

Проведено аналіз впливу основних параметрів газової фракції, яка виділена традиційною дистиляцією та із застосуванням мембранних технологій, як базової сировини, на якість авіаційного палива. За допомогою експериментальної мембранної установки із сирової нафти виділено газову фракцію. Дослідження фізико-хімічних властивостей газової фракції показали, що в отриманому за допомогою первапорації гасі відсутні кислоти, молекули води, вміст сірки знижено, а кількість аренів незначна

Ключові слова: авіаційний гас, первапорація, процеси переробки нафти, мембрана, полімер, суміш вуглеводнів

Проведён анализ влияния основных параметров керосиновой фракции, выделенной традиционной дистиляцией и с применением мембранных технологий, как базового сырья, на качество авиационного топлива. С помощью экспериментальной мембранной установки из сырой нефти выделена керосиновая фракция. Исследование физико-химических свойств керосиновой фракции показали, что в полученном с помощью первапорации керосине отсутствуют кислоты, молекулы воды, содержание серы снижено, а количество арен незначительно

Ключевые слова: авиационный керосин, первапорация, процессы переработки нефти, мембрана, полимер, смесь углеводородов

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A MEMBRANE TECHNOLOGY OF SEPARATING THE BASIC AVIATION KEROSENE FROM PETROLEUM

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1. Introduction

The organic fuel that is meant for refueling aircraft engines and aircraft turbines is a mixture of a large number of different hydrocarbons with various molecular structures that are determined by the basic requirements of physical and chemical parameters of the final product. Kerosene-based jet fuel or aviation kerosene (below here AK) contains compounds with carbon within a range of $C_8 - C_{15}$. All main parameters of AK depend on the qualitative and quantitative chemical composition of the fuel. Given the fact that AK is based on kerosene, a relationship between the basic kerosene and AK is obvious.

At present, the basic kerosene for AK is produced mainly by straight-run distillation or rectification. However, the existing technologies do not guarantee that the produced kerosene would have the necessary parameters that meet AK requirements. Various chemical additives help eliminate the shortcomings and achieve the required characteristics. The use of membrane technologies in separation of kerosene fraction with acceptable parameters for its subsequent use as AK without any additives can greatly facilitate and cheapen the cost of producing a high-quality jet fuel.

2. Analysis of the previous studies and formulation of the problem

Aviation kerosene is kerosene with certain additives or "steroids". There exist different types of AK, although they all contain chemicals that are meant to provide complete and efficient fuel combustion in turbines and extending the engine lifetime. Therefore, strictly determined requirements of certain types of AK and an available wide-range kerosene fraction (120–310 °C) allow extracting only those components of the latter that are most suitable for the type of base fuel and subsequent adding "steroids" to achieve the desired AK parameters [1, 2].

AK based on a wide kerosene fraction has physical and chemical parameters of kerosene. Kerosene, or paraffin oil, is intermediate between gasoline and diesel fractions. However, given that the range of distillation temperatures is 120–310 °C, we should note that if distillation temperatures are >120 °C, the components of the kerosene fraction begin mixing with components of the gasoline fraction (35–210 °C), and if the temperatures are >160 °C, the process incorporates components of the diesel fraction (160–350 °C) [3]. Thus, it can be concluded that the kerosene fraction means a mixture of components of all the three light fractions.

Traditional oil refining technologies, such as straight-run distillation or rectification, cannot ensure a clean separation of adjacent light fractions (without mixing their individual components) due to the proximity of the boiling points [3]. In order to determine whether the physical and chemical properties of the mixture correspond to those of kerosene, it is necessary to find basic parameters of the mixture and compare them with the requirements of kerosene. Although the values of the main parameters vary depending on the type of AK, the list of basic parameters remains the same for all AK types. The study focuses on some of the main parameters, compares them with analogous parameters that characterize kerosene and describes the technological ways of producing AK from kerosene without additives. The considered AK is Jet A fuel, commonly used in the USA [1, 2, 4].

For comparison, we choose only critical parameters of Jet A. These parameters depend on the chemical properties of the fuel rather than on its physical characteristics and, therefore, are largely subject to changes in the chemical composition of the fuel. The content of each class of hydrocarbon compounds, such as paraffins, naphthenes, aromatics, or other specific chemical compounds, largely determines the critical parameters presented below.

(A) *The heat of combustion* (engineering commonly uses a parameter of *the calorific value of a fuel*, however, these parameters do not physically differ from each other), the flying resource of aviation is directly dependent on this parameter, therefore, it is desirable to maximize its value. Hydrocarbon jet fuels, in particular kerosene-based ones, must have a heat of combustion of 37 000–47 000 kJ/kg. The studies have shown that the calorific value of jet fuel increases linearly with increasing hydrogen content. If a range of changes in sulfur concentration is acceptable 0–0.4 % the content of nitrogen and oxygen can slightly affect the value of combustion heat [4, 5].

(B) *The freezing point and the pour point*. During the flight, an aircraft is exposed to low temperatures. Given this, as a result of freezing, jet fuel should not clog filters during an aircraft operation. The Jet A specification postulates a requirement of the freezing point – the maximum value should be -40°C . Aviation kerosene comprises a plurality of individual hydrocarbons, each of which has its freezing point. Therefore, when the temperature starts to fall, first paraffin crystals appear in hydrocarbon compounds with higher freezing points. A further temperature drop leads to formation of more crystals and eventual obtaining of hydrocarbons that are very close to a solid-block state. The freezing point of AK is defined as temperature at which the last paraffin crystal melts during heating AK that has been pre-cooled to a state of crystal formation. Thus, the freezing point is much higher than the temperature of complete congelation of AK. The pour point should not be confused with the freezing point. The pour point is the lowest temperature at which oil still flows or is still pumped. The pour point maximum and minimum values provide a temperature range in which AK can be both liquid and solid. The pour point data are particularly useful for preventing a paraffin effect on the AK flow. Typically, the value of pour point is $4\text{--}15^{\circ}\text{C}$ lower than the freezing point of different AK types [4, 5].

