CHEMISTRY & CHEMICAL TECHNOLOGY

Vol. 10, No. 4, 2016 Chemical Technology

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PHYSICAL-CHEMICAL PROPERTIES OF JET FUEL BLENDS WITH COMPONENTS DERIVED FROM RAPESEED OIL

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Received: June 07, 2016 / Revised: June 23, 2016 / Accepted: September 30, 2016

Abstract. The work is devoted to the development of alternative jet fuel blended with rapeseed oil-derived biocomponents and study of their physical-chemical properties. The modification of conventional jet fuel by rapeseed oil esters was chosen for this work among the variety of technologies for alternative jet fuels development. The main characteristics of conventional jet fuel and three kinds of biocomponents were determined and compared to the standards requirements to jet fuel of Jet A-1 grade. The most important or identifying physical-chemical properties of jet fuels were determined for the scope of this study. Among them are: density, viscosity, fractional composition, freezing point and net heat of combustion. The influence of rapeseed oil-derived biocomponents on the mentioned above characteristics of blended jet fuels was studied and explained.

Keywords: jet fuel, alternative fuel, biocomponent, rapeseed oil, physical-chemical properties, density, viscosity, fractional composition, freezing point, net heat of combustion.

1. Introduction

Constant increase of aircraft fleet and exhausting crude oil deposits promote worsening of the world energy crisis. As a result we observe rise in prices for jet fuel that today comprise about 25–30 % of passenger travel [1]. Moreover, products of fuel combustion cause detrimental impact on environment [2]. Thus, the task of search and development of alternative jet fuels became especially important.

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

Today alternative fuels from various renewable feedstocks are actively developed and studied. Among them are fuels made of biomass, plant oils, animal fats, microalgae, and waste from agriculture, wood processing industry, municipal waste, *etc*. [3]. Thus, jet fuels produced from biomass *via* FT-synthesis and hydration of fats were successfully tested [4]. The standard ASTM D7566 that set requirements to this fuel was developed and the use of this fuel in aircrafts was allowed [5]. This alternative fuel possesses high quality; however its chemical structure looks as completely synthetic paraffinic kerosene [6]. It means that entering the environment the fuel causes negative impact on objects of environment similarly to conventional jet fuels.

There is also a considerable experience in the use of aviation biokerosene that is a mixture of conventional jet fuel and biocomponents produced from plants oil up to 50 % [7]. For many reasons today this kind of alternative jet fuel is the most promising for number of countries [5-7]. These biocomponents are methyl or ethyl esters of plant oils or animal fats, the most rational feedstock being rapeseed or camelina oils [8]. Primarily this biofuel also known as biodiesel has become popular as a fuel substitute for motor transport, but lately it has been proposed to be used as component for jet fuel. However, today application of rapeseed oil esters as components of jet fuel is at the early stage of development and needs to be studied more comprehensively.

The purpose of this work is to study the influence of biocomponents derived from rapeseed oil on physical-chemical properties of jet fuel and to consider the possibility of using jet fuel blended with biocomponents in aircrafts jet engines. The following tasks were set for reaching the purpose:

To study experimentally the main physical-chemical properties (density, fractional composition, viscosity, flash point, freezing point, and heat of combustion) of jet fuel and three kinds of biocomponents;

To study experimentally the mentioned above physical-chemical properties of jet fuels when blended with biocomponents up to 50 vol %;

To analyze and explain the influence of biocomponents on physical-chemical properties of jet fuels.

2. Experimental

2.1. Materials and Methods

Physical-chemical properties of jet fuel, tree kinds of biocomponents and their blends with jet fuel were investigated during the experiment. Jet fuel was presented by conventional oil-derived fuel for jet engines of Jet A-1 grade that meets the requirements of ASTM D1655. Conventional jet fuels are produced from middle-distilled oil fractions with the boiling temperatures of 413–553 K (ligroin-kerosene, gasoline-kerosene and gasoil fractions). They are obtained via direct distillation of low-sulfur and sulfur oils [9].

