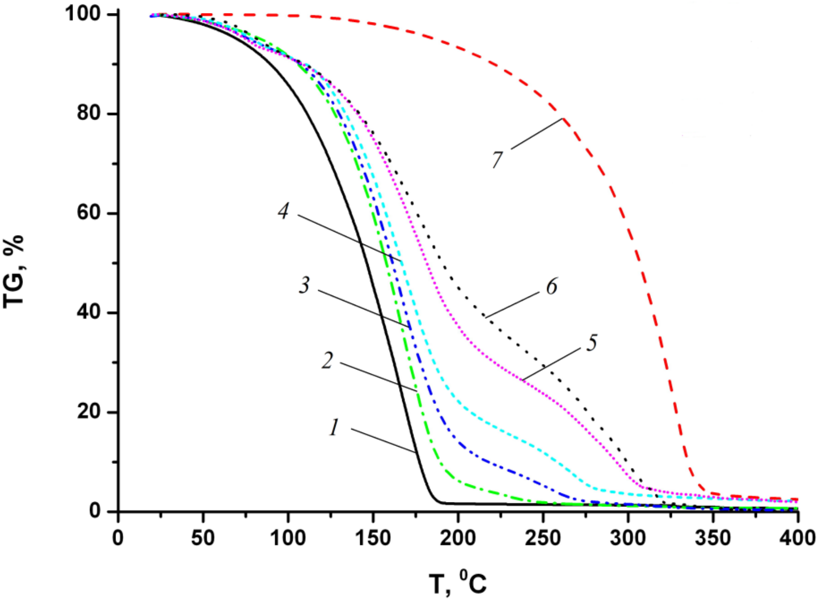


Fig. 5.74. The mass loss of fuel samples during its combustion: *1* – JF of grade Jet A-1; *2* – JF+10% modified FAEE; *3* – JF+20% modified FAEE; *4* – JF+30% modified FAEE; *5* – JF+40% modified FAEE; *6* – JF+50% modified FAEE; *7* – modified FAEE

The analysis of TG curves demonstrates that increase of bio-additive content in blended JF samples corresponds to increasing of its thermal stability. It is posible to make the general conclusion that thermal stability of blended JFs increases with the increase of content of bio-additives in fuel blends.

6.5. Comparative characteristics of quality indexes of new jet fuels blended with bio-additives and conventional jet fuels

Basing on the obtained experimental data the complex comparative characteristics of physical-chemical and exploitation properties of JFs blended with three kinds of bio-additives of plant origin were developed (Tables 5.11÷5.14).

Table 5.11

The comparative characteristics of quality parameters of JF of grade Jet A-1, RO FAME bio-additive and JFs blended with RO FAME in quantity up to 50 % (vol.)

No	Parameter	JF of grade Jet A-1	Bio-additive	JF +10 % of bio-additive	JF +20 % of bio-additive	JF +30 % of bio-additive	JF +40 % of bio-additive	JF +50 % of bio-additive
1	Density at t = 20 °C, kg/m^3	794.03	882.922	803.22	810.83	821.28	830.21	839.07
2	Fractional composition:							
	$T_{i.b.}$, °C	155.22	320.28	154.65	155.13	155.26	155.9	157.37
	10 % recovery at t, °C	169.15	334.91	169.07	170.87	172.33	173.73	176.19
	50 % recovery at t, °C	186.20	336.99	189.82	195.19	204.48	227.45	287.77
	90 % recovery at t, °C	217.13	347.09	293.74	336.08	338.29	339.17	339.72
	98 % recovery at t, °C	243.44	354.50	341.91	347.11	347.86	350.15	352.61
3	Kinematic viscosity, mm^2/s, at t:							
	- 20 °C	3.292	16.045 (-5)	3.804	4.572	5.684	8.668	13.954
	0 °C	2.117	13.352	2.404	2.815	3.365	4.588	6.474
	20 °C	1.5	7.202	1.685	1.934	2.251	2.851	3.685
	40 °C	1.134	4.472	1.264	1.432	1.636	1.968	2.396
	60 °C	0.895	3.062	0.993	1.116	1.258	1.46	1.706
	80 °C	0.729	2.25	0.806	0.899	1.006	1.138	1.291
	100 °C	0.608	1.741	0.671	0.745	0.828	0.918	1.02
4	Flash point, °C	43	130	43	44	46	48	49
5	Pour point, °C	minus 59	minus 15	minus 56	minus 54	minus 52	minus 35	minus 30
6	Net heat of combustion,kJ/kg	43218	37315	42569	41919	41329	40680	40089
7	Scuffing load, N	511	961	776	871	861	762	833
8	Copper strip test	1a	1a	1a	1a	1b	1b	1a

Table 5.12

The comparative characteristics of quality parameters of JF of grade Jet A-1, RO modified FAME bio-additive and JFs blended with RO modified FAME in quantity up to 50 % (vol.)

No	Parameter	JF of grade Jet A-1	Bio-additive	JF +10 % of bio-additive	JF +20 % of bio-additive	JF +30 % of bio-additive	JF +40 % of bio-additive	JF +50 % of bio-additive
1	Density at t=20 °C, kg/m^3	794.03	883.68	803.51	813.04	822.21	831.83	839.94
2	Fractional composition:							
	$t_{i.b.}$, °C	155.22	314.35	155.72	155.41	154.46	155.93	157.92
	10 % recovery at t, °C	169.15	327.23	169.73	170.92	172.25	174.12	177.17
	50 % recovery at t, °C	186.2	334.78	190.49	196.9	205.84	230.94	293.11
	90 % recovery at t, °C	217.13	343.35	304.6	335.67	337.44	338.42	339.31
	98 % recovery at t, °C	243.44	348.95	338.31	342.59	344.5	346.48	348.95
3	Kinematic viscosity, mm^2/s, at t:							
	- 20 °C	3.292	14.66 (-5)	3.995	4.969	6.011	6.349 (-15)	13.95 (-10)
	0 °C	2.117	12.265	2.482	2.972	3.49	4.174	4.911
	20 °C	1.5	6.734	1.72	2.005	2.304	2.683	3.084
	40 °C	1.134	4.234	1.28	1.466	1.66	1.895	2.142
	60 °C	0.895	2.926	0.999	1.131	1.268	1.429	1.596
	80 °C	0.729	2.165	0.808	0.906	1.009	1.127	1.248
	100 °C	0.608	1.741	0.671	0.745	0.827	0.918	1.02
4	Flash point, °C	43	167	44.5	45	46	48	50
5	Pour point, °C	minus 59	minus 19	minus 57	minus 54	minus 52	minus 38	minus 32
6	Net heat of combustion,kJ/kg	43218	37131	42548	41897	41270	40661	39992
7	Scuffing load, N	511	1154	791	869	835	967	1079
8	Copper strip test	1a	1a	1a	1a	1b	1b	1b

Table 5.13

The comparative characteristics of quality parameters of JF of grade Jet A-1, RO modified FAEE bio-additive and JFs blended with RO modified FAEE in quantity up to 50 % (vol.)

No	Parameter	JF of grade Jet A-1	Bio-additive	JF +10 % of bio-additive	JF +20 % of bio-additive	JF +30 % of bio-additive	JF +40 % of bio-additive	JF +50 % of bio-additive
1	Density at t=20 ^{o}C, kg/m^3	794.03	876.58	804.11	811.81	819.47	828.10	836.56
2	Fractional composition:							
	$t_{i.b.}$, ^{o}C	155.22	330.85	156.11	155.99	156.42	157.71	159.24
	10 % recovery at t, ^{o}C	169.15	336.86	168.12	169.22	170.32	172.13	174.61
	50 % recovery at t, ^{o}C	186.2	337.2	188.46	193.53	201.31	218.26	266.2
	90 % recovery at t, ^{o}C	217.13	336.14	249.1	340.66	344.04	344.43	344.53
	98 % recovery at t, ^{o}C	243.44	274.4	346.94	348.76	350.32	351.88	353.21
3	Kinematic viscosity, mm^2/s, at t:							
	- 20 ^{o}C	3.292	17.886 (-8)	4.027	4.957	6.088	7.589	9.624
	0 ^{o}C	2.116	13.381	2.503	2.988	3.544	4.258	5.18
	20 ^{o}C	1.5	7.355	1.734	2.025	2.343	2.742	3.239
	40 ^{o}C	1.134	4.621	1.29	1.486	1.689	1.939	2.242
	60 ^{o}C	0.895	3.188	1.008	1.149	1.291	1.463	1.665
	80 ^{o}C	0.7289	2.354	0.815	0.923	1.028	1.154	1.3
	100 ^{o}C	0.608	1.828	0.675	0.761	0.843	0.940	1.052
4	Flash point, ^{o}C	43	170	44.5	45.5	46.5	48.5	51.5
5	Pour point, ^{o}C	minus 59	minus 18.5	minus 57	minus 55	minus 52	minus 39	minus 33
6	Net heat of combustion,kJ/kg	43218	37550	42595	41971	41404	40781	40271
7	Scuffing load, N	511	763	680	794	840	887	1036
8	Copper strip test	1a	1a	1a	1a	1a	1a	1a

Table 5.14

The comparative characteristics of quality parameters of JF of grade Jet A-1, CamO FAEE bio-additive and JFs blended with CamO FAEE in quantity up to 50 % (vol.)

No	Parameter	JF of grade Jet A-1	Bio-additive	JF +10 % of bio-additive	JF +20 % of bio-additive	JF +30 % of bio-additive	JF +40 % of bio-additive	JF +50 % of bio-additive
1	Density at t=20 ^{o}C, kg/m^3	794.03	874.49	799.63	807.27	816.44	824.30	833.81
2	Fractional composition:							
	$t_{i.b.}$, ^{o}C	155.22	-	140.76	76.96	77.16	77.05	77.12
	10 % recovery at t, ^{o}C	169.15	-	169.33	169.77	171.39	173.48	176.32
	50 % recovery at t, ^{o}C	186.2	-	190.57	195.34	204.45	220.05	301.59
	90 % recovery at t, ^{o}C	217.13	-	286.63	343.37	344.69	344.45	344.23
	98 % recovery at t, ^{o}C	243.44	-	344.87	349.82	351.96	348.55	351.17
3	Kinematic viscosity, mm^2/s, at t:							
	- 20 ^{o}C	3.292	16.413 (-10)	4.094	4.898	5.434	7.547	9.2
	0 ^{o}C	2.116	11.48	2.58	2.948	3.29	4.194	4.968
	20 ^{o}C	1.5	6.422	1.803	1.997	2.233	2.686	3.115
	40 ^{o}C	1.134	4.09	1.351	1.464	1.639	1.893	2.161
	60 ^{o}C	0.895	2.852	1.06	1.132	1.269	1.424	1.608
	80 ^{o}C	0.7289	2.125	0.861	0.909	1.021	1.122	1.257
	100 ^{o}C	0.608	1.664	0.716	0.75	0.844	0.913	1.012
4	Flash point, ^{o}C	43	35	29.5	-	-	-	-
5	Pour point, ^{o}C	minus 59	minus 7	minus 62	Minus 51	minus 36	Minus 32	minus 29
6	Higher heat of combustion,kJ/kg	46368	39842	45683	44963	44123	43462	42718
7	Scuffing load, N	523	2644	696	677	1040	932	896
8	Copper strip test	1a	1b	1a	1a	1a	1b	1b

Later physical-chemical and exploitation properties of JFs blended with bio-additives based on FAME, modified FAME and modified FAEE were analyzed for satisfying requirements of modern specifications for JFs of grade Jet A-1 (Fig. 5.75÷5.78).

Basing on the results of analysis we have done the conclusion that content of bio-additives in blended JFs is limited by the values of such parameters as kinematic viscosity, PP, and net heat of combustion. According to experimental results on these parameters the content of FAME, modified FAME and modified FAEE in JF should not exceed 30 %.