(C) *Composition*. As noted above, kerosene-based AK consists of a large number of various hydrocarbons. Modern traditional technologies cannot distinguish and separate individual compounds present in AK. Thus, it is impossible to determine their number. The classes of these compounds

distinguished by the substance sizes (molecular weight, the number of carbons, and the shape of molecules) can be limited by distillation or rectification, as well as by requirements of the product basic parameters, such as the freezing point. Kerosene-based AK is composed of compounds of 8–16 carbons. However, some AK contains compounds with narrower ranges of carbons from 5–15 units [5, 6].

Basically, AK consists of paraffins, naphthenes, and aromatic hydrocarbons. When different types of AK are distinguished from each other by the values of the basic parameters, it mainly depends on the contents of various classes of hydrocarbons. We can confidently state that hydrocarbon composition determines the values of the set of AK basic parameters. It should be noted that the boiling point of the same class of hydrocarbon compounds increases with a rising number of carbons. In compounds with equal carbon numbers, the boiling point depends on the class of compounds and grows depending on isoparaffins, n-paraffins, naphthenes, and aromatics. For example, the difference between boiling points of aromatic hydrocarbons and isoparaffins with the same number of carbons is $40\text{--}50^{\circ}\text{C}$ [4]. This value is much higher than the difference between boiling points of compounds of the same class that differ from each other by one carbon (about 20°C). For example, a compound with the boiling point near 225°C , which is about mid-boiling point of kerosene-based QAV, can be aromatic with C_{10} , naphthene C_{11} , or paraffin C_{12} . The freezing point also rises with an increasing number of carbons in each class of substances. However, it strictly depends on the shape of molecular structure. Compounds such as normal paraffins and unsubstituted aromatic hydrocarbons are frozen (crystals are formed) at higher temperatures than other compounds with the same number of carbons due to the fact that their shape facilitates their packing into crystalline structures [4, 7].

As noted above, the main problem is crystallization of the fuel at low temperatures. All hydrocarbon compounds are essentially prone to crystallization, however, it is found that a higher concentration of long linear n-alkanes in AK increases the pour point. The AK hydrocarbon composition predetermines the density and the heat of combustion. The density increases with a rising number of carbons in the same class of substances. In classes of compounds with the same number of carbons, the density increases from paraffins to naphthenes, and further to aromatics. In compounds with equal numbers of carbons, the energy consumption per unit of weight (specific and mass energies) ranks the classes as follows: aromatics, then naphthenes, and then paraffins.

Diametrically opposite is situation with the energy consumption that corresponds to the unit of volume (specific bulk energy). Viscosity is dependent on the number of carbons more than on the substance class. A specified number of carbons make naphthenes slightly more viscous than paraffins or aromatics. Summing up the relationship between the classes of hydrocarbon compounds and AK properties, it can be added that normal paraffins have low bulk energy and very low low-temperature fluidity. Aromatic compounds have high bulk energy but low heat of combustion and low-temperature fluidity. The properties of isoparaffins and naphthenes make them intermediate between paraffins and aromatic compounds. In mixtures, the values of some parameters mainly become averaged depending on the values of individual components of the mixture. The parameters that are subject to this kind of approximation are called bulk properties or parameters. The values of some other properties

are determined by the presence of individual components in insignificant amounts and are not associated with the bulk composition of the mixture [4, 8] (Table 1).

Table 1

Bulk and local properties of kerosene

Properties	The interaction of components
Energy consumption	Bulk
Heat of combustion	Bulk
Fraction selection limits	Bulk
Density	Bulk
Fluidity	Bulk
Lubricity	Local
Stability	Local
Corrosion	Local
Purity	Local
Electroconductivity	Local

Table 2 presents requirements of AK basic parameters and shows that Jet A has limits on the content of aromatic hydrocarbons. The main adverse effect of these compounds is that they are a source of discharged solid particles and fumes in the exhaust gases. Higher concentration of aromatic hydrocarbons causes greater risks of contamination and clogging engines. Given the facts that the contents of arenes in various crude oils vary in a wide range between 15 and 50 % and that arenes are slightly hydrogenated, the importance of reducing the content of arenes in AK becomes obvious [9]. The article presents a brief consideration of the initial boiling point of AK. The initial boiling point is usually controlled to make a product that meets the requirements of the AK flash point. The boiling end point takes into account the requirements of the freezing point and the smoke point, and/or the content of naphthalene - a source of carbonate particles that impair the thermal stability of combustion processes in engines. It is recommended that the freezing point might be reduced by decreasing the boiling end point of AK.

(D) *Corrosion*. During its use, AK contacts with various materials. It is important that these materials, especially metal parts of turbines and other power units, might not be subject to corrosion. AK corrosion is caused by organic acids and mercaptans that are part of kerosene and AK. Acids appear not only as parts of petroleum, but also due to acid treatment during refining.

