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TRADITIONAL TECHNOLOGIES FOR PRODUCTION OF FUELS FOR AIR-JET ENGINES

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Available energy resources for various fuels, mainly for gas-turbine engines are presented in the given article. Traditional technologies for jet fuels production from nonrenewable raw materials, such as crude oil, coal, natural gas, oil-shales and others are analyzed in details. The timeliness and necessity for development of alternative technologies of aviation biofuels production are determined in the given article.

Introduction

At modern stage of population development liquid fuel is obtained mainly in a result of oil refining [1]. Products of oil refining are highly effective fuels, various lubricating materials, bitumen, paraffins and etc (fig. 1). Speaking about volumes of oil extraction, thus from the beginning of its industrial production (since the end of $1850th$) till the middle of $1970th$ world oil extraction was increasing twice approximately each ten years. Then, because of the world oil crisis its rates have decreased. At today's rates of consumption, the amounts of discovered oil will be enough for 40 years approximately, nondiscovered – for 10-50 years more. During last 35 years amounts of oil consumption increased from 20 to 30 billion barrels per year [1]. According to data of International Energy Agency (IEA) in year 2011 a new historical maximum of daily oil extraction volume was reached and was equal to 89 million barrels per day.

Today in the world there is great variety of resources for fuel production [2; 3]. This fact is firstly explained by limited world oil resources, causing its disruptive price growth, and secondly – by permanent worsening of ecological situation, because of oil extracting,

refining and using processes together with human will to save surrounding environment.

Taking into account the increasing scientifictechnical progress and sweeping development of technologies in fuels' production industry, we see the necessity to classify fuels that are manufactured today in the world in some particular way. However, fuels can be classified according to various properties. The most popular ways used for fuel classification are presented in table 1 [3–5].

We consider that the most reasonable and substantial is the attempt to classify fuels according to kinds of raw materials used in their production processes. Figure 3 shows a schematic classification of primary feedstock, which are used for fuels' production.

Classification of fuels

Since the mid 70's the humanity was in an active search of alternative energy sources with the aim of oil replacement. [1] In Canada and Venezuela, for example, oil sands were developed in an open way (oil sands, in which after the separation of light fractions, heavy oil, bitumen and asphalt still remain). Oil reserves in the oil sands of Canada and Venezuela are about 3400 billion barrels. [1] At the current rate of consumption this amount of oil may be enough for about 110 years. In the USA there are big reserves of oil-shales, which are also used to produce fuels. So, oil-shales totally contain about 2.8 - 3.2 trillion tons of oil [1]. Besides, natural gas, brown and black coal are widely used as a raw material for production of different fuels (fig.2) [3; 5; 6]. However, the most serious problem, connected with fuel manufacturing from the above mentioned feedstock is their negative impact on the environment [6].

Development of the aviation techniques has a constant trend for increasing of speeds and altitudes of aircrafts, improvement of economic efficiency, mass properties, reliability and life span of motor systems of aircraft engines [7]. The most part of the

aviation technics is equipped with gas turbine engines. The reliability and efficiency of the engine work and therefore of the aircraft requires high-quality fuel. Modern fuels for civil aviation should meet a number of requirements related to efficiency, reliability and durability of the aviation technics. Special attention is paid now to the environmental safety of the fuel [6]. Among the general technical requirements for fuels forgas turbine engines are the following [8]:

• High level of volatility that provides reliable flammability and complete combustion efficiency;

• 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 aircraft engine;

• Absence of negative impact on metal and non-metal parts of the engine fuel system, equipment for storage and transportation of;

Good lubricating properties that 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;

 \bullet 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.

Physicochemical and also ecological properties of fuels for gas-turbine engines is primarily determined by the origin and properties of raw materials used for their production, the method of basic fractions obtaining, the methods of their purification and mixing, properties of the additives applied [3].

However, despite the diversity of available natural resources, at the modern stage of development, oil remains the traditional and the most common feedstock for the production of aviation fuels, as well as other types of fuels. The majority of modern fuels for gas-turbine engines are received through the direct distillation, also destructive methods of oil refining are applied [4]. At the same time, fuel obtained during processing of the non-oil raw materials, such as coal and oil-shales became widespread in some countries [1, 6]. This is mainly connected with the presence of certain resources in the territory of producing country. Fig. 3 shows a schematic representation of generalized classification of ways for gas-turbine engines fuels production from various kinds of feedstock.

Jet fuel production by direct oil distillation

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 [4]. All of these products can partially come into jet fuels, produced by direct 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 highquality products [6].