Biocomponents used for blending with jet fuel were presented by fatty acids methyl esters (FAME) of rapeseed oil, meeting the requirements of EN 14214, fatty acids methyl esters of rapeseed oil and fatty acids ethyl esters that are specially modified for application as components of jet fuel. Fatty acids esters were produced by transesterification of rapeseed oil in the Institute of bioorganic chemistry and petrochemistry of the National Academy of Science of Ukraine. Methanol and ethanol were used for transesterification [10, 11]. The use of ethanol is more preferable as it is less toxic and derived from plant feedstock. In this case biocomponents are completely made of renewable raw materials and seem to be environmentally safe [12]. The modification of biocomponents was done by the method of *vacuum* distillation. It allows achieving higher level of biocomponents purification and improvement of physical-chemical properties. The method of biocomponents modification was developed by the authors of this article and described in earlier works [12].

For studying physical-chemical properties jet fuel was blended with biocomponents by mechanical mixing. Jet fuel blends contained up to 50 % of biocomponents. The list of tested samples and their designations are presented in Table 1.

Physical-chemical properties of jet fuels, which were pointed out in the tasks of this work, were estimated according to the standards methods that are determined by ASTM D1655. This document specifies requirements to jet fuels and standard test methods for controlling these requirements.

Density of fuel samples (denoted as ρ) was estimated according to ASTM D4052 Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter using device for density and concentration determination "Anton Paar", DMA 4500M. Density of fuel samples was determined at the temperature of 288 K that was specified by ASTM D1655.

Table 1

Fuels samples used for studying

Sample description	Sample designation
Jet fuel of grade Jet A-1	Jet A-1
Biocomponent – fatty acids methyl esters of rapeseed oil meeting the requirements of EN 14214	FAME
Jet fuel with 10 % of biocomponent	Jet A-1+10 % FAME
Jet fuel with 20 % of biocomponent	Jet A-1+20 % FAME
Jet fuel with 30 % of biocomponent	Jet A-1+30 % FAME
Jet fuel with 40 % of biocomponent	Jet A-1+40 % FAME
Jet fuel with 50 % of biocomponent	Jet A-1+50 % FAME
Biocomponent – modified fatty acids methyl esters of rapeseed oil	FAME(M)
Jet fuel with 10 % of modified biocomponent	Jet A-1+10 % FAME(M)
Jet fuel with 10 % of modified biocomponent	Jet A-1+20 % FAME(M)
Jet fuel with 10 % of modified biocomponent	Jet A-1+30 % FAME(M)
Jet fuel with 10 % of modified biocomponent	Jet A-1+40 % FAME(M)
Jet fuel with 10 % of modified biocomponent	Jet A-1+50 % FAME(M)
Biocomponent – modified fatty acids ethyl esters of rapeseed oil	FAEE(M)
Jet fuel with 10 % of modified biocomponent	Jet A-1+10 % FAEE(M)
Jet fuel with 10 % of modified biocomponent	Jet A-1+20 % FAEE(M)
Jet fuel with 10 % of modified biocomponent	Jet A-1+30 % FAEE(M)
Jet fuel with 10 % of modified biocomponent	Jet A-1+40 % FAEE(M)
Jet fuel with 10 % of modified biocomponent	Jet A-1+50 % FAEE(M)

Fractional composition of fuel samples was determined according to D86 Test Method for Distillation of Petroleum Products at Atmospheric Pressure using automatic fractional composition analyzer "Herzog Optidist".

Viscosity of fuel samples (denoted as v) was determined according to ASTM D445 Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity) using automatic device for viscosity determination "Herzog low-temperature viscometer", HVU 482. Viscosity of fuel samples was determined at the temperature of 253 K that is specified by ASTM D1655 and also in the temperature range from 253 to 373 K.

Freezing point of fuel samples (denoted as t_f) was determined according to ASTM D7153 Standard Test Method for Freezing Point of Aviation Fuels (Automatic Laser Method) using Automatic Freezing Point Analyzer ISL FZP 5Gs.

Net heat of combustion of fuel samples (denoted as Q) was determined according to D4809 Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter (Precision Method) using calorimeter system of determination higher and lower heat of combustion "IKA" C200.

Measurements were done for samples described in Table 1. Statistical processing of the obtained experimental data was done using Mathcad 15 software; graphical representation of results was done using Grapher 8 software.