Mercaptans or thiols (the basic chemical formula is R-SH, where R is an alkyl group radical) have very distinct acidic characteristics and, therefore, their concentration in AK is strictly limited. Given that the proportion of mercaptans in the initial kerosene is on average 0.1 % by weight of the total amount of sulfur compounds in kerosene, a need of after-treatment of the initial kerosene for its further use as basic AK becomes obvious. It should also be added that one of the main components of sulfur compounds in oil, such as sulfides and disulfides, are thermally unstable; thus, during the technological processes of producing and refining of the recovered kerosene fraction at temperatures of 130–150 °C, these compounds decompose to hydrogen sulfide and mercaptans, which has to be taken into account during preparation of the AK mixture. The above mentioned facts prove that many AK parameters depend on the hydrocarbon content, except those parameters that depend on the presence of any individual additives [4].

(E) *Additives*. Additives are chemical substances that are soluble in fuel and added in low concentrations to improve or maintain key performance properties of the fuel. Normally, additives are extracted from oil materials that form the basic AK, and their functions and chemistry are highly specialized. Additives are used in all products of oil refining in different quantities, however, the situation with AK is unique since one can use only previously specially tested additives.

(F) *Inhibitors of de-icing in the fuel system*. Ice can be formed in fuel tanks at low temperatures. Basically, ice is formed due to the presence of dissolved water in fuel. At low temperatures, water is separated from fuel, and ice is formed. Special inhibitors dissolve water, forming low freezing points of such compounds.

(G) *Antioxidants*. Even small quantities of oxygen dissolved in AK affect neutral compounds of fuel as a result of chemical oxidation reactions. Antioxidants interrupt the chains of chemical reactions and, thereby, prevent the formation of peroxides, soluble resins, or insoluble particles. It should be noted that antioxidants are not effective at increasing the thermal stability of fuel. Olefins are susceptible to oxidation more than other hydrocarbon compounds, thus, fuels with low concentrations of these compounds have higher stability. For example, straight-run fuels have low contents of olefins, and fuels subjected to hydrogen treatment contain no olefins. However, straight-run fuels are composed of natural antioxidants and, therefore, have good antioxidant properties, whereas hydrotreating that is aimed at removing mercaptans also removes natural antioxidants, and such fuels require antioxidant additives.

A *metal blocker* is represented by chemical compounds that form stable complexes with ions of some metals and inhibit the activity of metals such as copper and zinc that are effective as catalysts of oxidation reactions and, thereby, reduce the thermal stability of AK.

Additives that improve lubricity are used to compensate for low lubricity of some types of AK undergoing hydrogen treatment. They contain polar groups that exhibit good adhesion properties on metal surfaces by forming a thin layer and reducing the friction between two metal surfaces [4].

Processing technologies. Almost all types of AK are obtained from crude oil. Crude oil refining allows producing various petrochemicals, including AK. Modern technologies allow refining all types of oil. However, the smaller the density of the feed oil, the more light fractions and, therefore, fewer high-molecular compounds (in particular, resins, tars, and oxidation products) it contains. Light crude oil is easier refined and cost-efficient. All crude oils mainly consist of different hydrocarbon classes, such as paraffins, naphthenes, and aromatics. Each class consists of a wide range of substances with different molecular weights. Modern oil refining is a complex combination of independent technological processes. These processes can be divided into three basic categories that are listed below.

(1) *Separation processes*. During this process, the feedstock is separated into several components or fractions depending on their physical properties, as a rule, boiling points. These processes physically separate raw material, however, due to exposure to high temperatures (up to 450 °C), chemical changes are possible both in raw materials and extracted products. The main separation technique is distillation.

(2) *Refining processes* improve the quality of extracted fractions by chemical removing some compounds that have been present in negligible amounts although deteriorated

the product quality. During the chemical reactions, bulk properties of fractions usually do not change. The basic refining technology is hydrotreating.

(3) *Conversion processes* fundamentally change the molecular structure of raw materials due to the rupture of long molecules into smaller ones. Such processes mainly include catalytic cracking and hydrogen cracking.

Since oil refining processes affect many AK, they are briefly considered below.

Distillation is commonly used in oil processing, in particular, for extracting straight-run kerosene. As noted above, this technology is based on the difference between boiling points of various petroleum products. Using this difference in distillation allows separating various products with different boiling points. Separation of various products or fractions happens when the feed oil is gradually warmed up to the boiling point, which consequently leads to evaporation of some components and condensation of the vapor. Naturally, depending on the boiling point limits, initially separated products or fractions are those with lower boiling points. Gasoline, kerosene and diesel are recovered from oil in this way. Products that are obtained during distillation are referred to as straight-run products, and AK as straight-run fuel. All straight-run products are obtained in atmospheric distillation. In the study, there is no description of the types of distillation that are aimed at separating heavier products [10, 11].

Refining processes are typically used to remove sulfur compounds, including mercaptans. Some refining methods transform mercaptans into disulfides that are devoid of corrosive properties that are characteristic of mercaptans. A modern refining method is Merox (mercaptan oxidation) that uses cobalt-based catalysts, as shown below:



In most cases, Merox reaction does not change the total concentration of sulfur compounds in the fuel: it transforms one sulfur compounds into another. Hydrotreating involves the use of hydrogen and special catalysts to remove undesirable components. The process has mild modes to remove inactive compounds, such as olefins and some sulfur and nitrogen compounds. Some harder modes are used to saturate aromatic rings and remove all sulfur and nitrogen compounds. In this process, molecules containing sulfur are broken to form hydrogen sulfide and hydrocarbons [4, 10, 11]:



Conversion processes. High-molecular-weight hydrocarbon compounds with higher boiling points can be split by means of catalytic cracking: high temperatures and special catalysts make them split into low-molecular-weight compounds with low boiling points. Hydrocracking is a process similar to catalytic cracking. The only difference between these processes is that in hydrocracking reactions occur under high hydrogen pressure. In addition, the presence of hydrogen molecules reduces the amount of unsaturated hydrocarbon compounds that result from the breaking of carbon bonds.