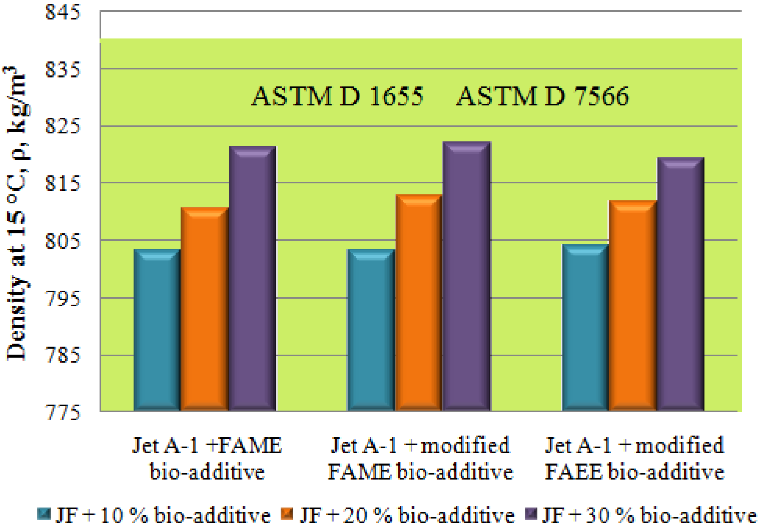


Fig. 5.75. Correspondence of JFs blended with bio-additives to requirement of specifications for JF of grade Jet A-1 by the parameter of density at *t* 15 °C

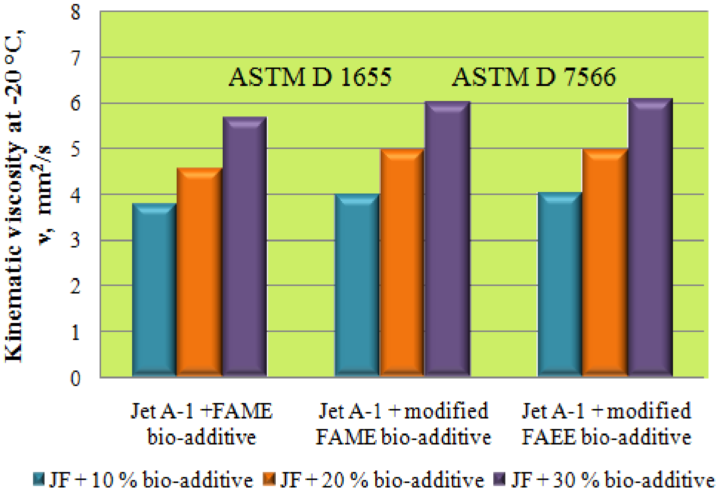


Fig. 5.76. Correspondence of JFs blended with bio-additives to requirement of specifications for JF of grade Jet A-1 by the parameter of viscosity at *t* -20 °C

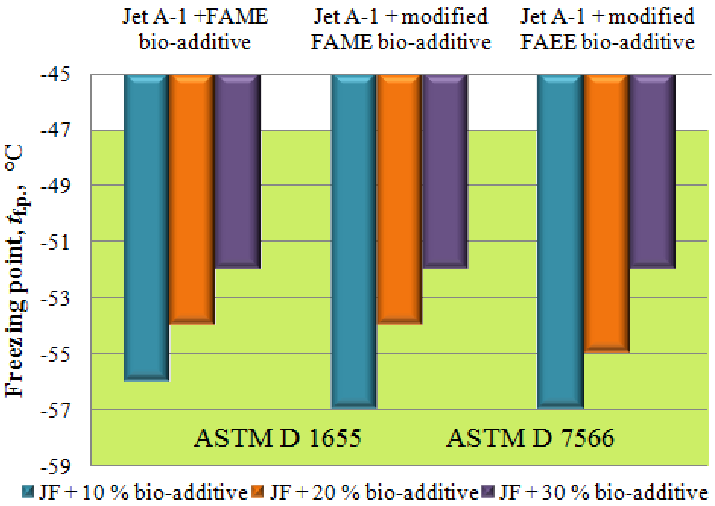


Fig. 5.77. Correspondence of JFs blended with bio-additives to requirement of specifications for JF of grade Jet A-1 by the parameter of FP

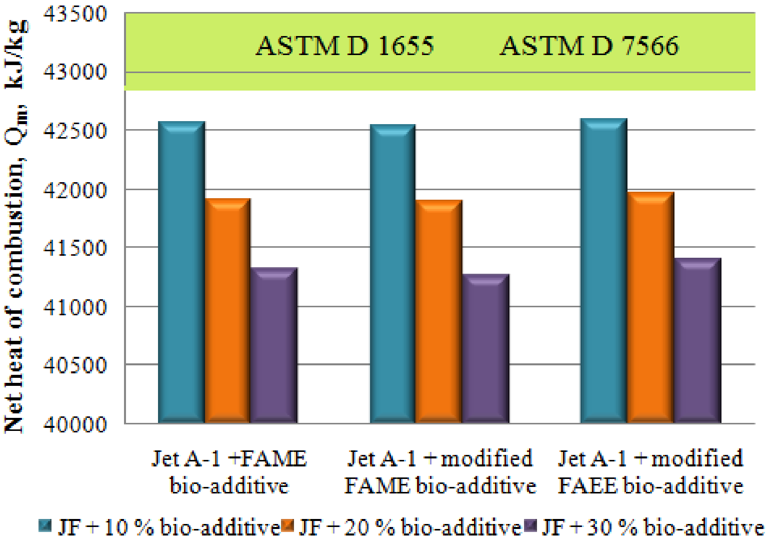


Fig. 5.78. Correspondence of JFs blended with bio-additives to requirement of specifications for JF of grade Jet A-1 by the parameter of net heat of combustion

In this case we observe rising of density of blended JFs in a range of 3.2÷3.55 %. Viscosity of JFs blended with bio-additives in quantity up to 30 % (v/v) becomes approximately in two times higher on about 50.02÷56.17 %. PP of blended JFs increases up to 11.86 %. These changes in quality parameters completely satisfy requirements of specifications for conventional JFs. Net heat of combustion of blended JFs changes in a range of 4.2÷4.5 %. At the same time it becomes possible to improve exploitation properties of blended JFs: FP rises on 6.93÷9.19 %, anti-wear properties increase on 6.73÷64.7 %.

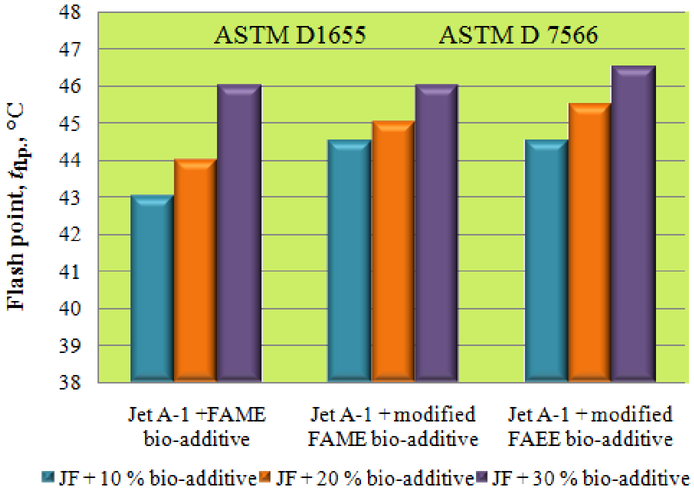


Fig. 5.70. Correspondence of JFs blended with bio-additives to requirement of specifications for JF of grade Jet A-1 by the parameter of FlP

The diagrams depicted on Fig. 5.66÷5.70 illustrate that JFs blended with components of plant origin in quantity up to 30 % (v/v) satisfy requirement of modern specifications for JFs. Decreased net heat of combustion of blended JFs (Fig. 5.69) may be compensated due to increased density of new fuels and rise of its energy value.

Taking into account insignificant difference in characteristics of JFs blended with methyl and ethyl esters it is more rational to use rather FAEE than FAME. The use of ethanol provides production of bio-additives of completely renewable feedstock. Analyzing comparative characteristic of quality parameters of conventional and blended JFs we came to conclusion that new blended JFs may be used as a working body of JEs. The receipts of environmentally friendly JFs blended with bio-additives were developed (Tables 5.15÷5.24). According to the receipts, new JFs should be produced by compounding hydrocarbon jet fuel with FAME and FAEE bio-additives. The content of bio-additives may be 10 %, 20 % and 30 % (v/v).

Table 5.15

The receipt of blended JF No 1

Initial components	Spesification	Composition, % (v/v)	Quantity, kg per 1 t of final product
1. Jet fuel of grade Jet A-1 2. Bio-additive of plant origin FAME	ASTM D 1655	90 ±0.5 10 ±0.1	900 ±5 100 ±1
Total:		100	1000

Table 5.16

The receipt of blended JF No 2

Initial components	Spesification	Composition, % (v/v)	Quantity, kg per 1 t of final product
1. Jet fuel of grade Jet A-1 2. Bio-additive of plant origin FAME	ASTM D 1655	80 ±0.5 20 ±0.1	800 ±5 200 ±1
Total:		100	1000

Table 5.17

The receipt of blended JF No 3

Initial components	Spesification	Composition, % (v/v)	Quantity, kg per 1 t of final product
1. Jet fuel of grade Jet A-1	ASTM D 1655	70 ±0.5	700 ±5
2. Bio-additive of plant origin FAME		30 ±0.1	300 ±1
Total:		100	1000

Table 5.18

The receipt of blended JF No 4

Initial components	Spesification	Composition, % (v/v)	Quantity, kg per 1 t of final product
1. Jet fuel of grade Jet A-1	ASTM D 1655	90 ±0.5	900 ±5
2. Bio-additive of plant origin modified FAME		10 ±0.1	100 ±1
Total:		100	1000

Table 5.19

The receipt of blended JF No 5

Initial components	Spesification	Composition, % (v/v)	Quantity, kg per 1 t of final product
1. Jet fuel of grade Jet A-1	ASTM D 1655	80 ±0.5	800 ±5
2. Bio-additive of plant origin modified FAME		20 ±0,1	200 ±1
Total:		100	1000

Table 5.20

The receipt of blended JF No 6

Initial components	Spesification	Composition, % (v/v)	Quantity, kg per 1 t of final product
1. Jet fuel of grade Jet A-1	ASTM D 1655	70 ±0.5	700 ±5
2. Bio-additive of plant origin modified FAME		30 ±0.1	300 ±1
Total:		100	1000

Table 5.21

The receipt of blended JF No 7

Initial components	Spesification	Composition, % (v/v)	Quantity, kg per 1 t of final product
1. Jet fuel of grade Jet A-1	ASTM D 1655	90 ±0,5	900 ± 5
2. Bio-additive of plant origin modified FAEE		10±0,1	100±1
Total:		100	1000

Table 5.22

The receipt of blended JF No 8

Initial components	Spesification	Composition, % (v/v)	Quantity, kg per 1 t of final product
1. Jet fuel of grade Jet A-1	ASTM D 1655	80 ± 0,5	800 ± 5
2. Bio-additive of plant origin modified FAEE		20±0,1	200±1
Total:		100	1000

Table 5.23

The receipt of blended JF No 9

Initial components	Spesification	Composition, % (v/v)	Quantity, kg per 1 t of final product
1. Jet fuel of grade Jet A-1	ASTM D 1655	70 ± 0,5	700 ± 5
2. Bio-additive of plant origin modified FAEE		30±0,1	300±1
Total:		100	1000

Basing on experimental results, theoretical and practical analysis of characteristics of feedstock used for bio-additives production and the analysis of requirements to conventional JFs we have formulated criteria for choosing rational composition of JFs blended with bio-additives of plant origin:

12) optimal (rational) ratio of saturated and unsaturated esters in the composition of bio-additives,
13) compatibility of bio-additives with conventional oil-derived JFs,
14) physical stability of blended JFs that is provided by mutual solubility of esters and hydrocarbons,
15) satisfactory density that have to provide necessary level of evaporability and formation of fuel-air mixture and completeness of fuel combustion,
16) satisfactory viscosity and low-temperature properties, which have to provide pumpability of JF and reliability of fuel system operation at low temperatures,
17) sufficient net heat of combustion that characterizes fuel flow and determines flight range,
18) chemical and thermochemical stability with minimal tendency to formation of sediments in JE systems,
19) absence of production by-products, water and other admixtures in bio-additives.

Chapter 6

STUDY OF OPERATION PARAMETERS OF JET ENGINE POWERED BY JET FUELS BLENDED WITH BIO-ADDITIVES

6.1. Aim and scope of the study

Bench tests of JE were done with the aim of testing newly developed JFs blended with bio-additives in conditions of engine operation and checking the hypothesis that these alternative JFs may be used as working body of JEs. Program of bench tests of JFs blended with bio-additives on JE foresees tests of two alternative JFs on certain operation regimes with checking acceleration response time of the engine with further comparing to result, using conventional JF. For this purpose the quality of fuel was determined according to throttle characteristic of the engine brought to ISA (by parameters of thrust, FF, jet pipe temperature, compressor delivery pressure, pressure in fuel manifold and acceleration response time depending on engine relative rotor speed).

6.2. Description of equipment and experiment realization

For fulfilling bench tests the gas-turbine engine of model RU19A-300 was used. Primarily this type of JE was developed for aircrafts of models Yak-30 and Yak-32. Later this JE was being installed on aircrafts on models An-24, An-26 and An-30 as auxiliary power unit (Fig. 6.1÷6.3, 6.5).