3. Results and Discussion

3.1. Requirements to Jet Fuels and Production of Biocomponents

Today there are strict requirements to jet fuels connected with efficiency, reliability, durability of aircraft equipment, and environmental safety [13]. Among the general technical requirements special attention should be paid to:

high level of evaporability that provides reliable flammability and completeness of fuels combustion;

good low temperature properties, which provide reliable fuel pumpability at low temperatures;

chemical and thermal stability with minimal tendency to form deposits in the fuel system of the aircraft engine;

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

good lubricating properties that eliminate excessive wearing of fuel assemblies friction parts;

the optimal level of electrical conductivity, which excludes fuel electrification and provides safe fuel transfer and filling of fuel tanks;

absence of toxic components, impurities and additives, minimum content of sulphur compounds, which lead to the formation of ecologically harmful products in the result of fuel combustion.

This complex of requirements is provided by physical-chemical, exploitation and ecological properties of jet fuels, which are determined by nature and properties of raw material, methods of basic fractions productions, methods of their purification and mixing, and additives applied [14].

The first step of our work was studying of physical-chemical properties of conventional jet fuel Jet A-1 and three kinds of biocomponents. Characteristics that are the most important for comparing conventional jet fuel and biocomponents are presented in Table 2.

As we can see from the Table, properties of jet fuel Jet A-1 completely meet the requirements of ASTM D1655. However, biocomponents differ from properties of conventional jet fuels. Therefore, the next step in our work was studying the compatibility of biocomponents with jet fuels and their influence on physical-chemical properties of blended jet fuel according to the following characteristics: density, fractional composition, viscosity, and freezing temperature.

Table 2

Physical-chemical properties of conventional jet fuel and biocomponents

Property	ASTM D1655	Jet fuel Jet A-1	FAME	FAME(M)	FAEE(M)
Density at 288 K, kg/m^3	775–840	794.03	882.92	883.68	876.58
Fractional composition, K :					
– 10 % distilled at temperature, max	478	442.15	607.91	600.23	609.69
– 50 % distilled at temperature, max	registered	459.2	609.99	607.78	610.2
– 90 % distilled at temperature, max	registered	490.13	620.09	616.35	609.14
– final boiling point, max	573	516.44	627.50	621.95	547.4
Kinematic viscosity, mm^2/s:					
– at 253 K, max	8.0	3.29	16.05 (-5)	14.67 (-5)	17.89 (-8)
– at 293 K, min	-	1.50	7.20	6.73	7.35
Freezing point, K, max	226	216	258	254	254.5
Flash point, K, min	311	316	403	440	443
Lower heat of combustion, kJ/kg, min	42800	43218	37315	37131	37550

3.2. Study of Biocomponents Influence on Physical-Chemical Properties of Blended Jet Fuels

Density and fractional composition directly influence fuel volatility – processes of evaporation, fuel-air mixture formation, completeness of combustion, net fuel flow, and absence of smoke and soot in combustion chamber. Density plays an important role for estimation of fuel energy properties, mainly heat value [15].

Viscosity causes impact on fuel pumpability in aircraft fueling system – it determines injection and spraying of fuel in combustion chamber. Viscosity influences fuel filters and nozzles efficiency at low temperatures, mainly degree of fuel spraying and droplets diameter. Increased viscosity causes worsening of fuel evaporability and completeness of combustion. At the same time viscosity stipulates anti-wear properties of jet fuels [16].

Freezing point allows estimating low-temperature properties of jet fuels, mainly fluidity at low temperatures during high-altitude flights of sub-sonic aircrafts.

Density. Methyl and ethyl esters of rapeseed oil are characterized by significantly high values of density ρ comparing to conventional jet fuels. It is explained by the chemical structure of esters. Hydrocarbon chains of esters contain 14–26 carbon atoms on average, on the contrary to conventional jet fuel that contains only 5–16 carbon atoms. It causes high values of esters molecular mass and thus their density. Fig. 1 shows that increasing of biocomponent content in samples of blended fuels causes increasing of their density.

It is clearly seen from the graph above that density dependence is linear. The density of blended jet fuels increases with the rise of biocomponents content. The reason for this is increasing of dispersion force between hydrocarbon molecules of jet fuel and acyl radical of ester molecules form one hand and induction force between hydrocarbons and carboxyl groups of esters.