Then oil is divided into fractions. Jet fuels are represented by middle distillation oil fractions with boiling range that partially overlaps with diesel one. They contain different classes of hydrocarbons, heteroatom compounds and inorganic impurities [5]. Fractions of jet fuel 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 jet fuel, is not the same. For example, to increase the fire safety of fuel, kerosene fraction is taken out with a higher initial boiling point, and to enlarge the resources the final boiling temperature of the kerosene fraction is increased or mixed with gasoline fraction, extracted from the top of the main distillation column [4, 5].

Crude oil fractions of the direct distillation are purified from the compounds worsening the quality of jet fuels. In order to remove some of these compounds, fractions are treated with a solution of sodium hydroxide and washed with water [6, 7]. 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 jet fuel 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 jet fuel, then it lead to a deterioration of anti-wearing properties. Mercaptans are the most undesirable compounds in the gasoline and kerosene fractions that are used for jet fuel. For removal of mercaptans the following processes are applied: plumbating cleaning, purification with copper chloride and process "Merox" [7].

Effective method for the removal of heteroatomic compounds from fuel is hydrotreatment. It means catalytic purification in the presence of hydrogen and catalyst [6]. 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 [7]. 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-wearing properties of fuels are also removed along with undesirable substances. Therefore hydrotreated fuels are injected with antioxidant and anti-wear additives. Or hydrotreated component (up to 70%) is mixed with the factions of direct distillation [6]. The further increasing of hydrotreating regime hardness leads to partial hydrogenation of aromatic hydrocarbons (hydrodearomatization process) [7]. 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 fuel [6].

Jet fuel production by destructive oil refining

In order to increase the yield of a higher quality light oil from crude oil the secondary oil refining processes are used [6]. This involves oil processing with cracking (destruction) of heavy hydrocarbons into lighter ones. Such processes are known as destructive ones [6]. 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 [5, 6]. The given process is used to produce jet fuels 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 jet fuels have freezing point below minus 60 \degree C and contain few ($\approx 10\%$) 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-weaing properties it is better to introduce the appropriate additives [5].

During the deep hydrogenation process jet fuel 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 fuel that contains mainly naphthenes of high density (840 kg/m³ at 20 $°C$), low sulphur content (<0.01%), alkenes (iodine value $\langle 0.2 \times 1/100 \times 1$) and existent gums $\left(\langle 3 \rangle \right.$ mg/100 ml). There is an assumption [6] 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 necessary to introduce additives into the fuel. Despite the absence of surfactants, product possesses satisfactory anti-wearing properties due to its relatively high viscosity.

Currently at the territory of Ukraine three types of jet fuel are adopted for the air jet engines: *RT, TS-1* and also *Jet A-1* [5]. All of them are produced by the primary and secondary oil refining processes.

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 straight-run and mixed with hydrotreated component. In the latter case, hydro-treated component is added to the straight-run fraction of oil [3]. Technical characteristics of the given fuel are defined by industrial standard of Ukraine ГСТУ 320.00149943.011-99 Fuel TS-1 for jet fuels. Specifications. Technological scheme of TS-1 fuel production is shown schematically in fig. 4 [3, 6].

RT fuel. RT fuel is hydrotreated usually. It meets the requirements that are applied to fuel TS-1, and can replace it. Additionally, it is more thermally stable and allows heating in the fuel system of aircraft to higher temperatures, and thus can be applied in more heat-stressed engines of aircraft with the increased length of supersonic flight [3]. Requirements to RT fuel are determined by the brand industry standard of Ukraine ГСТУ 320.00149943.007-97 Fuel for jet engines "RT". Specifications. Technological scheme of RT fuel production is shown schematically in fig. 5 [3, 6].

Jet A-1 fuel. Aviation fuel Jet A-1 is a kerosene oil-derived fuel and is used for the majority of gas-turbine engines. It is characterized by a little bit higher flash point temperature and self-ignition temperature comparing to fuels TS-1 and RT. This type of fuel is used throughout the world and meets the requirements of ASTM, DEF STAN, IATA Guidance Material (Kerosene Type), NATO Code F-35 [5]. In Ukraine, the quality of the fuel Jet A-1is defined by the state standard ДСТУ 4796:2007. Aviation fuel for gas turbine engines Jet A-1. Specifications. Technological scheme of Jet fuel A-1 production is shown schematically in fig. 6 [3, 5, 6].