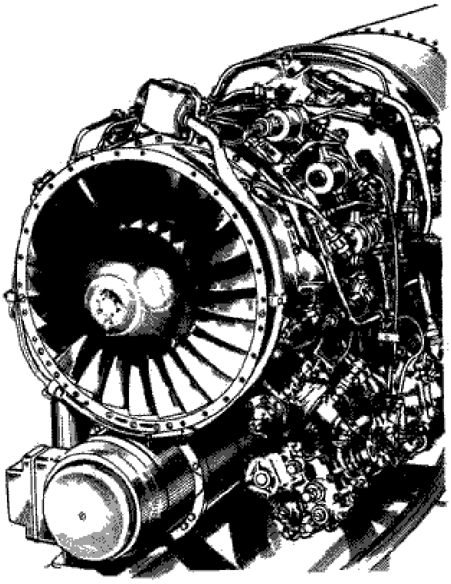


Fig. 6.1 External view of engine RU19A-300 (frontal view)

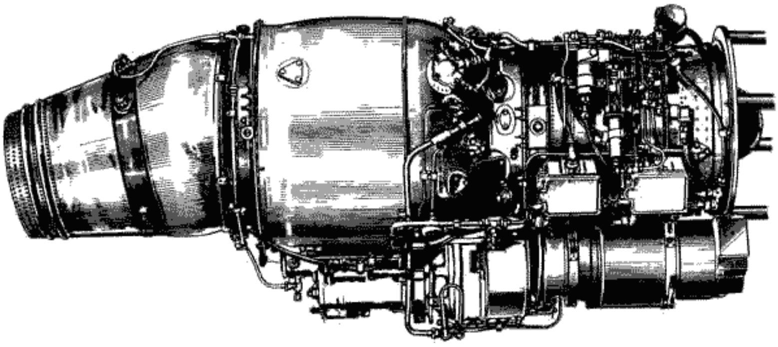


Fig. 6.2. External view of engine RU19A-300 (view from the right)

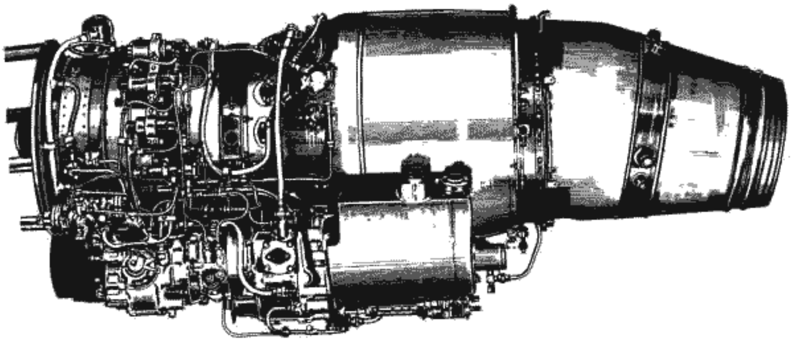


Fig. 6.3. External view of engine RU19A-300 (view from the left)

The bench tests were fulfilled on certified engine-test base with specific stand at State Enterprise 410 factory of Civil Aviation (Kyiv, Ukraine) (Fig 6.4). Main technical characteristics of tested engine are given in Table 6.1. The main regimes of the engine operation are described in Table 6.2.

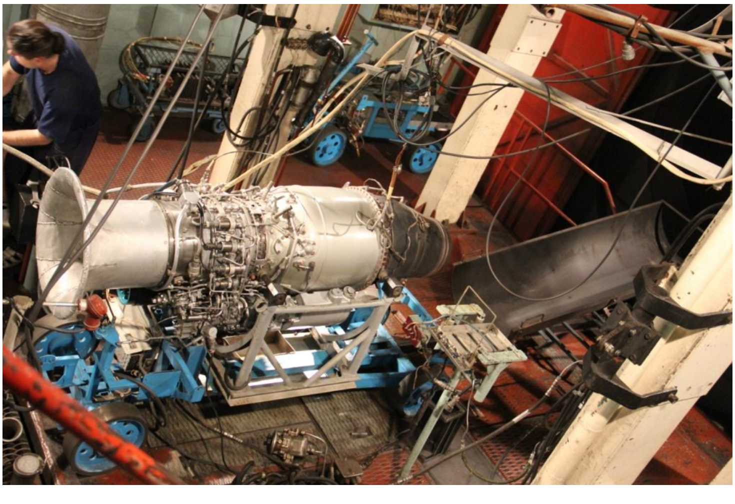


Fig. 6.4. Engine-test base with specific stand at State Enterprise 410 factory of Civil Aviation

Table 6.1

Main technical characteristics of the engine “RU19A-300”

1.	Engine model	РУ19А-300
2.	Type	Gas-turbine
3.	Direction of rotor spinning	Counterclockwise as viewed from jet pipe side
4.	Compressor:	
	- type	axial
	- number of stages	7
	- degree of pressure rise at nominal regime on ground	4.4
	- maximal air use	15.8 kg/s
	- acceptable air use that is taken from compressor for cooling of electric generator in the system of aircraft ejector:	
	At revolutions of 94%.	Not more than 400 kg/h
	On other regimes	Proportional to P_2
	Interstage air bleed tape behind the compressor:	
	- type	With hydraulic control
	- number	1
	- displacement	Behind the fourth stage
	- closing revolutions (when revolutions increases) and opening (when revolutions decreases)	63 ±2%
5.	Combustion chamber:	
	- type	Circular with slotted openings
	- number of heads	9
6.	Turbine:	
	- type	Axial, gas, jet, binded with fingers
	- number of stages	1
7.	Jet pipe:	
	- type	Subsonic, unregulated, with axis, inclined down on 10°
9.	External dimensions of the engine:	
	- length	1812 mm
	- diameter on a housing flange of nozzle assembly	552 mm
	- maximal height of the engine with aggregate	779 mm
10.	Coordinates of the gravity center:	
	- at X axis from the surface of the main mounts to the side of jet pipe	110 ±20 mm
	- at Y axis below the longitudinal section	120 ±15 mm
11.	Dry mass of the engine	222 kg

Engine control during the tests was done from the control room (Fig. 6.6) with the help of throttle control lever (TCL) connected with fuel pump through transmission. For reaching necessary regime of the engine operation TCL was stood into position of the required regime.

Table 6.2

Main operations regimes of the engine “RU19A-300”

Operation regime	Engine rotor speed		Thrust on stand, N	SFF, $\frac{\text{kgf of fuel}}{\text{kg/N h}}$	Time of constant operation, min	Operation time during resource, hours
	rpm	%				
Nominal	16000^{+83}_{-165}	$97^{+0,5}_{-1,0}$	Not less than 7845	Not more than 1.12	Not limited	Not limited
Cruise 0.9 of nominal	15100_{-83}	$94_{-0.5}$	Not less than 7061	Not more than 1.11	Not limited	Not limited
0.8 nominal	14850^{+83}_{-83}	$90^{+0.5}_{-0.5}$	-	-	Not limited	Not limited
Idling	5942^{+495}_{-415}	$36^{+3.0}_{-2.5}$	Not more than 490	-	Not more than 30 on ground, not limited at flight	Not limited

Fig. 6.6. Control room for engine’s operation control during the tests

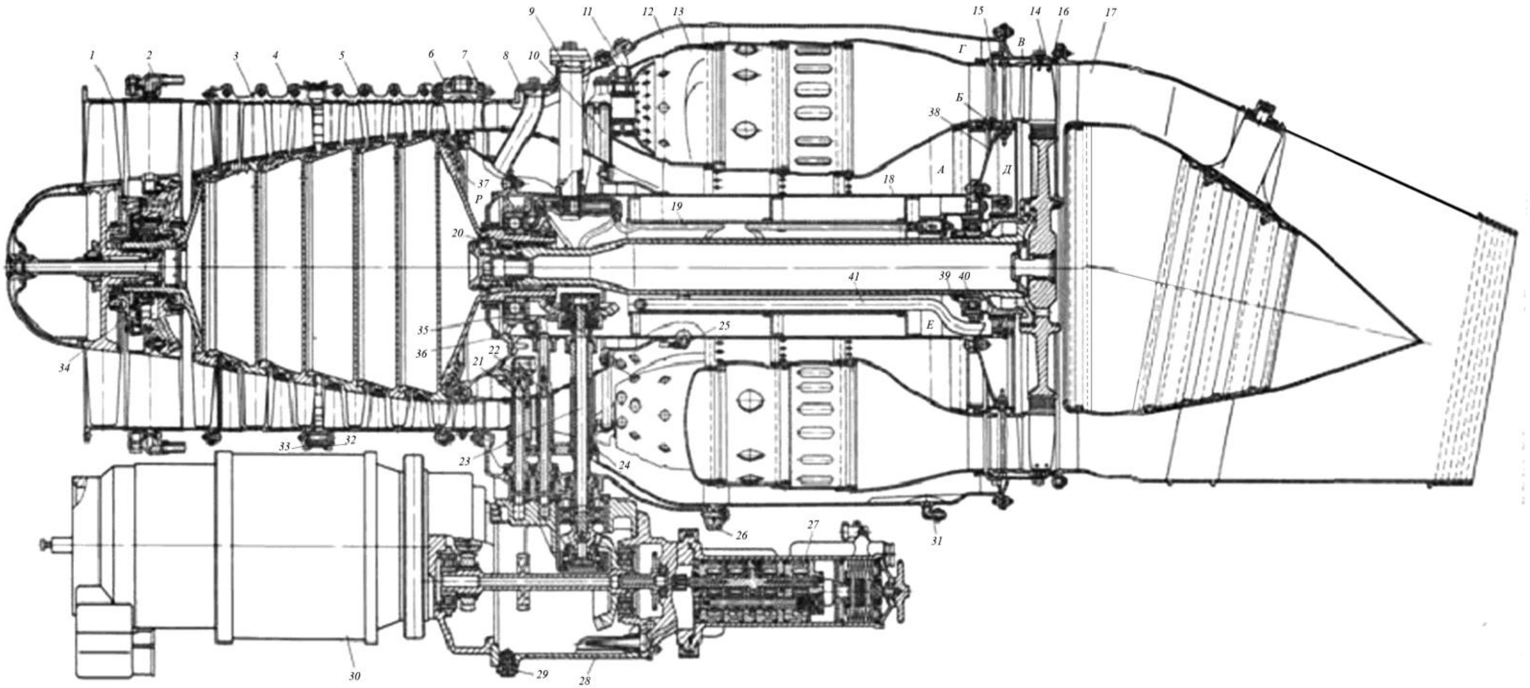


Fig. 6.5. Arrangement of JE “RU19A-300”:
1 – casing of the first stage of compressor; *2* – pipe of air supply for feeding up unloading cavities of front bearing and for warming of cowling; *3* – casing of the second and third stages of compressor; *4* – rotor of compressor; *5* – casing of the fourth and fifth stages of compressor; *6* – engine-mounting bracket; *7* – back casing of compressor; *8* – breathing air stack from unloading cavity; *9* – breathing stack of bearing housing; *10* – fuel collector; *11* – flame tube retainer; *12* – casing of ccombustion chamber; *13* – flame tube; *14* – turbine casing; 15 – nozzle guide vane; *16* – rotor of turbine; *17* – jet pipe; *18* – bearing housing; 19 – tube for supplying oil to center and rear bearings; *20* – socket for rotor connection; *21* – tube of oil drain from rear bearing; *22* – tube of oil drain from center bearing; *23* – shaft of accessory-gear box drive; *24* – shaft tube; *25* – tube of unloading cavity breathing; *26* – mounting bracket of bearing box; *27* – oil pump unit; *28* – accessory-gear box; *29* – oil drain valve; *30* – starter ГС-24Б; *31* – pressure tap; *32* – interstage air bleed tape; *33* – controllers of interstage air bleed tape; *34* – front bearing; 35 – center ball-bearing; *36* – center bearing; *37* – lab seal of unloading cavity; *38* – supporting wall of nozzle assembly; *39* – rear bearing box; *40* – rear bearing; *41* – tube of oil pumping from rear bearing

Before starting the bench tests the engine was installed onto stand with supplying to stand systems and normal fuel system. Next the engine was connected to vessels with JF blended with bio-additives. After that complex of checking works were done: checking of engine for absence of failures, cracks, rubbish, etc, checking of oil and fuel system for absence of failure or leakages and level of oil in oil tank, checking operation of control systems, including TCL. Later the testing was done according to the following testing program:

1) Start the engine with the help of "START" button. Automatic starting panel gives commands for switching on the starting device, switching on the electric shutoff valve, switching on the ignition system. After some time fuel comes to igniters, where it is fired by plugs. Then fuel comes to combustion chamber, where it is burned by plume of starting igniters, the turbine starts working and fuel automatic regulator makes fuel metering. After some time the ignition system and system of FF starting. After turbine excessive momentum significantly exceeds resistance torque of the JE, the starting device switches off. It happens, when relative rotor speed reaches 31±2 %. Further bring out of the engine to the idling regime is done due to excessive turbine moment. Engine start on JF or JFs blended with bio-additives should be done in accordance to the graph of checking engine operation on ground (Fig. 6.7.) After successful start of the engines its operation must be tested in the main regimes for accordance to certain parameters (exploitation norms), which are listed in the Table 6.3.

2) Later the engine is warmed up at idling regime (relative rotor speed is n = 36 %); duration of regime is not less than 40 s with registration of parameters.

3) The engine is brought out to cruise regime 0.8 of nominal (n = 90 %); duration of regime is not less than 40 s with registration of parameters. When relative rotor speed reaches 63±2 % tachometric signal equipment gives command for closing interstage air bleed tape.

4) The engine is brought out to nominal regime (n = 97 %); duration of regime is not less than 40 s with registration of parameters.

5) The acceleration response time is checked: engine is being brought to idling regime during 25 s, parameters are registered and engine is being brought to nominal regime during 1÷2 s and holding at regime during 10 s with registration of parameters.

6) The engine is brought out to 0.75 of nominal regime (n = 80 %); duration of regime is not less than 40 s with registration of parameters.

7) The engine is brought out smoothly to idling regime during 25 s with further stop, measuring of engine rotor run-out and registration of parameters. When rotor speed reaches 63±2 % tachometric signal equipment gives command for opening interstage air bleed tape. The engine is stopped by moving TCL from 80+5 % relative rotor speed to "STOP" position. During engine stopping the rotor run-out should be checked from idling revolutions to rotor stop. The runout time should be not less than 35 s.

8) Repeat the works, described in items 1÷7 for engine operation for two kinds of JFs blended with bio-additives.

9) Perform the protocol of bench tests.

The bench tests were fulfilled for 3 kinds of JF:

1. conventional JF of grade Jet A-1,
2. JF + 10% of RO modified FAEE bio-additive,
3. JF + 20% of RO modified FAEE bio-additive.