Fractional composition. As it is known conventional jet fuel is a mixture of hydrocarbons of different structure. Due to this they do not have a defined boiling temperature, but rather evaporate in a wide range of temperatures. At the same time biocomponents are also a mixture of organic compounds. They belong to the class of aliphatic fatty acids esters and differ from each other by geometric structure, molecular mass and thus boiling temperature. Boiling temperatures of esters (Fig. 2) significantly differ from fractional composition of conventional jet fuels and do not coincide with them [16].

Boiling temperatures of biocomponents are within a very narrow range; moreover the most part of the volume (about 75–80 %) boils even in more narrow range – about 293–298 K. It is explained by that fact that about 80 % of studied biocomponents belong to esters of oleic, linoleic, and linolenic acids. Significant decrease of final boiling point of FAEE up to 547 K may be explained by its chemical destruction. Presence in FAEE molecules of additional methyl group increases their molecular weight (comparing to FAME) and dispersion forces of interaction between molecules. Thus boiling temperature of FAEE is higher than temperature of molecules thermal destruction. So, during the process of distillation we may observe formation of products of ***cis-trans***-isomerization, polymerization and pyrolisis of esters, which results in decrease of boiling temperatures.

Study of fractional composition of blended jet fuels has shown that addition of fatty acids esters to jet fuels causes widening of their fractional composition. It is clearly seen that final boiling point of blended fuels is significantly higher than that of the conventional jet fuel. (Figs. 3a, b, c).

Fractional composition curves mean that boiling temperature ranges of conventional jet fuels and fatty acids esters do no coincide even partially. Increasing of biocomponent content by each 10 % causes output of high boiling fractions, respectively. The increase of boiling temperatures of blended fuels is explained by significantly higher heat of evaporation of esters comparing to jet fuel hydrocarbons.

Addition of biocomponents to jet fuel may negatively influence the completeness of combustion and soot formation from one side [17]. But from the other side decreasing of light boiling fractions content may decrease its evaporability [18]. This will allow decreasing of fuels losses from evaporation, minimizing possibility of vapor locks formation and increasing of fuel fire safety. At the same time it may improve energy content of jet fuel.

Viscosity. Biocomponents made of FAME and FAEE of rapeseed oil have significantly higher viscosity ν values comparing to conventional jet fuel. The reason of this is length of hydrocarbon chain that determines the big size of compounds [19]. Due to this the speed of chaotic molecules movement decreases and as a result viscosity increases. Moreover, about 80 % of biocomponents are esters of unsaturated fatty acids with one or two double bonds. Due to the presence of double bonds esters molecules take curved-shape form, that additionally increases their viscosity. Viscous-temperature characteristics of conventional jet fuel and biocomponents sample are shown in Fig. 4.

The sizes of esters molecules are bigger comparing to hydrocarbon molecules, which causes formation of stronger energy of their intermolecular interaction. This explains stronger dependence of esters viscosity on temperature that is described by the graph above.

Addition of biocomponents to jet fuel causes increasing of blended fuels viscosity, which is shown in Fig. 5.

The increase of blended jet fuels viscosity is explained by the rise of intermolecular forces between hydrocarbons and esters molecules. It may negatively influence fuel pumpability through the aircraft fueling system, decreasing productivity of fuel pumps and quality of fuel spraying. At the same time increased viscosity positively influence antiwear properties of jet fuels [16].

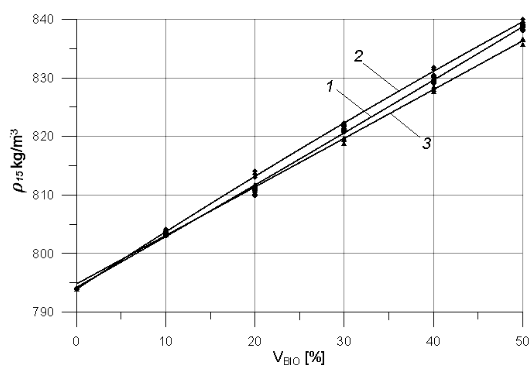

Fig. 1. Dependence of blended jet fuels density on the content of biocomponents: jet fuel Jet A-1 + FAME (1); jet fuel Jet A-1 + FAME(M) (2) and jet fuel Jet A-1 + FAEE(M) (3)