Jet fuel production by oil-shale refining

Technology of jet fuel production from oilshales is well-known and established one. Oilshales are solid sedimentary rocks composed mainly of carbonate and silicate minerals. There is 50-80% of inorganic substances and 20-35% of kerogen (sometimes up to 50%) in the dry matter of oil-shales [2]. Kerogen contains aromatic, acyclic, and also organic oxygen-and sulphur-containing compounds, practically insoluble in organic solvents. The base part of the oil-shales' refining process is dry distillation in a retort, where oil-shale itself is subjected to the pyrolysis at temperature of about 480-540 °C. Shale kerogen decomposes with formation of gasoline gas, pyrogenetic water, flammable gases and vapours of shale tar. In the following processes, shale tar can be distilled like traditional oil. Processes of oil-shale dry distillation can be divided into two types – with direct and indirect heating [9]. Process, where the resulting gas is burned, is a typical process with direct heating. Retort for dry distillation of oil-shales is a vertical veneered in the middle part refractory brick chamber, where crushed shale is constantly moved down and heated to a temperature of dry distillation with hot gases, rising up and contacting with the solids. At the same time kerogen is thermally decomposed, releasing vapours of shale tar and exhaust gases, which during moving up, are cooled with new oilshale, coming from the top, then are removed from the retort and sent to the cooling system and the separation. Separation of shale tar is done by passing of cooling vapours and gases through a special refrigerator, from which part of the fuel gas returns to the retort of dry distillation [10].

Dry shale's distillation can be performed both after their extraction on the surface, and directly in the places of natural occurrence of layers. In the last case, underground oil-shales

are heated to a temperature of dry distillation of 450-540 °C by burning some part of the shale or introduction of exhaust gases, such as natural gas, or overheated water stem. Subsequently, the product is pumped to the surface [9]. The main advantage of underground oil-shales processing is absence of need for its extraction, transportation to installation of the dry distillation and removal of the ash, remaining in the form of wastes.

Shale tar is applicable for mid-distillate fuels production like diesel and kerosene. However, it has a high density, medium sulphur, nitrogen and unsaturated hydrocarbons content. Density and freezing point of shale tar is higher than of many oil fractions with the same viscosity. Production of jet fuels from oil-shales by the method of high-temperature dry distillation requires hydrotreating to reduce the content of mentioned organic compounds and to improve its quality. For this purpose, such additional processes as visbreaking, catalytic hydrotreating and hydrocracking that should be implemented at the facility or in the vicinity of the installation for oil-shales dry distillation. In general, production of jet fuel from oil-shales of appropriate quality is connected with deeper processing and higher expenses than the production of fuels from crude oil [9]. Today, there is an already developed and approved oil-shale processing technology that includes fractionation, prolonged coking and hydrocracking. This technology is schematically presented in fig. 7 [9].

Fuel for gas turbine engines, obtained by processing of oil-shales has average content of aromatic hydrocarbons (10-25%) and does not cause problems associated with lubricating qualities. Moreover, it shows a high level of stability during long-term storage [2; 9]. Jet fuels produced as a result of oil-shales processing are now approved for use in both civil and military aviation.

Volumes of greenhouse gases emitted in a result of oil-shales refining depend mostly on applied technology of processing. Totally, processes of oil-shales refining and fuel manufacturing require considerably larger energy inputs than during crude oil refining, and consequently emissions of greenhouse gases are also more significant. Moreover, formation of greenhouse gases is influenced by such factors as construction of installation for oil-shales refining, use of electric power for installation heating, way of energy receipt, value and quality of by-products, availability of device for $CO₂$ and other gases catching [2].

As it was already mentioned, production processes of jet fuels from oil-shales include stages of deep hydrotreatment. Finally, we obtain product with low content of sulphur and in some cases (depending on applied purification method) product with low content of aromatic hydrocarbons. Thus, implementation of aviation fuels, produced from oil-shales, provides considerably low content of sulphur oxides and particulate matter in exhaust gases of aircrafts [2, 10].

Jet fuel production by coal processing

Method or process of Fisher-Tropsh (FTprocess) is a widely known technology of fuel production since the II World War [11]. The main feedstock, used for this technology is black and brown coal. Moreover, natural gas and biomass are also successfully used today [12]. FT-process includes four main stages. The first one is obtaining of synthetic gasthat is a mixture of hydrogen and carbon monoxide $(CO+H₂)$. Syngas is received as a result of coal gasification, other words its treatment with saturated water vapour at high temperatures and average pressure. Syngas, coming from coal gasifier contains considerable amount of carbon dioxide and

certain percentage of gaseous substances, formed by additives, taking place in raw material, for example, sulphur. Both $CO₂$, and other compounds negatively influence on FTprocess proceeding. That is why the next important stage is elemination of harmful substances from synthetic gas flow. This process is connected with considerable emissions of $CO₂$ into the atmosphere. The next stage is catalytic process of carbon monoxide hydration with application of iron and cobalt catalysts with further formation of mixtures of liquid hydrocarbons: alkanes, olefins, paraffins, alcohols and etc.