Table 6.3

Exploitation norms of regime parameters

Operation regimes	Relative rotor speed,%	Jet pipe temperature, °C	Oil pressure at engine inlet, MPa	Time of engine constant operation, min
Nominal	$97^{+0.5}_{-1.0}$	Not more than 720	0.34÷0.39	Not more than 5 min
Cruise 0.9 of nominal	$94_{-0.5}$	Not more than 700	0.34÷0.39	Not limited
0.8 of nominal	90±0.5	Not more than 700	0.34÷0.39	Not limited
Idling	$36^{+3.0}_{-2.5}$	Not more than 730	Not less than 0.1	Not more than 30 on ground, not limited at flight
Rotation	Not less than 11	-	Appears at the end of rotation	

During the bench tests the following engine operation parameters were measured:

1) relative rotor speed n, %,
2) engine inlet temperature $t_{\text{e.in.}}$, °C,
3) barometric pressure, B_{atm}, mm Hg
4) thrust, R, N
5) pressure in fuel manifold, $P_{\text{f.m.}}$, MPa,
6) jet pipe temperature, $t_{\text{j.p.}}$, °C,
7) fuel flow, G, l/hour,
8) acceleration response time, s.

Values of rotor speed, thrust and fuel consumption, which were measured during bench tests need to be recalculated to the ISA using formulae presented below. ISA is considered to be: barometric pressure $B_o = 760$ mm Hg and external temperature $t_o = 15$ °C.

Relative rotor speed:

$$n_{ISA} = n_{exp.} \cdot \sqrt{\frac{288}{t_0+273}}, \text{ rpm}; \tag{6.1}$$

where:

n_{ISA} – relative rotor speed at ISA,%

$n_{\text{exp.}}$ – experimental value of rotor speed,%

t_0 – temperature at ISA, °C.

Engine thrust:

$$R_{ISA} = R_{exp.} \cdot \frac{760}{B_0 - \frac{\Delta P_a^*}{13{,}6}}, \text{ N}; \tag{6.2}$$

where:
R_{ISA} – thrust at ISA, *N*,
$R_{\text{exp.}}$ – experimental value of thrust, *N*,
B_0 – barometric pressure, mm Hg,
ΔP_{a}^* – stagnation pressure reduction, mm w.g., kg/m^2.

Fuel consumption:

$$G_{ISA} = G_{exp.} \cdot \frac{760}{B_0 - \frac{\Delta P_a^*}{13.6}} \cdot \sqrt{\frac{288}{t_0 + 273}}, \text{ l/h}; \tag{6.3}$$

where:
G_{ISA} – fuel flow at ISA, l/h,
$G_{\text{exp.}}$ – experimental value of fuel flow, l/h,
B_0 – barometric pressure, mm Hg,
ΔP_{a}^* – stagnation pressure reduction, mm w.g., kg/m^2,
t_0 – temperature at ISA, °C.

Jet pipe temperature [116]:

$$t_{\text{j.p. } ISA} = \left(t_{\text{j.p. } exp.} + 273 \right) \cdot \frac{288}{t_0 + 273} - 273, \text{ °C}. \tag{6.4}$$

where:
$t_{\text{j.p. ISA}}$ – jet pipe temperature at ISA, °C,
$t_{\text{j.p. exp.}}$ – experimental value of jet pipe temperature, °C,
t_0 – temperature at ISA, °C.

Experimental volumetric FF may be translated into standard mass FF by its multiplication by fuel density:

$$G = G_{exp.} \cdot \rho. \tag{6.5}$$

where:
$G_{\text{exp.}}$ – experimental value of fuel flow, l/h,
ρ – JF density, kg/m^3.

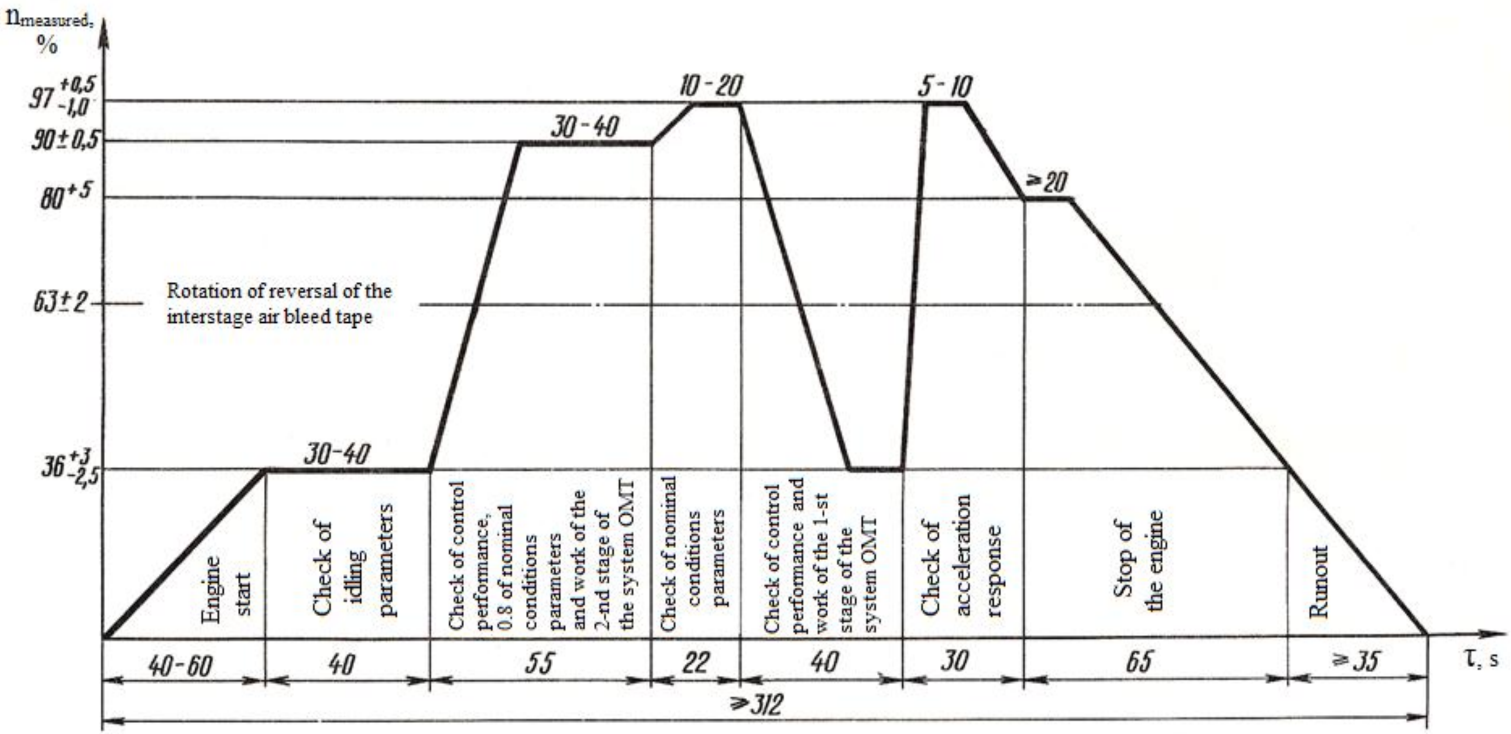


Fig. 6.7. Graph-cyclogram for checking engine operation on ground

6.3. Results and discussion

Experimental results on listed above parameters were brought into protocols. Generalized results for conventional JF and two kinds of blended JFs are presented in Table 6.4. The table includes both experimental data and data on rotor speed, engine thrust, FF and jet pipe temperature, brought to ISA conditions, which were calculated using formulae 6.1÷6.4.

6.3.1. Thrust

The following Fig. 6.8 shows the result on JE's thrust determination using conventional JF, JF blended with 10 % of RO modified FAEE bio-additive and JF blended with 20 % of RO modified FAEE bio-additive. Thrust evolution is presented as a function of engine operation conditions – angle α of the throttle control lever.

From the graph above it is clearly seen that all the tested fuels produced almost the same JE's thrust. At JE acceleration to 0.8 of nominal regime (α ≈ 80) JFs blended with 10 % and 20 % of RO modified FAEE show higher thrust values. At the same time during acceleration to nominal regime better thrust is produced by conventional JF. However the variations in JE's thrust are insignificant and are within the acceptable limits.

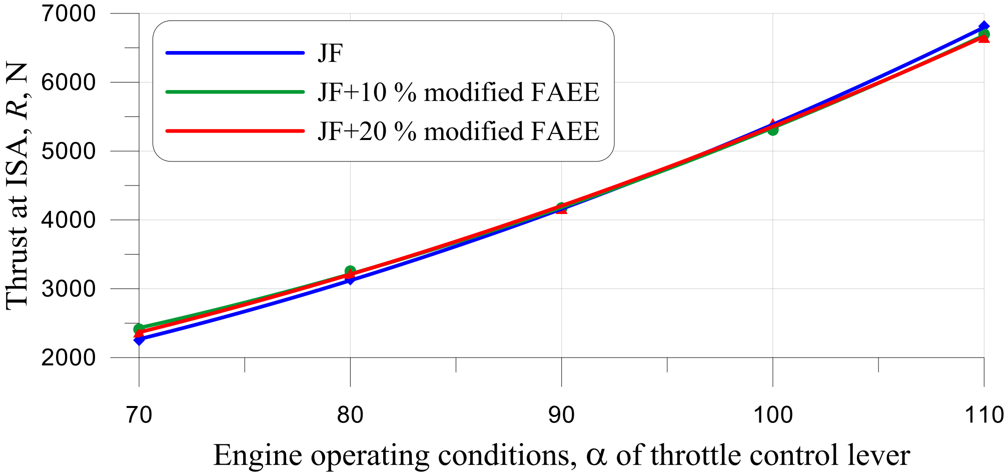


Fig. 6.8. JE's thrust as a function of engine operating conditions

Table 6.4

Experimental results of JFs bench tests on engine “РУ19А-300”

Fuel sample	Parameter of engine operation, α TCL	Relative rotor speed, %	Relative rotor speed at ISA, %	Engine inlet temperature, °C	Barometric pressure, mm Hg	Thrust, N	Thrust at ISA, N	Pressure in fuel manifold, MPa	Jet pipe temperature, °C	Jet pipe temperature at ISA, °C	Fuel flow, l/h	Fuel flow at ISA, l/h	Acceleration response time, s
JF of grade Jet A-1	Start	-	-	-	748		-	-	590	569.5	-	-	7.0
	Idling	36	-	22		392.3	-	1.47	600	579.3	-	-	
	70	70.5	57	23		1863	2256	1.96	522	500.5	473	388	
	80	78.0	62	23		2599	3138	2.20	525	503.4	571.5	459	
	90	84.3	65	25		3452	4178	2.45	550	522.4	690	543	
	100	90.5	67	25		4433	5345	2.84	600	570.7	841	637	
	110	92.6	69/70	29		5590	6816	3.43	661	617.7	1049.8	767	
JF+10% bio-additive	Start	-	-	31	747.5		-	-	590	544.6	-	-	7.575
	Idling	36	-	31		382.5	-	-	632	584.4	-	-	
	70	72.1	48.5	33		1991	2412	2.06	521.5	474.8	491.8	337	
	80	78.75	53	33		2687	3256	2.26	546	497.8	567.7	389	
	90	85.0	57	33		3447	4173	2.55	550	501.6	696	477	
	100	90.5	61	33		4384	5310	2.84	597	545.8	841.1	577	
	110	96.2	65	33		5546	6698	3.43	661	606	1045.6	717	
JF+20% bio-additive	Start	-	-	-	747.5	-	-	-	570	523	-	-	7.36
	Idling	39	-	32		402.1	-	1.47	620	570.2	-	-	
	70	72.2	48,5	33		1961	2368	2.04	524	477.1	499.1	342.5	
	80	79.1	53	33		2648	3221	2.26	528.5	481.4	590.4	404.5	
	90	85.2	57	33		3437	4163	2.45	552	475.2	704.1	482.5	
	100	90.8	61	33		4903	5403	2.84	599	547.7	854.1	585.5	
	110	96.2	65	33		5492	6649	3.43	661.5	606.5	1036.5	710.5	

At the same time the graph at Fig. 6.8 doesn't characterize the absolute value of thrust produced by the JE. It describes only response of JE operation to the position of the throttle control level. It is known that thrust of the JE is stipulated by the degree of air compression produced by the compressor. The work of the compressor is provided by the rotor spinning. Thus, the JE's thrust is directly proportional to the work performed by the rotor that is characterized by rotor speed. Taking into account the above mentioned, the JE's thrust was considered as a function of rotor speed (Fig. 6.9).

The results on Fig. 6.9 show the significant difference in thrust produced by conventional JF and blended JFs. Acceleration of JE from idling regime to 0.8 of nominal and producing thrust about 4000 N when powered by blended JFs is provided by less relative rotor speed (48.5 %) comparing to conventional JF, when the same thrust is provided by higher relative rotor speed (about 58 %). It is seen that the same values of JE's thrust are reached at lower rotor speed when JE uses blended JFs, comparing to conventional JF. Less work is done by the JE for producing the same thrust. The results show that blended JFs are more efficient comparing to conventional JF of grade Jet A-1. At the same time it was found no significant difference in JE's thrust produced by both JFs blended with RO modified FAEE bio-additives.