Fig. 1 shows a technological scheme of oil processing and refining at a modern oil refinery. Certainly, a lot of plants, especially minirefineries, do not have all the equipment that is shown in Fig. 1. Crude oil is fed to a distillation column, where atmospheric pressure is used to separate straight-run

components of light fractions, such as naphtha, kerosene, diesel, and light distillates. The atmospheric column residue is a vacuum distillate used to produce gasoline after hydrocracking or catalytic cracking. Cracking is followed by hydrotreating to reduce the concentration of sulfur and nitrogen compounds. AK that is produced at a plant can be either straight-run, hydrotreated, or a mixture of both these products and hydrocracking products. A small amount of heavy gasoline components can also be mixed up in AK. Straight-run kerosene recovered from low-sulfur crude oil can have AK properties. However, most often straight-run kerosene passes all of the above treating processes and only then becomes AK. The scheme is presented below.

Table 2 presents some of the main parameters of aviation kerosene Jet A. It shows that properties of this type of AK are strictly limited. Naturally, production of such AK requires substantial refining of feedstock, i. e. kerosene base [4].

Table 2

A list of parameters	Jet A
The total content of acids (mgrTAN/gr) max	0.10
Aromatics (bulk %) max	25
The total sulfur content (weight %) max	0.30
Mercaptan sulfur (weight %) max	0.003
Volatility	
Distillation temperature:	
The initial boiling point (°C)	–
10 % boils away (°C) max	205
50 % boils away (°C) max	To be determined
90 % boils away (°C) max	To be determined
The end boiling point (°C) max	300
The residue (bulk %) max	1.5
The loss (bulk %) max	1.5
The flash point (°C) min	38
The density at 15°C (kg/m ³)	775–840
Fluidity	
The freezing point (°C) max	–40
The heat of combustion	
The net calorific value (MJ/kg) min	42.8
The fuming point (mm) min	25
Naphthalenes (bulk %) max	3.0
Admixtures	
Resins (mg/100ml) max	7

Processing crude oil by the scheme presented in Fig. 1 allows producing kerosene with various characteristics, which depends on the type of crude oil. In addition, when the temperature rises up to 140 °C, it is necessary to take into account the mixing of kerosene with gasoline and diesel fractions. It should be remembered that at a temperature of 140–300 °C, the kerosene composition may contain long linear alkanes and aromatic compounds that are part of the gasoline fraction as well as complex paraffin compounds as part of the diesel fraction. Unfortunately, distillation process can separate a multicomponent mixture, such as crude oil, only by different boiling points, which leads to the mixing (for example, kerosene) of various components of neighboring fractions [12]. Therefore, the selection of hydrocarbon compounds that meet the requirements of AK based on the initial kerosene depends on a single criterion – the boiling point. Fig. 2, 3 show compositions of the initial kerosene (Fig. 2) and Jet A (Fig. 3) depending on the number of carbons that form various hydrocarbon compounds with different properties [6].

