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EXPERIMENTAL STUDY OF LOW-TEMPERATURE PROPERTIES OF ALTERNATIVE AVIATION FUELS

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Abstract. The work is devoted to the investigation of low-temperature properties of alternative jet fuels mixed with bio-additives derived from rapeseed oil, methanol and ethanol. For the scope of this work modification of conventional jet fuel with bio-additives derived from rapeseed oil, methanol and ethanol were chosen to develop alternative jet fuels. The main low-temperature characteristics – freezing point and pour point of conventional jet fuel and three types of bio-additives were identified and compared with the requirements to conventional Jet A-1 fuel. The influence of bio-additives derived from rapeseed oil, methanol and ethanol on low-temperature characteristics of new jet fuels has been studied and explained. The necessity of studying new technologies is grounded. Mathematical dependencies of freezing point and viscosity of alternative fuels on bio-additives content were proposed.

Keywords: jet fuel, alternative fuel, bio-addittive, rape oil, low-temperature properties, freezing point, pour point, viscosity.

Introduction

The jet fuel Jet A/Jet A-1, the product used in today's airliners, has been largely refined from crude oil feedstock. In recent times, however, the aviation industry became aware of emissions and its contribution to climate change. It has also raised concerns over future supply security and operational costs. These factors have led to interest in the development of product produced from alternative sources. A drop-in product may be defined as one that can replace today's Jet A-1 and can be incorporated into the existing jet fuel (JF) specification.

Advancement in process technology is providing alternative means of producing traditionally distilled crude products, through the conversion of coal, gas or biomass. The processing techniques provide production of fuels, which have similar properties to conventional Jet A-1 fuel.

Significant progress in the development and deployment of alternative aviation fuels has been achieved over the last ten years (Hileman 2014). While a wide variety of alternative aviation fuels production pathways have been developed and solutions to most technical challenges to alternative aviation fuels implementation still can be found, the political and economic boundary conditions still require further development to allow the large-scale production of alternative aviation fuels at affordable prices for airline customers.

Literature overview

The promising feedstock for alternative JFs production is plant biomass (corn, rapeseed, soybean, camelina, algae, etc), animal fats, industrial, household and municipal waste, etc (Abu-Taieh 2011). Today, one of the main tasks in the field of production and use of aviation fuels and lubricants is to expand the resource base and to develop progressive technologies for its production. At the same time, alternative aviation fuels must meet a number of requirements related to efficiency, reliability and durability of transport vehicles (Iakovlieva 2013). These factors stipulate an intensive search for energy efficient and environmentally safe alternative motor fuels (Chuck 2014).

Operational fuel requirements, which determine reliability and durability of air transport and, thus, its safety, have led to the creation of a quality control specification which aims to ensure that different refinement techniques and crude sources are indistinguishable to aircraft operators (Hileman 2014). The specification controls product quality through a series of simple lab based tests to quickly establish if crude derived kerosene meets a range of predetermined values. Usually, lab tests are not a direct measure of gas turbine performance parameters (i.e. fuel spray atomization quality or thermal stability), but instead provide confidence built on extensive operational experience (Yanovskii *et al.* 2005).

Production of a drop-in product refined from non-traditional petroleum sources, such as coal, gas or biomass, therefore raises concern as, although the product may meet the specification pass off tests, the actual performance in a gas turbine is unknown. This is due to the fact that the specification provides for quality control of crude product only and does not provide the complete picture in terms of assessing the suitability of an alternative aviation fuel. For example, residual heavy metals, not currently tested for within the specification, in a certain biomass product may damage the gas turbine hot section or the lack of a certain hydrocarbon group may affect the fuel system performance.

During previous studies the samples of new alternative JFs were developed and first lab test of its physical chemical properties were fulfilled. This kind of alternative JF is a mixture of conventional JF of grade Jet A-1 and bio-additives produced from plants oil up to 50 %. New fuels were obtained using bio-additives produced from rapeseed oil (RO). It is known that today rapeseed is one of the promising types of feedstock within the European region (Yakovleva *et al.* 2017).

At the same time it is well-known that one of the key operational parameters of JF is its low temperature properties. These properties determine aircraft reliable and sable operation at wide range of conditions and thus provide flight safety that is a main principle of modern civil aviation. Today much works are devoted to the question of studying low-temperature properties of alternative JF (Pankin *et al.* 2011).