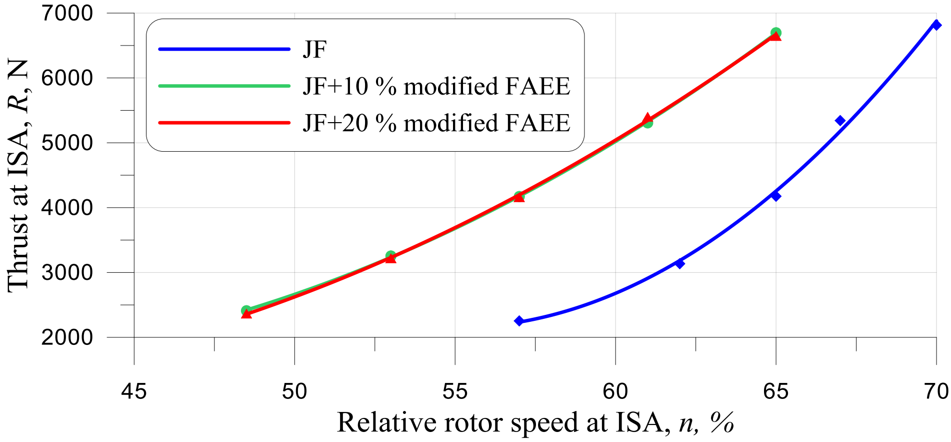


Fig. 6.9. JE's thrust as a function of engine rotor speed when powered with *1* – JF Jet A-1; *2* – JF + 10% of modified FAEE; *3* – JF + 20% of modified FAEE

6.3.2. Fuel flow

The following Fig. 6.10 shows the result on JE's FF determination using conventional JF, JF blended with 10 % of RO modified FAEE bio-additive and JF blended with 20 % of RO modified FAEE bio-additive. The parameters of FF are presented as a function of engine operation conditions – angle α of a throttle control lever. The graph represents data on volumetric FF of the JE.

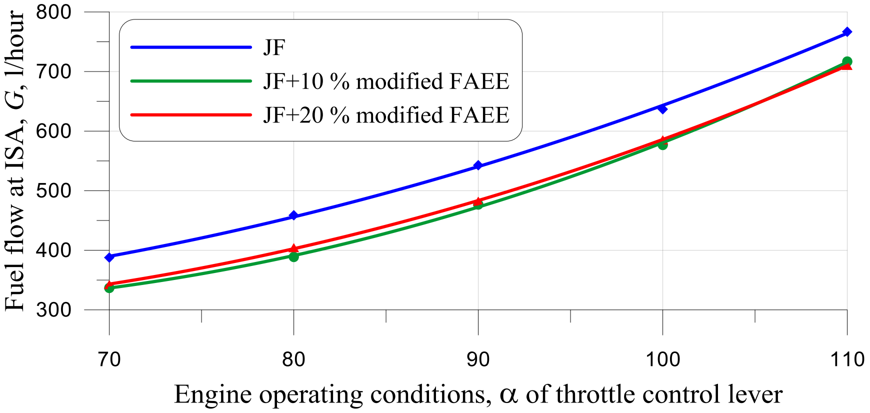


Fig. 6.10. JE's thrust as a function of engine rotor speed when powered with *1* – JF Jet A-1; *2* – JF + 10% of modified FAEE; *3* – JF + 20% of modified FAEE

From the graph above it may be seen that JFs blended with 10 % and 20 % of RO modified FAEE have presented a significant reduction in FF comparing to conventional JF. The FF for JF blended with 10 % of RO modified FAEE bio-additive is on 50÷70 l/h less that comparing to conventional JF. At the same time JF with higher content of bio-additive (20 %) has provided slightly greater FF, that is on 5÷15 l/h more than for JF with 10 % of bio-additive. Evidently this positive result on FF reduction was achieved due to the higher densities of blended JFs.

The graph at Fig. 6.10 describes response of JE operation to the position of the throttle control level. The JE's FF was also considered as a function of rotor speed (Fig. 6.11). Results at Fig. 8.11 show the difference in FF provided by conventional JF and blended JFs. It is seen from the graph that the same values FF are provided at lower rotor speed when JE uses blended JFs, comparing to conventional JF. We can see that FF at 0.9 of nominal operation regime (provided by relative rotor speed = 61 %) is equal to 577 l/h for blended JF with 10 % of bio-additive and 585 l/h for blended JF with 20 % of bio-additive, while the same regime for conventional JF (provided by relative rotor speed = 67 %) is reached at FF = 637l/h.

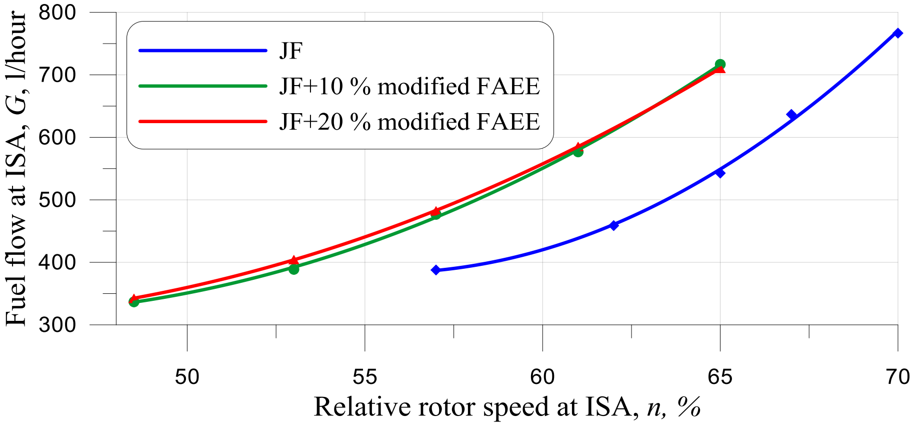


Fig. 6.11. JE's thrust as a function of engine rotor speed when powered with *1* – JF Jet A-1; *2* – JF + 10% of modified FAEE; *3* – JF + 20% of modified FAEE

When correlating the obtained results on FF with results on JE's thrust we can make a general conclusion that less work should be done by the JE to reach the same performance characteristics (thrust and FF) when it is powered by JFs blended with bio-additives. Thus, this result allows us concluding on greater energy and fuel efficiency of new blended JFs.

6.3.3. Pressure in fuel manifold

The following Fig. 6.12 shows the result on determination pressure in fuel manifold before injection into combustion chamber using conventional JF (*1*), JF blended with 10 % of RO modified FAEE bio-additive (*2*) and JF blended with 20 % of RO modified FAEE bio-additive (*3*). The studied parameter is presented as a function of engine operation conditions – angle α of the throttle control lever.

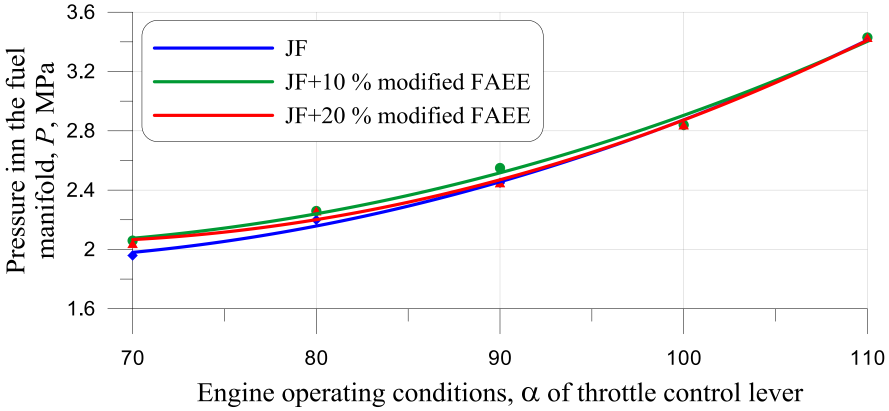


Fig. 6.12. Pressure in fuel manifold as a function of engine operating conditions when powered with *1* – JF Jet A-1; *2* – JF + 10 % of modified FAEE; *3* – JF + 20 % of modified FAEE

From the graph above it is clearly seen that pressure in fuel manifold that is generated during supply all the tested fuels doesn't show significant differences. During JE acceleration from idling regime to 0.8 of nominal regime (α ≈ 80) JFs blended with 10 % and 20 % of RO modified FAEE cause higher pressure in fuel manifold. Probably this may be explained by greater viscosity values of blended JFs. At the same time during acceleration to 0.9 of nominal regime (α ≈ 90→100) the difference in pressure becomes less. And at nominal regime (α ≈ 110) all the tested fuels cause the same values of pressure in fuel manifold. In general all the experimental values of pressure in fuel manifold are within the acceptable limits.

8.3.4. Jet pipe temperature

The Fig. 6.13 shows the result on measuring gas temperature in the jet pipe of the JE using conventional JF, JF blended with 10 % of RO modified FAEE bio-additive and JF blended with 20 % of RO modified FAEE bio-additive. The studied parameter is presented as a function of engine operation conditions – angle α of a throttle control lever.

From the graph above it is clearly seen that using conventional JF generate higher gas temperature in the jet pipe comparing to JFs blended with bio-additives. Here we can observe a gradual decrease of jet pipe temperature with increasing content of bio-additive in JF blends. This effect is considered to be positive because of the several reasons.

First of all temperature decrease may positively influence on materials and structure of JE exhausts system. It is well known that metal alloys, used for jet pipe construction, have to be resistant to extremely high temperatures, produced by hot gas stream. Thus, using blended JFs may contribute to durability of JE's construction.

It is also known that high temperature, produced by gas stream is the reason for atmospheric nitrogen oxidation and formation of NO_x emissions. There is a direct dependence between gas temperature and amounts of NO_x emissions. From this statement we can conclude that decreasing of jet pipe temperature may positively contribute to overall reduction of NO_x emissions.

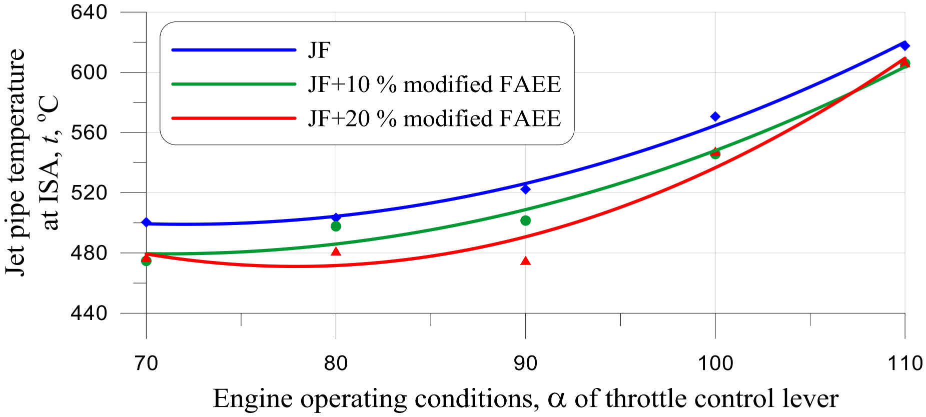


Fig. 6.13. Jet pipe temperature as a function of engine rotor speed when powered with *1* – JF Jet A-1; *2* – JF + 10% of modified FAEE; *3* – JF + 20% of modified FAEE

6.3.5. Relative rotor speed

The following Fig. 6.14 shows the result on studying relative rotor speed of the JE using conventional JF, JF blended with 10 % of RO modified FAEE bio-additive and JF blended with 20 % of RO modified FAEE bio-additive. The studied parameter is presented as a function of engine operation conditions – angle α of a throttle control lever.

From the graph at Fig. 6.14 it may be seen that JFs blended with 10 % and 20 % of RO modified FAEE have presented a significant reduction in relative rotor speed generated by the JE comparing to conventional JF. When correlating the obtained results on relative rotor speed with results on JE's thrust and FF we can make a general conclusion that using blended JFs is more efficient comparing to conventional JF as less work should be done by the JE to reach the same performance characteristics (thrust and FF). Thus, this results allows us concluding on greater energy and fuel efficiency of new blended JFs.

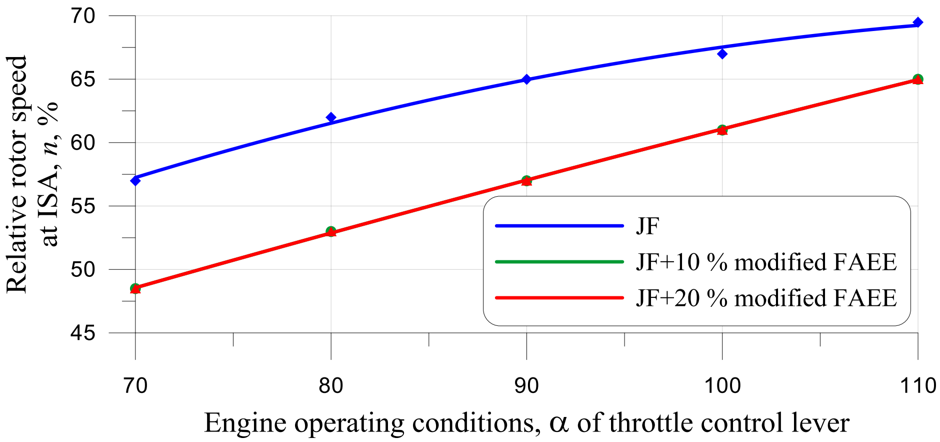


Fig. 6.14. Rotor speed as a function of engine rotor speed when powered with *1* – JF Jet A-1; *2* – JF + 10 % of modified FAEE; *3* – JF + 20 % of modified FAEE

8.3.6. Acceleration response time

The final parameter that was controlled during bench tests of JF samples is acceleration response time. This parameter characterizes the time necessary for the JE to reach its maximal power (maximal thrust). Acceleration response time was measured as a time for acceleration from idling regime to nominal regime. The results of measurements are shown at Fig. 6.15.