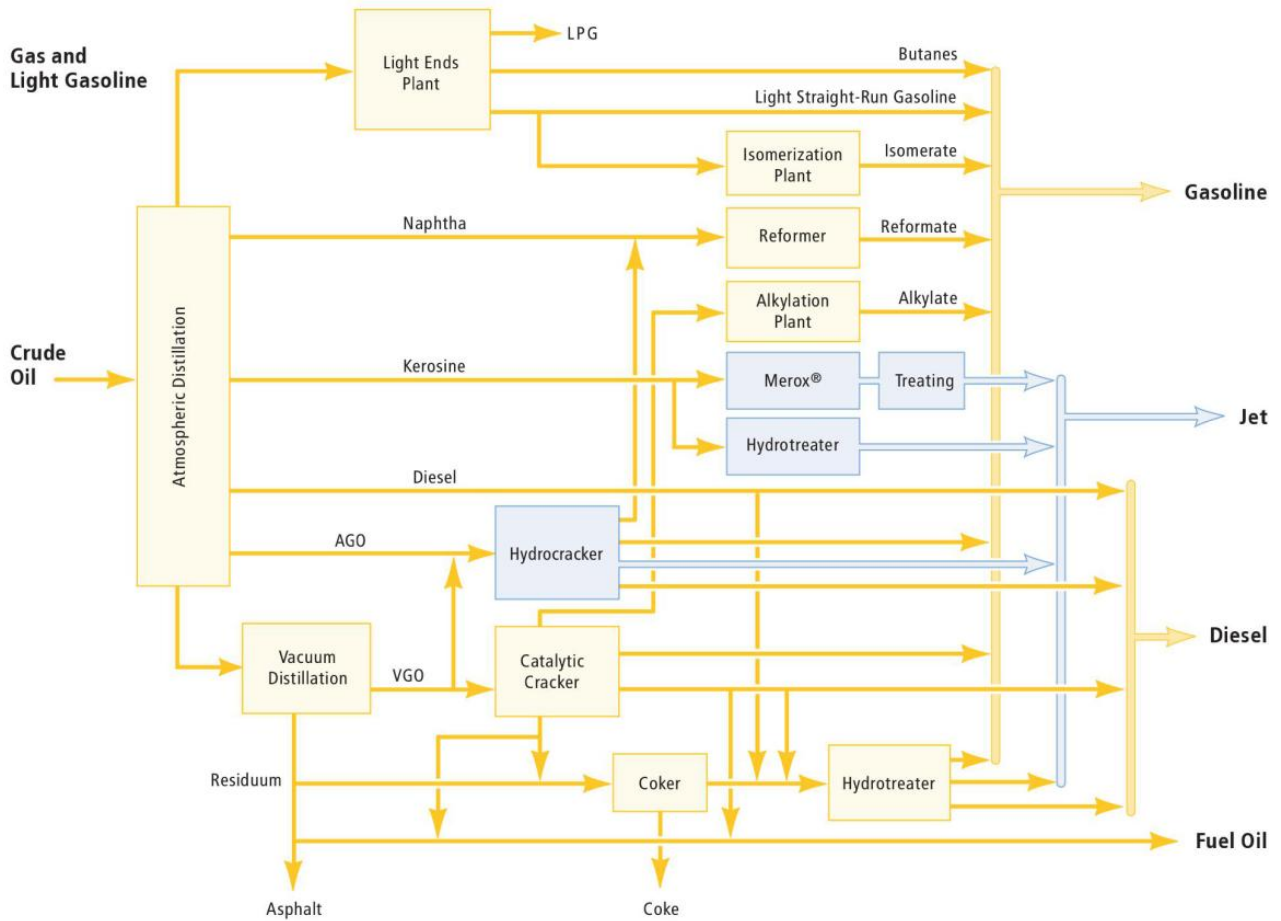


Fig. 1. A typical technological scheme of oil processing and refining

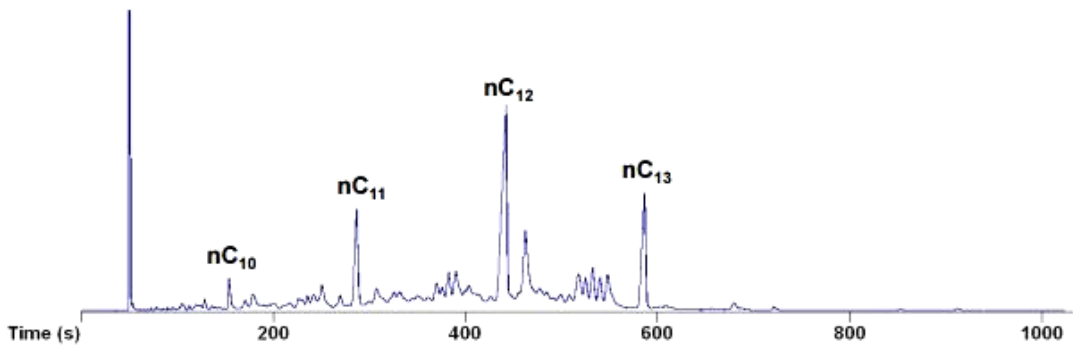


Fig. 2. Gas chromatographic spectra of commercial kerosene distillate

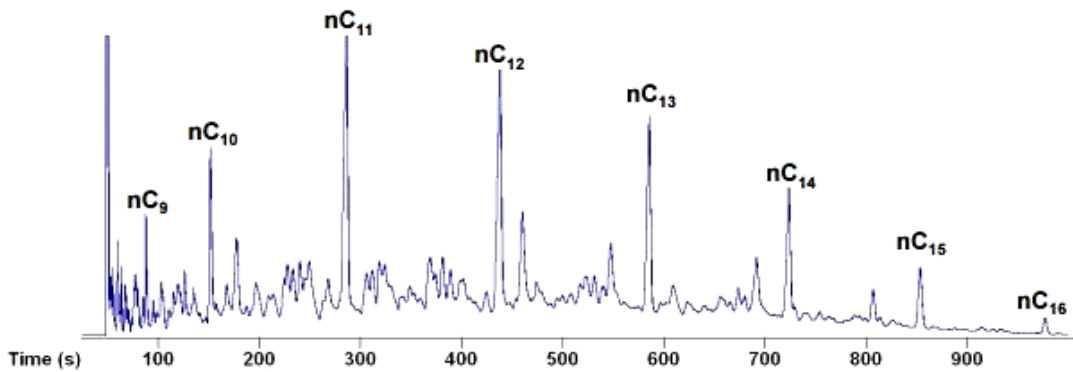


Fig. 3. Gas chromatographic spectra of commercial Jet A

Then typical and essential features of a particular type of AK are achieved by means of additional treatment and special additives. In addition to the risk of kerosene dilution with gasoline and diesel components, there is a problem of transformation of hydrocarbons and other specific compounds during thermal exposure in the presence of oxygen, which means decomposition of certain molecules with weak bonds and oxidation of the others. Kerosene processing at high temperatures in the presence of hydrogen also leads to breaking of the bonds of hydrocarbon compounds and formation of new chemical compounds.

The authors of the study have aimed at extracting a kerosene fraction from crude oil within a temperature range of 120–310 °C with the help of membrane pervaporation at low temperatures between 55 and 90 °C and under atmospheric pressure. A membrane kerosene separation technology was chosen because it has certain significant advantages over distillation. The separation of a multicomponent mixture takes place at the molecular level. Vaporization of any component occurs not due to the boiling point, but because of the “dilution” of the component molecules in the surface layers of a polymeric membrane, followed by their diffusion in the membrane body and evaporation from its reverse surface. Application of the low-temperature separation process does not allow decomposition and oxidation of components of the feedstock and the separated product [13, 14]. Therefore, the values of the main parameters of the reconcered kerosene are likely to be within admissible values of AK.