Changing conditions of reaction proceeding it is possible to vary ratios of obtained fractions. At the end, after finishing the FTprocess, synthesized fractions of hydrocarbons are treated in the way similar to processes of fuel production from crude oil (fig. 8) [2] Received fractions are characterized by almost zero content of sulphur heteroatom compounds. The major part of received products is used for production of jet and diesel fuels. Fuels, received by FT-process, contain paraffin hydrocarbons, comparing to conventional kerosene, aromatic hydrocarbons are practically absent [2]. As a result, their tendency to soot formation is considerably lower, and they are more thermally stable. In addition, jet fuel, obtained during coal processing possesses higher combustion value, so, its consumption during flight is less. However, the results of experiments indicate [6–8] that such fuel has worse lubricating properties, and this fact requires application of additives.

As it was already mentioned, natural gas is widely used along with coal for jet fuel production by FT-process [11]. The main component of natural gas is methane. In a result of FT-process the above mentioned synthetic gas $(CO+H₂)$ is obtained, then by

the method of catalytic hydration a mixture of various hydrocarbons is formed and used for jet fuel manufacturing. Technological scheme of fuel for air jet engines production from natural gas is similar to thescheme, where coal is used, but the exception is absence of first preparatory stage of coal gasification. This technology is described in detailes in scientific works [2; 5; 9; 11].

As it is known [2; 5; 11] implementation of technologies for both natural gas and coal processing leads to considerable emissions of $CO₂$ and other substances. Thus, according to data [2], during process of synthetic jet fuel production from gas, volume of discharged greenhouse gases is in 1,8 times and from coal is in $2 - 2.4$ times higher than resulting from oil refining. Except the peculiarities of technological process of coal refining, its chemical composition also plays an important role. For example, use of bituminous coal as a raw material is accompanied by emissions CH⁴ that also is a greenhouse gas. It should be mentioned that during combustion of fuel, produced from natural gas, sulphur emissions are absent.

Conclusion

In given article the analysis of traditional technologies, applied for jet fuel production is done. Thus, the most popular and wide spread ones are the methods of fuel production by direct oil distillation and secondary (destructive) oil refining. Moreover, there are already known and well developed technologies of aviation fuel production from non-oil feedstock – oil-shales, coal and some other resources. Each of technologies, described in the article, has its own peculiarities and advantages. However, the discussed technologies are usually more complicated, expensive and require considerable investments comparing with traditional oil refining. Besides, the common thing for these methods of fuel production is

use of fossil raw material, which sources are finally limited. Another aspect of fossil fuel usage for aviation fuel production is connected with emissions of harmful exhaust gases during combustion in aviation engines. Therefore, today scientists are actively engaged in development of alternative technologies of jet fuel production from renewable sources, being able to substitute traditional fuel and decrease negative impact on the environment in the future.

On the base of carried out analysis, the existing nowadays methods of fuels for gas turbine engines production were classified, depending on the primary raw material, used for production process. Given classification scheme presents a set of methods for jet fuel production from renewable feedstock. These technologies suppose application of biomass, vegetable oils and animal fats, oils of microand macroalgae, various agricultural and wood processing industry waste, and etc. The most investigated and widely known alternative technologies of jet fuel production are represented by synthetic aviation kerosene, received from biomass by FTprocess, biokerosene based on ethers of plant oils or animal fats, and also hydrotreated vegetable oils. Peculiarity of given types of fuel is consumption of natural, renewable, mostly plant raw material. At the same time general carbon dioxide balance in the nature is not disturbed because plants consume carbon dioxide required for their development from the atmosphere. Also it is worse mentioning that use of aviation biofuel allows considerable decreasing the toxicity of aircrafts' exhaust gases. First of all it is explained by the absence of heterogenic compounds in biofuels, such as sulphur, nitrogen and others that negatively influence the composition of exhaust gases. Thereby, use of natural plant raw material during jet fuel production processes will help to solve

the problem of dependence on non-renewable energy sources and minimize impact on natural environment.

Taking into account all above mentioned factors, we see the necessity for future investigation and development of alternative technologies of fuel for gas turbine engines production from renewable plant feedstock.

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Fig. 1. Variety of crude-oi

Fig.3. Classification of ways for jet fuel production from various kinds of feedstock

Fig.4. Technological scheme of TS-1 fuel production

Fig.5. Technological scheme of RT fuel production

Fig.6. Technological scheme of Jet A-1fuel production

Fig. 7. Production of jet fuels from oil-shales by processing

Fig. 8. Scheme of jet fuel production by coal processing