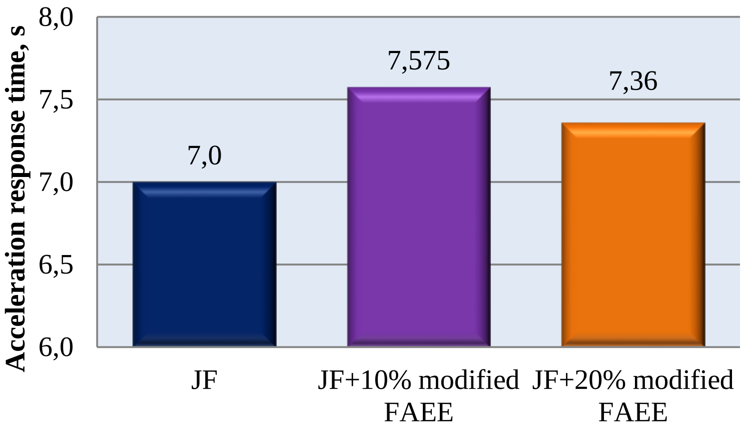


Fig. 6.15. Acceleration response time for JE when powered with: *1* – JF Jet A-1; *2* – JF + 10 % of modified FAEE; *3* – JF + 20 % of modified FAEE

From the graph at Fig. 6.15 it may be seen that using JFs blended with bio-additives results in slightly higher acceleration response time of JE comparing to conventional JF. However, the time difference is not significant and completely within exploitation norms for the tested JE.

Chapter 7

EVALUATION OF EMISSIONS FROM JET ENGINE POWERED BY JET FUELS BLENDED WITH BIO-ADDITIVES

7.1. Aim and scope of the study

It is well known that qualitative and quantitative composition of aircrafts' emissions is determined by construction and efficient operation of JEs and also environmental properties of JFs, which in its turn are determined mainly by containing in them heteroatomic compounds such as sulfur. Sulfur compounds influence on the content of sulfur oxides in exhaust gases of aircraft and consequently on their toxicity. The presence of aromatic hydrocarbons in JFs is an important indicator in assessing its environmental properties. Policyclic aromatic compounds are the source of soot in exhaust gases of aircrafts.

For emissions estimation purposes, ICAO has defined a specific reference landing – take-off (LTO) cycle below a height of 915 m (3 000 ft) (Fig. 7.1).

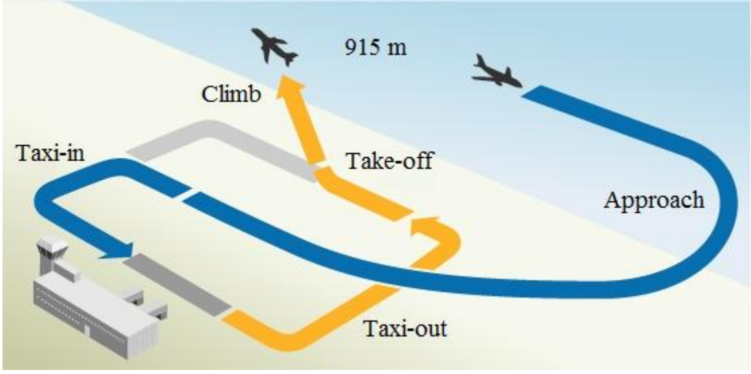


Fig. 7.1. The ICAO landing and take-off cycle [168]

This cycle consists of four modal phases chosen to represent approaching, taxiing/idling, take-off and climbing and is a much simplified version of the operational flight cycle (Table 7.1).

Table 7.1

Reference LTO cycle of an aircraft

LTO phase	Duration of LTO phase, min	Relative engine thrust, %
Take-off	0.7	100
Climb up to height 915 m	2.2	85
Approach and landing from height 915 m	4.0	30
Taxiing and ground idling	26.0	7

This reference emissions LTO cycle is intended to address aircraft operations below the atmospheric mixing height or inversion layer. While the actual mixing height can vary from location to location, on average it extends to a height of approximately 915 m (3 000 ft). Pollutants emitted below the mixing height can potentially have an effect on local air quality concentrations, with those emitted closer to the ground having possibly greater effects on ground level concentrations.

The main aircrafts emissions, which are estimated according to ICAO recommendations is: CO_2, H_2O, SO_2, CH_4, CO, C_nH_m, NO_x and SN. Taking into account that aircrafts emissions can lead to significant local air pollution that is dangerous for humans, certain emissions norms of the mentioned above substances are introduced for each LTO operation regimes.

Levels of emission of each substance depends on the temperature, concentration of fuel and residence time in the combustion chamber. Moreover, the enumerated factors may have the opposite effect on emissions of various substances, which is the main problem in the design of JEs' combustion chambers with low emissions. In addition, due to the variations of these factors on different regimes of engine operation, emissions of poluttants change also differently (Fig. 7.2).

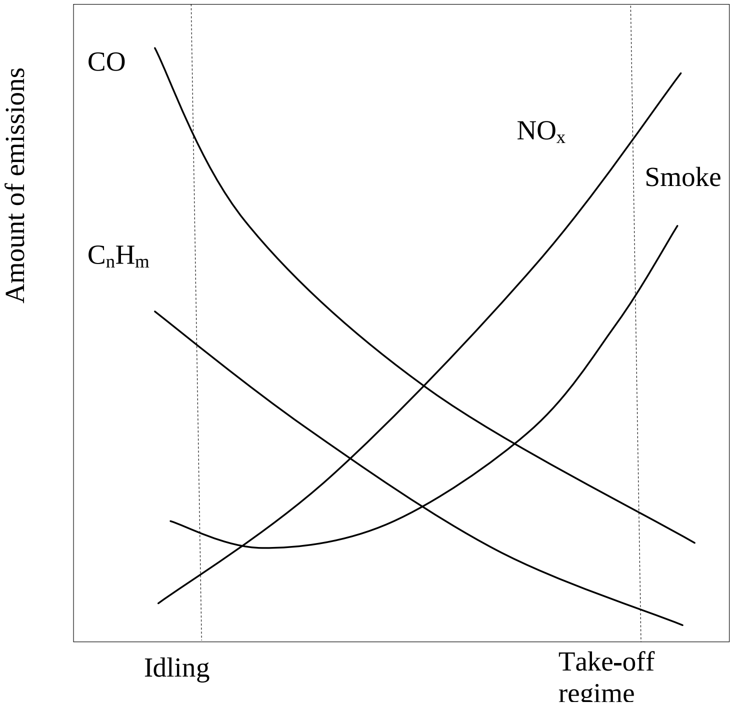


Fig. 7.2. Influence of JE operation regimes on amount of emissions

It is clearly understood that different types of JEs produce different amounts of emissions. Moreover, amount of exhaust gases also depends on the type of JF, mainly its hydrocarbon and element composition. Numerous studies, devoted to estimation of aircrafts emission in most cases do not take into account chemical composition of JFs.

7.2. Description of the method

Usually levels of aircrafts emissions may be determined applying two approaches: experimentally – using special measuring equipment and analytically – calculating, having a set of initial data. However, the first approach is used very rarely, because the experimental equipment is usually available for JE and aircraft producers, moreover, it is very expensive and complex in operation. That is why analytical approach is applied in most cases.

The level of emissions is evaluated in grams of pollutant per cycle for 1 kN of take-off thrust and determined by the formula:

$$\frac{M_j}{R_{t.th}} = \sum_{i=1}^{4} \left(EI_j\right)_i \frac{G_i \tau_i}{R_{t.th.}} = \frac{1}{3600} \sum_{i=1}^{4} \left(EI_j\right)_i G_s \bar{R}_i \tau_i \qquad (7.1)$$

where:

M_j – mass of pollutant *j*, emitted during standard LTO cycle that consists of *i* regimes, g,
$R_{t.th.}$ – take-off thrust, kN,
EI_j – emission index (EI) of pollutant, g/kg of fuel,
G_i – fuel flow, kg/s,
τ_i – duration of *i* regime, s,
G_s – spesific fuel consumption, kg/N h,
$\bar{R}_i$ – relative thrust.

Relative thrust may be found as [116]:

$$\bar{R}_i = \frac{R_i}{R_{t.th.}} \qquad (7.2)$$

where:

R_i – thrust at *i* regime, kN.
$R_{t.th.}$ – take-off thrust, kN.

In case when real (measured) FF is known this formula may be simplified to:

$$M_j = \sum_{i=1}^{4} EI_j \cdot G_i \cdot \tau_i \qquad (7.3)$$

where:

EI_j – emission index (EI) of pollutant, g/kg of fuel,
G_i – fuel flow, kg/s,
τ_i – duration of *i* regime, s.

From the formula above it is seen that level of emissions depends on the efficiency of combustion chamber that is characterized by EI EI_j and on specific FF G_s at each regime of the LTO cycle.

Taking into consideration typical technical requirements of ICAO to JFs, the quantities of products of complete fuel combustion may be calculated using equations of chemical reaction of burning. The products of complete fuel combustion include CO_2, H_2O, and SO_2. The equation of chemical reaction of complete oxidation of fuel (complete combustion) is considered to be stoichiometric.

The reaction of complete combustion of carbon has the following form:

$$C + O_2 \rightarrow CO_2 \qquad (7.4)$$

Taking into account that the molecular mass of carbon (C) is equal to 12 and molecular mass of oxygen (O_2) is equal to 32, we can derive:

$$12\text{ kg (C)}+32\text{ kg (}O_2\text{)}=44\text{ kg (}CO_2\text{)} \quad (7.5)$$

dividing by 12 we obtain the:

$$1\text{ kg (C)}+\left(\frac{32}{12}\right)\text{ kg (}O_2\text{)}=\left(\frac{44}{12}\right)\text{ kg (}H_2O\text{)} \rightarrow 1\text{ kg (C)}+C\text{ kg (}O_2\text{)}=\left(\frac{11}{3}\right)C\text{ kg (}CO_2\text{)} \quad (7.6)$$

Thus, knowing the coefficients of chemical reaction equation, EI of CO_2 can be calculated as following:

$$EI_{CO_2} = \frac{11}{3} \cdot m_{\mathrm{C}} \quad (7.7)$$

where:

m_{C} – content of carbon in fuel, % (m/m).

Analogously the reaction of complete combustion of hydrogen may be written:

$$2H_2 + O_2 \rightarrow 2H_2O \quad (7.8)$$

Taking into account that the molecular mass of hydrogen (H) is equal to 1 and molecular mass of oxygen (O_2) is equal to 32, we can derive:

$$4\text{ kg (}H_2\text{)}+32\text{ kg (}O_2\text{)}=36\text{(}H_2O\text{)} \quad (7.9)$$

dividing by 4 we obtain the:

$$1\text{ kg (}H_2\text{)}+\left(\frac{32}{4}\right)\text{kg (}O_2\text{)}= \left(\frac{36}{4}\right)\text{kg (}H_2O\text{)}\rightarrow 1\text{ kg (}H_2\text{)}+ 8H\text{ kg (}O_2\text{)}=9H\text{ kg (}H_2O\text{)} \quad (7.10)$$

Knowing the coefficients of chemical reaction equation, EI of H_2O can be calculated as following:

$$EI_{H_2O} = 9 \cdot m_{\mathrm{H}} \quad (7.11)$$

where:

m_{H} – content of hydrogen in fuel, % (m/m).

Analogously the reaction of complete combustion of sulfur may be written:

$$S + O_2 \rightarrow SO_2 \quad (7.12)$$

Taking into account that the molecular mass of sulfur (S) is equal to 32 and molecular mass of oxygen (O_2) is equal to 32, we can derive:

$$32\text{ kg S}+ 32\text{ kg }O_2=64\text{ kg (}SO_2\text{)} \rightarrow 1\text{ kg S }+S\text{ kg (}O_2\text{)}=2\text{ S kg (}SO_2\text{)} \quad (7.13)$$

Knowing the coefficients of chemical reaction equation, EI of SO_2 can be calculated as following:

$$EI_{SO_2} = 2 \cdot m_{\mathrm{S}} \quad (7.14)$$

where:

m_{S} – content of sulfur in fuel, % (m/m).

These calculations of EIs are maximal since they correspond to complete combustion of fuel. Its error at existing combustion efficiency values usually does not exceed 2 %. Formulae for calculating EIs of CO_2, H_2O, and SO_2 require data on mass ratio of hydrogen, carbon and sulfur in fuels. These data may be found in Table 7.3 of this work.

In order to predict NO_x emissions, basing on generalization of experimental data, the dependence on duration time in the combustion chamber τ_c and turbine inlet temperature $t_{\text{t.in.}}$ that mostly determines temperature of fire, AFR $\alpha_{c.z.}$ in combustion zone and degree of mixture distortion.

Thus, EI of NO_x was calculated by the following formula:

$$EI_{NO_x} = (0{,}06 + 0{,}005 \cdot \tau_c) \cdot e^{0{,}00736 \cdot t_{\text{t.in.}}} \tag{7.15}$$

where:

τ_c – FAM residence time in the combustion chamber before combustion, $\tau_c = 2 \div 10$ ms,

$t_{\text{t.in.}}$ – turbine inlet temperature.

Within the scope of this work the average value of τ_c was taken – $\tau_c = 6$ ms. From the literature sources it is known that the value of turbine inlet temperature $t_{\text{t.in.}}$ is usually higher than jet pipe temperature $t_{\text{j.p.}}$ on ~200 °C. Absence of the dependence of NO_x emissions on pressure in the combustion chamber is explained by the stability of pressure during oxidation reaction of nitrogen.