3. The purpose and objectives of the study

The study was aimed at membrane pervaporation of light crude oil and recovery of kerosene, some basic parameters of which correspond to AK properties. In addition, it is necessary to show that technological parameters of the membrane oil separation technology allow a significant surpassing of the traditional technologies of oil refining, including atmospheric distillation that is the core technology of producing straight-run kerosene as the base of AK.

To achieve this goal, we set the following tasks:

- 1) to recover the basic kerosene for AK from crude oil with the use of a membrane technology;
- 2) to determine experimentally the main parameters of the basic kerosene and compare them with those of the aviation kerosene Jet A;
- 3) to point out the main advantages of membrane technologies in producing the basic kerosene in comparison with traditional separation methods.

4. Experimental research on the use of the membrane technology in extracting separating the basic AK from petroleum

The experimental research focused on kerosene that was extracted from light ($\rho=0.848 \text{ gr/cm}^3$) low-sulfur ($N_s=0.15\%$, by weight) crude oil by means of polymeric pervaporation membranes.

After recovering kerosene from petroleum, there were determined the values of some basic parameters of the aviation kerosene Jet A, namely: its fractional composition, the content of arenes, the concentration of sulfur compounds, acidity, and freezing temperature. Furthermore, the values

of these parameters were compared with those of kerosene that was extracted from the same crude oil by distillation. The data are shown in Table 3. A hardware and technological circuit of the experimental pervaporation membrane unit is shown in Fig. 4. The technological process of membrane pervaporation with the use of various polymeric membranes is specified in previous articles [3, 12], so here we briefly describe the sequence of separation processes.

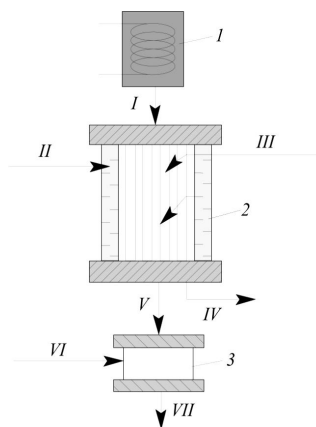


Fig. 4. A scheme of the pervaporation membrane unit:
1 – a heater; 2 – a pervaporation membrane unit;
3 – a refrigerator; I – inert gas; II – a hot coolant;
III – raw material; IV – a residue; V – a gas-vapor mixture;
VI – a cold coolant; VII – an extracted fraction

The feed oil is preheated by means of a hot coolant (hot water) in a temperature range of 30–50 °C. The heated oil is fed to the membrane unit. At the first stage of separation, a gasoline fraction (that is a mixture of components with boiling points in a range of 35–215 °C) is extracted from crude oil. After the first stage, the feedstock temperature is raised from 55 to 90 °C. In this temperature range, a kerosene fraction (that consists of components with boiling points in a range of 140–300 °C) is extracted. It should be noted that temperature modes of membrane separation can control not only the initial and the end boiling points of kerosene but also the fraction composition.

After extraction of the kerosene fraction, its composition was analyzed by means of fractional distillation and gas chromatographic studies, which was aimed at determining the content of arenes in the above fraction. An X-ray spectroscopy allowed determining sulfur content in kerosene. There were also measurements of the freezing point and acidity of the fraction.

After research on the kerosene fraction that was extracted in the pervaporation membrane unit, there were made exactly the same analyses of the kerosene fraction extracted by distillation. The results are shown in Table 3.

Before discussing the results, let us specify each experimental procedure. The content of arenes in the kerosene fraction was determined by using a gas chromatograph with a 15-meter nonpolar separation column (its internal diameter is 0.5 mm). Nitrogen served as carrier. The experiments were conducted in a temperature range of 40–300 °C, with an interval of 10 °C/min. In addition, distillation allowed determining the boiling point limits of the fraction. The results are given in Table 3.

The amount of sulfur was determined with the use of an X-ray fluorescence spectrometer SPECTROSCAN that has

energy dispersion. Diesel samples with sulfur contents of 100 and 50 ppm were used as calibration samples. The amount of mercaptans was determined on the basis of the following empirical correlation:

$$N_{\text{merc.}} \leq 1/3N_s, \quad (3)$$

where $N_{\text{merc.}}$ is concentration of mercaptans, and N_s is total sulfur in the sample [15].

The results of the experiments

A list of parameters	Jet A	Pervaporated-kerosene	Distilled kerosene
The total content of acids (mgrTAN/gr)	0.10	Not detected	>0.10
Aromatics (bulk %)	25	3	27
The total sulfur content (weight %)	0.30	0.008	0.055
Mercaptan sulfur (weight %)	0.003	≤0.0025	≥0.003
Distillation temperature:			
The initial boiling point (°C)	–	134	140
10 % boils away (°C)	205	175	195
50 % boils away (°C)	To be determined	195	225
90 % boils away (°C)	To be determined	235	275
The end boiling point (°C)	300	245	298
The residue (bulk %)	1.5	0.5	2.5
The loss (bulk %)	1.5	1.0	1.5
The density at 15 °C (kg/cm ³)	775–840	795	815
The freezing temperature (°C)	–40	–58	–38

The acidity was determined exclusively by means of qualitative assessment of the presence of acids in the extracted kerosene. Water was added to the flask with the test sample of kerosene, and then the flask with its content was shaken. Acidity was measured in the aqueous layer with the use of methyl orange (red) indicator.