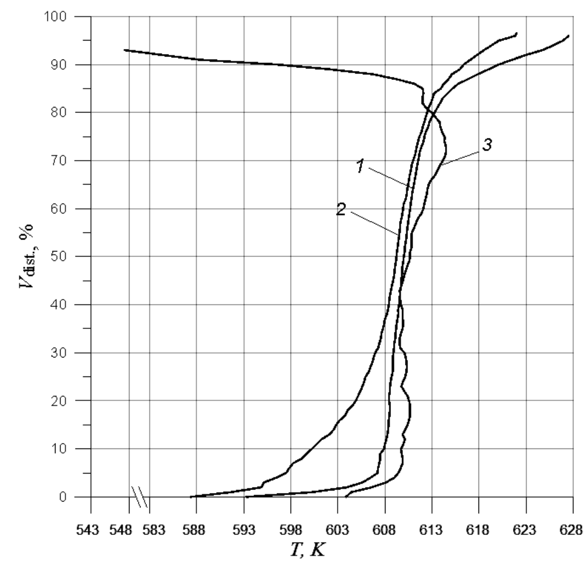

Fig. 2. Fractional composition of FAME (1); FAME (M) (2) and FAEE(M) (3)

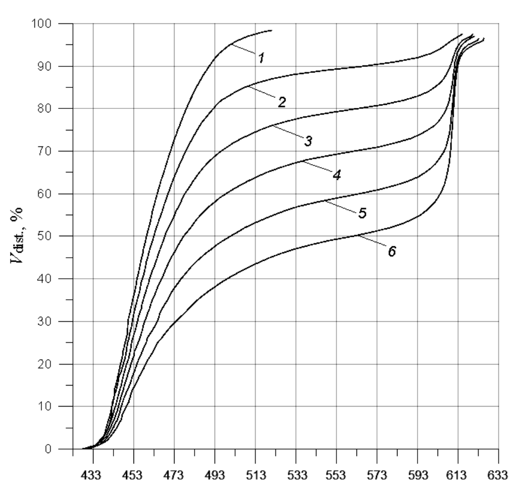

Fig. 3a. Fractional composition of fuel Jet A-1 (1); fuel Jet A-1+10 % of FAME (2); fuel Jet A-1+20 % of FAME (3); fuel Jet A-1+30 % of FAME (4); fuel Jet A-1+40 % of FAME (5); fuel Jet A-1+50 % of FAME (6)

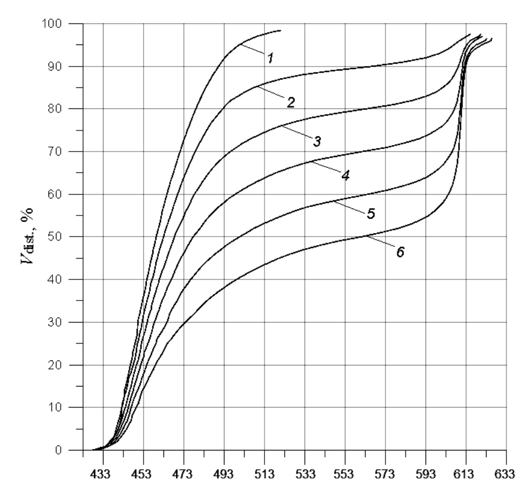

Fig. 3b. Fractional composition of fuel Jet A-1 (1); fuel Jet A-1+10 % of FAME(M) (2); fuel Jet A-1+20 % of FAME(M) (3); fuel Jet A-1+30 % of FAME(M) (4); fuel Jet A-1+40 % of FAME(M) (5); fuel Jet A-1+50 % of FAME(M) (6)

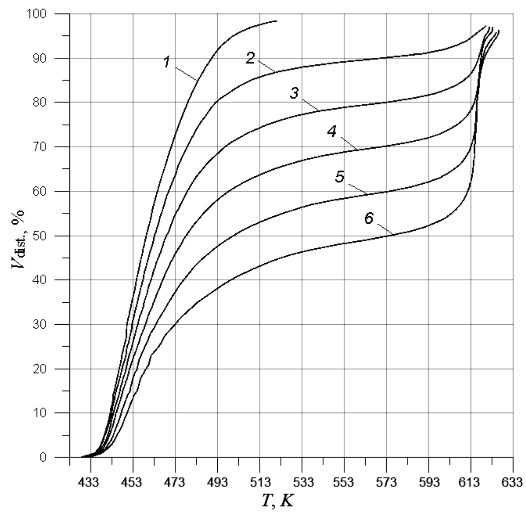

Fig. 3c. Fractional composition of fuel Jet A-1 (1); fuel Jet A-1+10 % of FAEE(M) (2); fuel Jet A-1+20 % of FAEE(M) (3); fuel Jet A-1+30 % of FAEE(M) (4); fuel Jet A-1+40 % of FAEE(M) (5); fuel Jet A-1+50 % of FAEE(M) (6)