7.3. Results and discussions

7.3.1. CO_2 emissions

Using the data from Table 5.3 mass ratio of carbon, hydrogen and sulfur in samples of JF and JF blended with 10 % and 20 % of modified FAEE bio-additives were derived (Table 7.2).

EI of CO_2 was calculated using data from the table above by the formula (7.7). The results of calculation are presented on Fig. 7.3.

Table 7.2

Mass ratio of chemical elements in fuel samples

Fuel sample	Content, % (v/v)			
	Carbon (C)	Hydrogen (H)	Sulfur (S)	Oxygen (O)
JF	84.975	14.0	0.025	-
JF+ 10% modified FAEE	84.1668	13.7095	0.02335	1.1008
JF+ 20% modified FAEE	83.3586	13.419	0.0217	2.2015
Modified FAEE	76.889	12.095	0.0085	11.0075

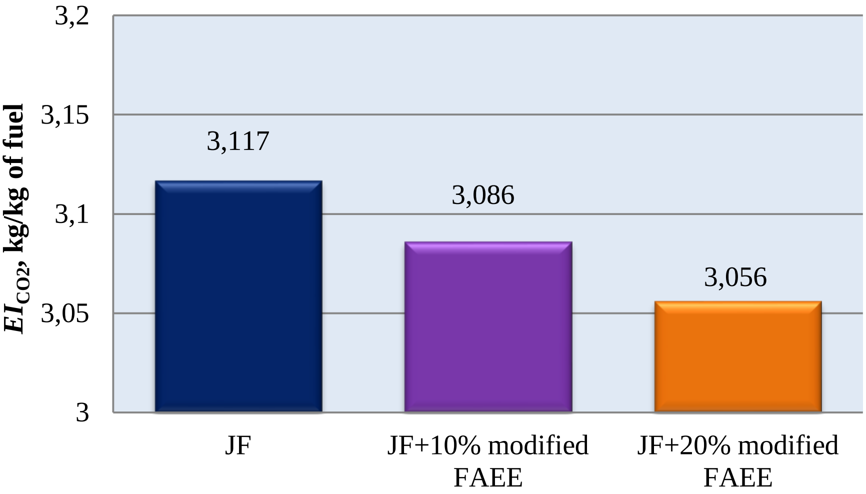


Fig. 7.3. EI of CO_2 during combustion of tested fuel samples

It was found that combustion of JFs blended with RO FAEE bio-additives in quantities 10 % and 20 % (v/v) results in lower values of CO_2 emissions comparing to combustion of conventional fuel. This may be explained by differences in chemical and element composition of RO bio-additives and conventional JF. Typical JF contains about 85 % of carbon in its composition. At the same time bio-additives contain less than 77 % of carbon. It means that adding RO modified FAEE bio-additives into JF decreases total content of carbon in fuel blends. Thus in a result of blended JFs combustion, which contain 20 % of bio-additives, the amount of CO_2 emissions may be decreased by 1.96 %. Here special attention should be paid to the comparatively high content of oxygen (~11 %) in bio-additives, while it is almost absent in JF. Presence of oxygen in fuel allows rising its completeness of combustion. It means that from one side we observe decrease of CO_2 emission due to the decrease of carbon content in blended JF. And from other side, increase mass content of oxygen in blended JFs raises completeness of fuel combustion.

7.3.2. H_2O emissions

EI of H_2O was calculated using data from the table above by the formula (7.11). The results of calculation are presented on Fig. 7.4.

It was found that combustion of JFs blended with RO FAEE bio-additives in quantities 10 % and 20 % (v/v) results in lower values of H_2O emissions comparing to combustion of conventional fuel. This may be also explained by differences in chemical and element composition of RO bio-additives and conventional JF. Typical JF contains about 14 % of hydrogen in its composition. At the same time bio-additives contain about 12 % of hydrogen. It means that adding RO modified FAEE bio-additives into JF slightly decreases total content of hydrogen in fuel blends. Thus in a result of blended JFs combustion, which contain 20 % of bio-additive, the amount of H_2O emissions may be decreased by 4.04 %.

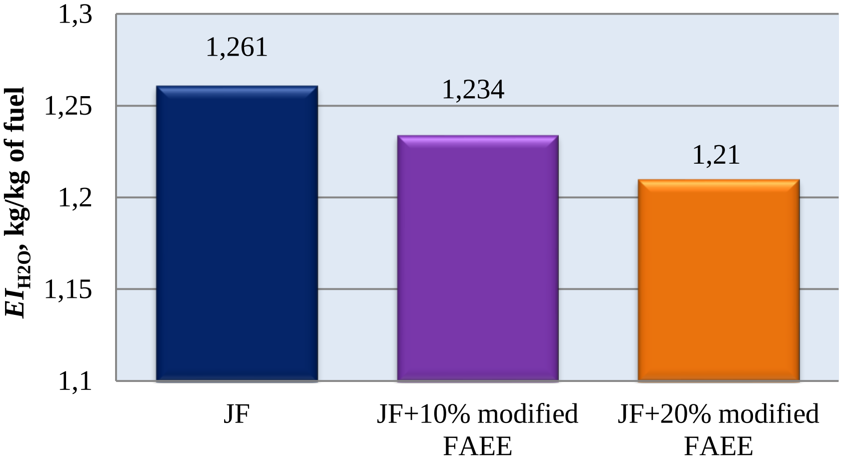


Fig. 7.4. EI of H_2O during combustion of tested fuel samples

7.3.3. SO_X emissions

EI of SO_2 was calculated using data from the table above by the formula (7.11). The results of calculation are presented on Fig. 7.5.

It was found that combustion of JFs blended with RO modified FAEE bio-additives in quantities 10 % and 20 % (v/v) results in lower values of SO_2 emissions, comparing to combustion of conventional fuel. This may be explained by that fact that RO and consequently bio-additives produced from RO contain significantly smaller (negligible) amount of sulfur compounds comparing to conventional JF. It means that adding RO modified FAEE bio-additives into JF decreases total content of sulfur in fuel blends. Thus SO_2 emissions in a result of blended JFs combustion, which contain 20 % of bio-additive, may be decreased by 14.0 %.

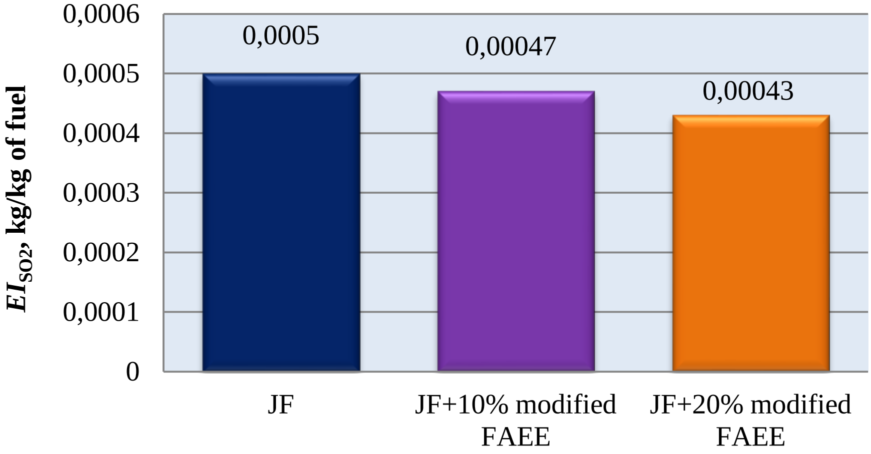


Fig.7.5. EI of SO_2 during combustion of tested fuel samples

7.3.4. NO_X emissions

EIs of NO_X were calculated by the formula (7.15). Taking into account that values of turbine inlet temperature $t_{t.in.}$ depend on JE operation regime, EIs were calculated for each regime of the standards aircraft LTO cycle. The results of calculations are presented on Fig. 7.6.

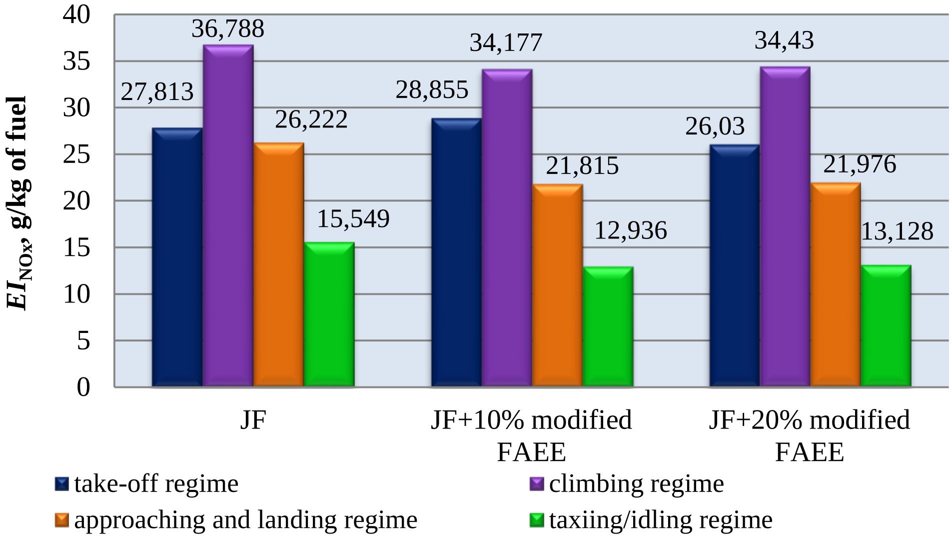


Fig. 7.6. EI of NO_X during combustion of tested fuel samples on different regimes of the standard LTO cycle

The results of calculations have shown that combustion of JFs blended with RO FAEE bio-additives in quantities 10 % and 20 % (v/v) results in lower values of NO_X emissions at all stages of standard LTO cycle comparing to combustion of conventional fuel. However, analyzing formula 7.15 and theoretical data from Chapter 2.4 it is clearly seen that values of NO_X emissions almost don't depend on chemical (element) composition of JFs. Both types of fuels – conventional and blended with bio-additives may contain only trace amounts of nitrogen compounds that is not crucial for total NO_X emissions formation. NO_X emissions, which are the products of atmospheric nitrogen oxidation, are determined by FAM residence time in combustion chamber and mainly by turbine inlet temperature. Thus, analyzing the experimental data on JE's operation parameters testing, it may be clearly seen that use of JF blends results in lower turbine inlet and jet pipe temperatures comparing to conventional JF. This decrease in temperature consequently affects the amounts of NO_X emissions at each JE operation regime, i.e. standard LTO cycle regimes. Thus, NO_X emissions in a result of blended JFs combustion, which contain 20 % of bio-additive, may be decreased during take-off regime by 6.41 %, during climbing regime by 7.10 %, during approaching and landing regime by 16.81 % and during taxi/idling regime by 16.80 %.

7.4. Comparative characteristics of emissions from jet engine powered by jet fuels blended with bio-additives and conventional jet fuel

In order to summarize the obtained results on evaluation of exhaust gases emissions from JE powered by JFs blended with bio-additives and conventional JF the comparative characteristic of emission levels was developed.

As it was previously explained emission levels are determined not only by EI of certain pollutant, but also by specific FF at each regime of the LTO cycle and duration of these regimes. Because of that the comparative characteristic of emission levels was developed basing on the total mass of pollutants that is emitted during complete standard LTO cycle (Table 7.3.). Masses of pollutants were calculated using formula (7.3). The data about net FF were used from the results of JE operation parameters testing. Standard duration time of LTO cycle regimes was taken as it is recommended by ICAO.

Table 7.3

Comparative characteristics of aircraft exhaust gases in fuel samples

Fuel samples	Characteristics of aircraft exhaust gases – mass of pollutant, kg/standard TLO cycle							
	CO_2	Change of parameters, %	H_2O	Change of parameters, %	SO_2	Change of parameters, %	NO_x	Change of parapmeters, %
JF	228.914	-	92.608	-	0.037	-	1.826	-
JF + 10 % modified FAEE	177.148	-22.61	70.836	-23.51	0.016	-56.95	1.285	-29.59
JF + 20 % modified FAEE	199.903	-12.67	79.150	-14.53	0.028	-23.43	1.441	-21.07

Basing on the results of analysis we can make the conclusion that blending conventional JFs with RO modified FAEE bio-additive in quantity up to 20 % (v/v) allows decreasing total level of exhaust gases emissions form aircraft JE. The obtained results allowed us concluding that aircraft's emission level is a complex characteristic that depends on both type of JF used (it quality, element and hydrocarbon composition) and JE operation parameters (efficiency of combustion process, FF).

Is of products of complete JF combustion – CO_2, H_2O and SO_2 – may be predicted (calculated) basing on data about fuel's chemical and element composition and do not require fulfilling JE's bench test. At the same time evaluation of EI of NO_x requires JE's testing as it is determined by the characteristics of JE operation and calculation is based on these data. The results have shown that increasing ratio of bio-additive in JF blends causes corresponded decreasing of studied pollutants EIs. Adding 20 % (v/v) of RO modified FAEE bio-additives may results in decreasing CO_2 EI up to 1.96 %, H_2O EI up to 4.04 %, SO_2 EI up to 14.0 %, and NO_x EIs up to 6.41 % during take-off regime and up to 16.80 % during taxi/idling regime.