The freezing point (temperature) was determined as follows: sample kerosene was poured into a test tube with a jacket, stirrer, and thermometer. The tube was placed in a vacuum flask with a coolant (liquid nitrogen) environment. During cooling, the sample was continuously stirred. The temperature, at which crystals appeared, was fixed. The sample was then removed from the flask and, thereby, allowed to warm while its content was continuously mixed, and the temperature at which the crystals completely disappeared was fixed.

5. Discussion of the research results on the use of the membrane technology of the basic AK separation from petroleum

Resources of petroleum with low acid content are practically limited, thus, reducing acidity in the basic raw material for AK, i. e. kerosene, is particularly important and necessary to prevent corrosion in aircraft engines. However, none of the conventional methods of reducing acidity guarantees invariability of other important parameters of AK. In this regard, the absence of acids, which is indicated by the orange-yellow color of aqueous solutions of the tested samples ($7 \leq \text{pH} \leq 8$) of kerosene that was recovered in the pervaporation membrane unit, shows a favorable benefit of this technology. Meanwhile, the distilled kerosene is not devoid of acids, as indicated by the red color of aqueous solutions of the tested samples ($0 \leq \text{pH} \leq 4$). Taking into account the fact that the boiling points of light naphthenic acids begin at 190–210 °C, whereas those of heavier ones at 240–300 °C and higher, it becomes obvious that

kerosene distillation embraces both light and heavier acids. As to the pervaporated kerosene, the polymeric membranes are resistant to penetration of oxygenated acids.

The data (on the contents of sulfur compounds) that are shown in Table 3 are considered and analyzed below. Table 3 shows that the total sulfur content in pervaporated kerosene falls considerably (compared to the concentration of sulfur in the feed oil) and allows meeting the requirements of the content of mercaptans for their subsequent use in AK. The

Table 3

content of sulfur compounds in the distilled kerosene is much higher, which does not allow its use as the basic AK material without pre-removal of the sulfur compounds. The distribution of sulfur compounds in the feed oil with regard to their boiling points qualitatively explains the research results. In a temperature range of 140–300 °C, there are sulfur compounds that make up approximately one third of the total sulfur.

The results on the sulfur content in the pervaporated kerosene are explained by the peculiarities of membrane processes and work of polymeric membranes. Polymeric membranes are pre-calibrated in order the macromolecular grid might perceive and “remember” how pure kerosene molecules pass through it. Thereafter, the feed oil passes through membranes, and those compounds

which contain sulfur in their molecules easily pass through the channels which have earlier “memorized” macromolecular chains, whereas the passage of molecules with “extraneous” atoms is rather complicated and reduced to a minimum.

It should also be noted that at low temperatures (≤ 90 °C) of pervaporation, sulfur compounds do not decompose.

As noted above, one of the important criteria for AK is the content of arenes. Table 3 shows that in the pervaporated kerosene the content of arenes is negligible, whereas in the kerosene distillate the concentration of arenes is only slightly lower than in the feedstock (32 %) and exceeds the standard concentration specified for Jet A. Obviously, during extraction of the gasoline fraction (35–215 °C) in the membrane unit, almost all compounds of aromatic hydrocarbons were removed.

Crude oil distillation allows obtaining kerosene in a boiling point range of 140–298 °C, however, it is this temperature range that contains most arenes, both singly charged with substituents and multiply charged. In other words, the membrane pervaporation ensures removal of most arenes during gasoline separation at a temperature of 30–50 °C, which fully guarantees their minimum content in kerosene, i. e. meets the requirements of AK.

Furthermore, consider the results of fractional distillation. The pervaporated kerosene contains both aromatic and aliphatic hydrocarbons. Only in comparison with the distilled kerosene, they are almost free from components of gasoline and diesel fractions, therefore, the end boiling point corresponds to the temperature at which kerosene compounds are absent. It should be especially stressed that the volume of residue is minimal in kerosene recovered in the membrane unit (which, undoubtedly, indicates the absence of resins), whereas the residue is much higher in the kerosene distillate. The relatively low density of the pervaporated kerosene indicates the absence of diesel components (160–350 °C) and resins.

The obtained results well correlate with the experimental data on determining the freezing point. As Table 3 shows, the

low-temperature fluidity of the kerosene distillate is noticeably lower than the freezing point (in subzero temperatures) of the pervaporated kerosene. Since the kerosene distillate contains a considerable amount of high-molecular-weight arenes (including bicyclic and tricyclic compounds, as well as paraffins that are more prone to the formation of crystals at low temperatures), a relatively high freezing point of such kerosene becomes obvious. A high low-temperature fluidity of the pervaporated kerosene is caused by the absence of complex arenes and paraffins.

It should also be added that the hydrophobicity of polymeric membranes causes a complete absence of water molecules in the pervaporated kerosene. Since the use of the membrane technology for the basic AK separation from petroleum allows waiving some refining methods, such as hydrotreating and Merox (Fig. 1), the advantages of membrane separation in comparison with convection technologies of producing the basic AK are obvious.

6. Conclusions

1. The membrane technology of separating crude oil is one of the most promising technologies of oil refining, and in the near future, it is likely to replace most of the convection oil refining technologies. The technological process of

separating crude oil into fractional components has obvious advantages, namely: the separation happens at relatively low temperatures and under atmospheric pressure, extraction of particular fractions (such as kerosene) occurs at the molecular level, which excludes any "pollution" with components of adjacent fractions (in this case, the components of gasoline and diesel fractions) (Table 3).