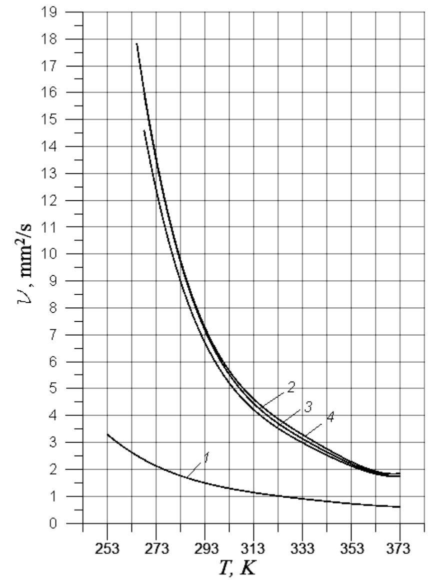

Fig. 4. Influence of temperature on viscosity: fuel Jet A-1 (1); FAME (2); FAME(M) (3) and FAEE(M) (4)

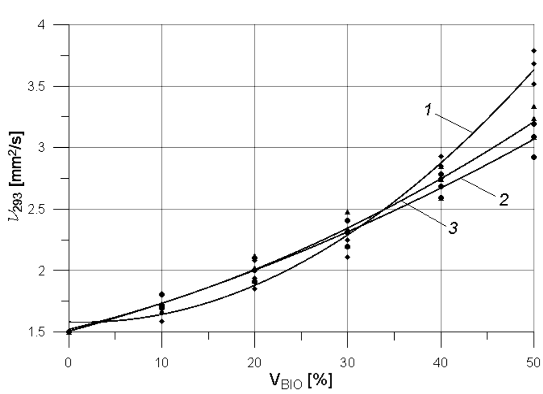

Fig. 5. Dependence of blended jet fuels viscosity on the content of biocomponents: jet fuel Jet A-1+FAME (1); jet fuel Jet A-1+FAME(M) (2) and jet fuel Jet A-1+FAEE(M) (3)

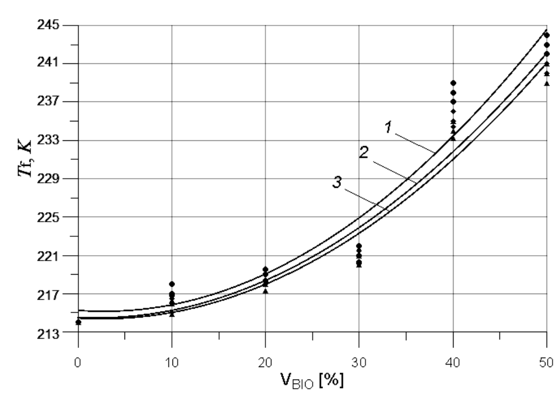

Fig. 6. Dependence of blended jet fuels freezing point on the content of biocomponents: jet fuel Jet A-1+FAME (1); jet fuel Jet A-1+FAME(M) (2) and jet fuel Jet A-1+FAEE(M) (3)

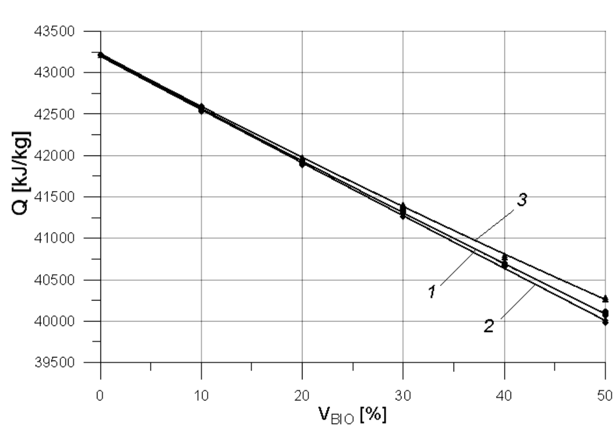

Fig. 7. Dependence of blended jet fuels net heat of combustion on the content of biocomponents: jet fuel Jet A-1+FAME (1); jet fuel Jet A-1+FAME(M) (2) and jet fuel Jet A-1+FAEE(M) (3)