At the same time evaluation of total mass of pollutants emitted during standard LTO cycle has shown different results. Blending conventional JFs with RO modified FAEE bio-additive generally decreases the total mass of emissions. However adding 10 % (v/v) of bio-additives allows reaching more reduction of mass of emissions than in case when 20 % (v/v) of bio-additive is added to conventional JF. This result is explained by that fact that FF, measured during bench tests, was higher for JF blend containing 20 % of bio-additives (especially at idling and 0.8 of nominal regimes of JE operation). Thus, finally we can make the conclusion that adding 10 % (v/v) of RO modified FAEE bio-additives may results in decreasing mass of CO_2 emissions up to 22.61 %, mass of H_2O emissions up to 23.51 %, mass of SO_2 emissions up to 56.95 %, and mass of NO_X emission up to 29.59 %.

CONCLUSIONS

This study allowed solving an important present day research and utility task that is characterized by scientific novelty and possesses practical importance. The main task of the study has foreseen developing of alternative jet fuel by means of blending conventional jet fuel with plant-derived bio-additives and studying properties of new alternative jet fuels.

The review and systematization of the variety and classification of JFs used all over the world was done during literature overview. The technologies of JFs production from various non-renewable energy sources are discussed. The list of technical requirements to modern JFs is given in chapter 3. Analyzed data allowed outlining the factors, which stipulate development and implementation of alternative JFs: limitation of crude-oil deposits, decreasing of its energy efficiency, global warming that is intensified by processes of extraction, processing and use of fuels and exhaust gases that negatively affect atmosphere.

Perspective technologies and feedstock for alternative JFs production were analyzed, as well as advantages and disadvantages of each of them. It was concluded that the most perspective and easily available way for development alternative JFs is blending conventional JFs with products of plant oil esterification (fatty acids esters).

Fundamentals of JEs operation and exploitation are considered within this study. Basic principles of JE construction are presented with aim of comprehensive understanding of the JE performance and the role of JFs for its providing. It was shown how certain fuel properties may affect or improve JE performance. It was discussed, how JF quality and composition may affect the life span, reliability and durability of JEs.

Chapter 4 of the work is devoted to development of method for bio-additives production from RO fatty acids esters. The method of vacuum distillation allows obtaining high quality bio-additives based on FAME and FAEE of RO and CamO oils, which were used for blending with conventional JFs.

The results of experimental studies of physical-chemical and exploitation properties of new blended JFs are shown in Chapter 5:

20) blending conventional JF with bio-additives causes rising of JFs density; this change may be explained by rising energy of dispersive interation between molecules of hydrocarbon JF and bio-additives; at the same time it was found that density of new blended JFs sample satisfy requirements of specifications,
21) blending conventional JF with bio-additives leads to extending fractional composition of JFs toward the final boiling point, that is explained by much stronger intermolecular bonds between esters molecules and higher heat of evaporation values of ester consequently; analyzing the requirements of specification for JFs, which are characterized by increased final boiling points, it can be concluded that bio-additives can be used also for blending with conventional JFs of heavy fractional composition,
22) blending JFs with bio-additives causes consequent decreasing of net heat of combustion of JFs, that is explained by the lower content of hydrogen in bio-additives and presence of significant quantity of oxygen; at the same time the

change of energy value of new blended JFs is minimal due to it increased density; the energy value of blended JFs is at the level, typical for conventional JFs,

23) blending conventional JF with bio-additives leads to significant rising of JFs kinematic viscosity, that happens due to the appearance of forces of intermolecular interaction between JF's and esters' molecules;
24) specifications to conventional JFs determines requirement to kinematic viscosity at -20 °C and all the tested fuel samples satisfy standard requirements,
25) blending conventional JF with bio-additives leads to general worsening of low-temperature properties of JFs that is revealed by rising of PP, this limits using of bio-additives in JFs' blends; the analagous tendency was observed during investigation of CFPP; thus maximal content of bio-additives may be 30 % (v/v). JFs' blends of such composition completely satisfies requirements of specifications to conventional JFs,
26) blending JFs with bio-additives showed positive results on improving antiwear properties of JFs, increasing content of bio-additives in JF cause rising the amount of surfactants in fuel and, consequently, strengthening of boundary film between friction pairs and thus improves antiwear properties of blended JFs,
27) blending JFs with bio-additives leads to improvements of JFs fire safety, that is provided by increased FlP due to rising the ratio of components with higher heat of evaporation comparing to conventional JFs,
28) blending JFs with bio-additives has not shown negative effect on JFs' corrosiveness. Corrosiveness of blended JFs satisfies requirements of specifications;
29) In order to study thermal stability and combustion characteristics of blended JFs the thermogravimetric analysis of conventional JF, RO modified FAEE and samples of JF blends was done. It was found that thermal stability of blended JFs increases with the increase of content of bio-additives in fuel blends.

In the result of experimental studies described in Chapter 5, the comparative characteristics of physical-chemical and exploitation properties of JFs blended with FAME and FAEE bio-additives produced from RO and CamO was developed. The properties of new alternative JFs were considered for satisfying requirements of standards for JFs of grade Jet A-1. It was concluded that maximal content of bio-additives in blended JFs is 30 % (v/v), which is limited by the values of such parameters as kinematic viscosity, PP, and net heat of combustion. Taking into account insignificant difference in characteristics of JFs blended with methyl and ethyl esters it is more rational to use rather FAEE than FAME. The use of ethanol provides production of bio-additives of completely renewable feedstock.

The results of bench tests of operation parameters of JE using conventional JF and two receipts of blended JFs, which contained 10 % and 20 % of RO modified FAEE bio-additive are shown in Chapter 6:

30) using JFs blended with bio-additives leads to improvement of JE thrust characteristics, as the same values of JE's thrust may be reached at lower rotor speed when JE powered with blended JFs, comparing to conventional JF; blended JFs are more efficient comparing to conventional JF of grade Jet A-1; at the same time it was found no significant difference in JE's thrust produced by both blended JFs samples,

31) using JFs blended with bio-additives leads to significant reduction of FF comparing to conventional JF; evidently this positive result on FF reduction was achieved due to the higher densities of blended JFs,
32) using JFs blended with bio-additives leads to reduction of gas temperature in the jet pipe comparing to conventional JFs (Fig. 6.13); temperature decrease will have positive effect on materials and structure of JE exhaust system improving its durability to high gas temperature; decreasing of jet pipe temperature will also contribute to overall reduction of NO_x emissions,
33) using JFs blended with bio-additives leads to reduction of relative rotor speed of JE comparing to conventional JF (Fig. 6.14); it was found that less work is done by the JE for producing the same thrust, thus blended JFs stipulate more efficient JE operation,
34) using JFs blended with bio-additives results in slightly bigger acceleration response time of JE comparing to conventional JF (Fig. 6.15); however the time difference is not significant and completely within exploitation norms for the tested JE.

In the result of bench tests it was concluded that operational parameters of the JE powered with new blended JFs completely satisfy exploitation norms, which are set in specification for tested JE. Thus, the proposed JFs blended JFs, which contain 10 % and 20 % of modified FAEE bio-additive may be used as a working body of the JE and do not require its design changes.

The results of evaluation of emissions from JE powered with conventional JF and two receipts of blended JFs, which contained 10 % and 20 % of modified FAEE bio-additive are shown in Chapter 7:

35) combustion of JFs blended with bio-additives results in lower EI of CO_2 comparing to conventional JF (Fig. 7.3); this is explained by lower content of carbon and comparatively high content of oxygen in bio-additives, comparing to conventional JF, that allows rising completeness of blended JFs combustion,
36) combustion of JFs blended with bio-additives results in lower EI of H_2O comparing to conventional JF (Fig. 7.4); this is explained by lower content of hydrogen in bio-additives comparing to conventional JF,
37) combustion of JFs blended with bio-additives results in lower EI of SO_2, comparing to conventional JF (Fig. 7.5); this is explained by trace amount of sulfur compounds in bio-additives comparing to conventional JF,
38) combustion of JFs blended with bio-additives results in lower EIs of NO_X at all stages of standard LTO cycle comparing to conventional JF (Fig. 7.6); this is explained mainly by lower turbine inlet and jet pipe temperatures comparing to conventional JF; this decrease in temperature consequently affects the amounts of NO_x emissions at each JE operation regime, i.e. standard LTO cycle regimes.

In the result of emissions evaluation it was concluded that blending conventional JFs with bio-additives allows improving its environmental properties: decreasing amounts of CO_2, H_2O, SO_2 and NO_x emissions in JE exhaust gases. Thus it was proved the improvement of environmental properties of JFs by means of introducing RO derived bio-additives.

Thus, in a result of this study it was shown and proved that the application of bio-additives derived from rapeseed oil in jet fuel, for a specified limit of configured blends, does not exceed the values of current standard requirements with reference to jet fuel.

It was confirmed that the bio-additives percentage in JF, until the current standard requirements are met, does not require design changes in JE.

It was also confirmed in a result of the work that the application of bio-additives, derived from RO, in JF reduce exhaust gases emissions from JE.

Utility conclusions

The improvement of exploitation properties of JFs, when blended with bio-additives in quantity up to 30 % was achieved: lubricity was increased by ~64 % and FlP was increased by 9.19 % and 6.93 % when blended with FAEE and FAME bio-additives respectively.

The improvement of operational parameters of JE, powered with JFs blended with modified FAEE bio-additives was achieved: FF was reduced by 7÷12 %, thrust produced by the JE was enforced by 60÷85 % and the same relative rotor speed and jet pipe temperature were reduced ~2 %.

The improvement of environmental properties of JFs, when blended with bio-additives in quantity up to 20 % was achieved: EI of CO_2 in exhaust gases was decreased by ~2 %; EI of H_2O in exhaust gases was decreased by 4 %; EI of SO_2 in exhaust gases was decreased by 14 % and EI of NO_x in exhaust gases was decreased during take-off regime by 6 %, during climbing regime by 7%, during approaching and landing regime by ~17 % and during taxi/idling regime by ~17 %.

The receipts of new JFs blended with bio-additives, which possess improved exploitation and environmental properties were developed. According to developed receipts JF blends may contain 10 %, 20 % and 30 % of modified FAME or modified FAEE bio-additives.

Future development conclusions

This study has created necessary and sufficient condition for future development of technologies of alternative JFs production and application. At the same time development and implementation of bio-based JFs requires solving the range of tasks.

The new bio-additives from various plant feedstock (i.e. UCO, sorghum, algae, etc) should developed in future. This is stipulated by the need to provide sufficient amounts of jet biofuel and requirements to prodive sustainability of alternative JFs production process. Except that, new bio-additives should possess satisfactory physical-chemical and exploitational properties.

Future studies on blended JFs should be directed to increasing the maximal content of bio-additives in conventional JFs at least up to 50 % (v/v). This may be achieved by the improvement of physical-chemical and exploitation properties of RO bio-additives. The fulfilled studies have shown that low-temperature properties (PP, FP) of blended JFs have to be improved. Also there is a need to improve energy properties (net heat of combustion) of RO bio-additives.

New studies have to be devoted to investigation of blended JFs stability: physical, chemical and thermal oxidation stability. These parameters are considered to be highly important as they provide proper quality of blended JFs during long term storage, transportation, other handling operations, as well as impact of external conditions like sunlight, moisture and high temperatures.

At the same time there is a need to develop new or updated methods for studying and control of some quality parameters of blended JFs. This is mainly stipulated by the differences in chemical composition and some chemical characteristics of bio-additives. Thus, development of new methods may help to may blended JFs quality control more accurate and precise.

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MODIFICATION OF JET FUELS COMPOSITION WITH RENEWABLE BIO-ADDITIVES

ABSTRACT

The study is devoted to developing of alternative jet fuel by means of blending conventional jet fuel with plant-derived bio-additives and studying properties of new alternative jet fuels. The review and systematization of the variety and classification of jet fuels used all over the world was done. The technologies of jet fuels production from various non-renewable energy sources are discussed. Factors, which stipulate development and implementation of alternative jet fuels were shown: limitation of crude-oil deposits, decreasing of its energy efficiency, global warming that is intensified by processes of extraction, processing and use of fuels and exhaust gases that negatively affect atmosphere. Perspective technologies and feedstock for alternative jet fuels production were analyzed, as well as advantages and disadvantages of each of them. Fundamentals of jet engine operation and exploitation are considered within this study. It was discussed how jet fuels quality and composition may affect the life span, reliability and durability of jet engines. The method for bio-additives production from rapeseed oil and camelina oil fatty acids esters was developed. High quality bio-additives based on FAME and FAEE of rapeseed and camelina oil were used for blending with conventional jet fuels. In the result of experimental studies the comparative characteristics of physical-chemical and exploitation properties of new alternative jet was developed. The properties of new jet fuels were considered for satisfying requirements of standards for fuels of grade Jet A-1. It was shown that maximal content of bio-additives in blended jet fuels is 30 %. In the result of bench tests it was concluded that operational parameters of the jet engine powered with new blended jet fuels completely satisfy exploitation norms, which are set in specification for tested jet engine, may be used as a working body of the jet engine and do not require its design changes. In the result of emissions evaluation it was concluded that blending conventional jet fuels with bio-additives allows improving its environmental properties: decreasing amounts of CO_2, H_2O, SO_2 and NO_x emissions in jet engine exhaust gases. The results of the study will contribute to reducing the energy dependence of air transport, improve its environmental friendliness and will promote improvement of the sustainability and safety of modern civil aviation.

Key words: jet fuel, jet engine, alternative fuel, bio-additive, rapeseed oil, camelina oil, physical-chemical properties, exploitation properties, environmental properties, emissions, operation parameters.