2. The pervaporated kerosene has physical and chemical properties that meet the requirements of the aviation kerosene Jet A since all the main parameters of such kerosene base have values that meet the requirements of Jet A (Table 3).

3. The use of the membrane technology in producing AK considerably facilitates formation of the required AK properties and parameters and significantly reduces the cost of transforming the basic kerosene in AK without any additives. This can be exemplified with the following: if the amounts of mercaptans and acids present in the kerosene base exceed admissible limits of AK, it is necessary to carry out additional technological processes, such as hydrotreating and Merox, which undoubtedly involves additional consumption of heat energy as well as hydrogen, catalysts and chemicals to neutralize the acid; besides, this involves disposal costs to utilize toxic waste resulting from the above refining methods. According to rough estimates, the cost of a ton of basic kerosene can reach USD 50–60.

References

1. Cookson, D. J. Investigation of the Chemical Basis Kerosene (Jet Fuel) Specification Properties [Text] / D. J. Cookson, C. P. Lloyd, B. E. Smith // *Energy & Fuels*. – 1987. – Vol. 1, Issue 5. – P. 438–447. doi: 10.1021/ef00005a011
2. Investigation of By product Application to Jet Fuel [Text]: Final Report. – U.S. Department of Energy, 2001. – 28 p.
3. Burtina, I. A. Membrane recovering of kerosene and diesel fractions from mix of heavy oil and gas condensate [Text] / I. A. Burtina, D. V. Litvinenko, O. O. Gachechiladze, N. V. Shafarenko // *Industrial service*. – 2012. – Vol. 4, Issue 49. – P. 2–4.
4. Chevron Corporation Technical Review [Text]. – *Aviation Fuels*, 2008. – P. 1–94.
5. Affens, W. A. Effect of Composition on Freezing Points of Model Hydrocarbon Fuels [Text] / W. A. Affens, J. M. Hall, S. Holt, R. N. Hazlett // *Fuel*. – 1984. – Vol. 63, Issue 4. – P. 543–547. doi: 10.1016/0016-2361(84)90294-1
6. Steinecker, W. Analysis of Kerosene Based Fuels Using Variable Geometry Columns Featuring Variable Stationary Phase Thickness (VSPT) [Text] / W. Steinecker. – VGC Chromatography LLC. USA, 2012. – P. 1–3. – Available at: http://www.vgchromatography.com/documents/VGC_Application_Note-Kerosene_Analysis.pdf
7. Friedman, R. High Freezing Point Fuels Used For Aviation Turbine Engines [Text]: material 24 – the Annual International Gas Turbine Conference / R. Friedman. – San Diego, California, 1979. – P. 1–12.
8. Shafer, L. Chemical class composition of commercial Jet Fuels and other specialty Kerosene Fuels [Text] / L. Shafer, R. Striebich, J. Gomach, T. Edwards // 14th AIAA/AHI Space Planes and Hypersonic Systems and Technologies Conference. – 2006. – Vol. 44, Issue 11. – P. 2433–2814. doi: 10.2514/6.2006-7972
9. Colket, M. Development of an Experimental Database and Kinetic Models for Surrogate Jet Fuels [Text] / M. Colket, T. Edwards, N. Cernansky, F. Dryer, F. Egolfopoulos, D. Friend et. al. // 45th AIAA Aerospace Sciences Meeting and Exhibit. – 2015. – Vol. 53, Issue 1. – P. 1–21. doi: 10.2514/6.2007-770
10. Separation Technology for the Industries of the Future, chapter 3 Petroleum Industry [Text]. – The National Academies Press. – Washington: D.C., 1998. – P. 28–35.
11. Odebunmi, E. O. Characterization of Crude Oils and Petroleum Products: (I) Elution liquid chromatographic separation and gas chromatographic analysis of oils and petroleum products [Text] / E. O. Odebunmi, E. A. Ogunskin, P. E. P. Ilukhor // *Bull Chem. Soc. Ethiop*. – 2002. – Vol. 16, Issue 2. – P. 115–132. – Available at: <http://www.ajol.info/index.php/bcse/article/view/20934/18846>
12. Burtina, I. A. The membrane separation of liquid hydrocarbons [Text] / I. A. Burtina, O. O. Gachechiladze, L. I. Ruzhinskaya // *Theoretical and applied problems of service*. – 2010. – Vol. 1, Issue 34. – P. 8–11.
13. Burtinaya, I. A. Transfer processes in polymer membranes. Part 1 [Text] / I. A. Burtinaya, L. I. Ruzhinskaya, O. O. Gachechiladze, N. V. Shafarenko // *Eastern-European Journal of Enterprise Technologies*. – 2013. – Vol. 1, Issue 6(61). – P. 4–6. – Available at: <http://journals.uran.ua/eejet/article/view/9181/7972>
14. Burtinaya, I. A. Transfer processes in polymer membranes. Part 2 [Text] / I. A. Burtinaya // *Eastern-European Journal of Enterprise Technologies*. – 2013. – Vol. 2, Issue 11 (61). – P. 41–44. – Available at: <http://journals.uran.ua/eejet/article/view/11731/9873>
15. Al-Harashsheh, A. Sulfur distribution in the oil fractions obtained by thermal cracking of Jordanian El-Lajjun oil shale [Text] / A. Al-Harashsheh, A. Y. Al-Otoom, R. A. Shawabkeh // *Energy*. – 2005. – Vol. 30, Issue 15. – P. 2784–2795. doi: 10.1016/j.energy.2005.01.013