Freezing point. Biocomponents are characterized by significantly high values of freezing point tf comparing to conventional jet fuel. The length of esters molecules stipulates their high viscosity and its dependence on temperature. Because of the molecules size their mobility is low (comparing to jet fuels). When temperature decreases, due to the depression of heat motion from one side and reduction of heat motion between molecules from the other side, association between molecules quickly rises. When temperature continues decreasing esters cool down and completely lose their mobility. Fig. 6 describes the rise of freezing point of blended fuels with increasing content of esters.

Studying the influence of biocomponents on freezing temperature of jet fuels we determined that up to 30 vol % of esters in jet fuel blends does not influence the temperature essentially. But with increasing of biocomponents content freezing temperature starts rising approaching values typical for pure esters.

Thus we may predict that blended jet fuel with esters additives will possess increased freezing temperature. It may negatively influence aircrafts fueling system operation, mainly fuel pumpability at low temperature. So, the content of biocomponent in blended jet fuel should not exceed 30 vol %.

Net heat of combustion. Biocomponents are characterized by lower net heat of combustion *Q* comparing to conventional jet fuels (Fig. 7).

Increasing of biocomponent content in blended jet fuel leads to linear decreasing of combustion heat. It is explained by the difference in elemental composition of esters and jet fuel: esters contain ~2 % less hydrogen and 11–11.5 % of oxygen, that is almost absent in jet fuel. At the same time low net heat of combustion of blended jet fuels may be compensated due to the increased density of esters.

4. Conclusions

As the result of the work the complex of physical-chemical properties and quality parameters of jet fuel and rapeseed oil esters were studied. The results have shown that the main characteristics of biocomponents differ from conventional jet fuels.

The dependencies of jet fuel density, fractional composition, viscosity and freezing temperature on the content of biocomponents were obtained. It is found that blending jet fuel with rapeseed oil esters results in increasing of fuel density and viscosity, rising of freezing temperature and widening of fractional composition due to the rise of final boiling point. It was determined that jet fuel modification by biocomponents will have controversial effect on exploitation properties of new fuels. On one hand it may have negative influence on combustion process, and on the other hand it allows improving certain exploitation characteristics and making new jet fuel more environmentally clean.

It may be concluded that modification of conventional jet fuel by rapeseed oil derived components is possible. At the same time there is a need in more detailed study of the influence of biocomponents on fuel properties for optimization of jet engines operation using new kind of fuel. The next step in the study of biocomponents influence on jet fuels properties is research of exploitation properties of new blended jet fuels and fulfilling of bench test of jet engines.

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ФІЗИКО-ХІМІЧНІ ВЛАСТИВОСТІ СУМІШЕВИХ ПАЛИВ ДЛЯ ПОВІТРЯНО-РЕАКТИВНИХ ДВИГУНІВ З КОМПОНЕНТАМИ НА ОСНОВІ РІПАКОВОЇ ОЛІЇ

Анотація. *Робота присвячена розробленню альтернативного авіаційного палива з біокомпонентами на основі ріпакової олії та вивченню їх фізико-хімічних властивостей. Серед різноманіття технологій отримання альтернативних авіаційних палив для даної роботи було обрано модифікування традиційного палива для повітряно-реактивних двигунів естерами ріпакової олії. Було визначено основні характеристики традиційного авіаційного палива та трьох видів біокомпонентів та порівняно їх зі стандартними вимогами до авіаційного палива марки* Jet A-1. *У рамках даної роботи було досліджено найбільш важливі, або ідентифікаційні властивості палив для повітряно-реактивних двигунів. До них належать: густина, в'язкість, фракційний склад, температура замерзання та нижча теплота згорання. Вивчено та пояснено вплив біокомпонентів на основі ріпакової олії на зазначені характеристики сумішевих палив для повітряно-реактивних двигунів.*

Ключові слова: *паливо для ПРД, альтернативне паливо, біокомпонент, ріпакова олія, фізико-хімічні властивості, густина, в'язкість, фракційний склад, температура замерзання, нижча теплота згорання.*