Purpose of this study is to investigate the basic low-temperature properties of alternative aviation fuels, and to determine how they correspond to the norms of traditional aviation fuels and to what extent they can replace them. Objectives of the study are: to measure parameters of such properties of fuels as a viscosity and freezing point (FP) and derive mathematical dependencies for its calculation. Based on the results of the research, construct diagrams.

Requirements to low-temperature properties of jet fuels

Low-temperature properties of JFs are characterized by its behaviour at low temperatures and are strictly controlled by specifications. During exploitation JFs usually have to work at very low temperatures, especially in winter and during high-altitude flights at altitudes of 9–12 km, where temperature reaches -50–-70 °C (Kulik *et al.* 2015).

Cooling of JFs may be accompanied with clogging of fuel filters that may be associated with aircrafts accidents and disasters. Cooling of fuel also affects reduction of spraying efficiency by fuel nozzles and worsening fuel pumps operation. It is knows that the filtering ability of fuels at low temperatures depends on the fractional and chemical composition and also water content.

Low-temperature properties of fuels are characterized by complex of physical and chemical phenomena, which occur in fuels at temperatures below 0 °C. At low temperatures insoluble sediments of organic nature appear and affect the operation of the fuel system. The main reasons for their occurrence are sharp decrease of some fuel components solubility with a temperature decrease and phase transitions. Such sediments are a composed of amorphous and crystalline substances. The amorphous part includes high-molecular-weight heteroorganic compounds and salts of organic acids, crystalline part is hydrocarbons having high freezing point.

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

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

Description of equipment and experiment realization

For fulfilling experimental studies conventional JF of grade Jet A-1 was used. Its quality meets requirements of specifications ASTM D1655, Def Stan 91-91.

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

- FAME of RO quality parameters meet requirements of specifications EN 14214, and ASTM D6751;
- FAME of RO that were specially modified by vacuum distillation according to the method described in (Iakovlieva *et al.* 2017);
- FAEE of RO that were also modified by vacuum distillation according to the mentioned method.

Within the scope of this work we have studied low-temperature properties of pure JF, pure samples of bio-additives and JF blends, which contained 10 %, 20 %, 30 %, 40 % and 50 % of each type of bio-additives.

PP and FP of fuel samples were determined using Petroleum products low-temperature properties analyzer UTF 70 according to GOST 5066-91 (ISO 3013-74).

Viscosity of fuel samples was determined using automatic device for viscosity determination "Herzog Low temperature viscometer", HVU 482 according to the standard ASTM D445.

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

Bio-additives based on FAME and FAEE of RO are characterized by higher values of PP comparing to conventional JF (Table 1). High values of bio-additives PP are stipulated by chemical structure of molecules and by Van der Waals interactions between them. The length of the hydrocarbons chain (C_{15}–C_{25}) defines the large size of the compounds and due to this binding energy between molecules is higher comparing to conventional JFs.

Table 1. PP of JF and bio-additives samples

Designation of fuel sample	**Pour point, ºC**
Jet fuel of grade Jet A-1	- 59.0
FAME of rapeseed oil	- 15.0
Modified FAME of rapeseed oil	- 19.0
Modified FAEE of rapeseed oil	- 18.5

Due to the existence of forces of intermolecular interaction the speed of random motion of esters molecules is insignificant. With a decrease of temperature its association grows fast: on the one hand, because of decrease in thermal motion of molecules, which weakens the bonds between them, and on the other – because of decrease in mobility of esters molecules, which are "bounded" with each other.

Further temperature decrease causes viscosity rise to such a degree that esters freeze and loose its mobility. Presence of double bonds in esters' molecules makes them curve-shaped, that makes it difficult to locate compactly.

The experimental results have shown that blending JFs with bio-additives increased its PP (Fig. 1). When concentrations of bio-additives are less than 30% (v/v), their effect on the FP is relatively insignificant. At low concentrations they are uniformly distributed in the volume of JF and distances between esters' molecules are not enough for interaction appearance. Further increase of esters content causes rise of PP that gradually approaches to values typical for pure esters.

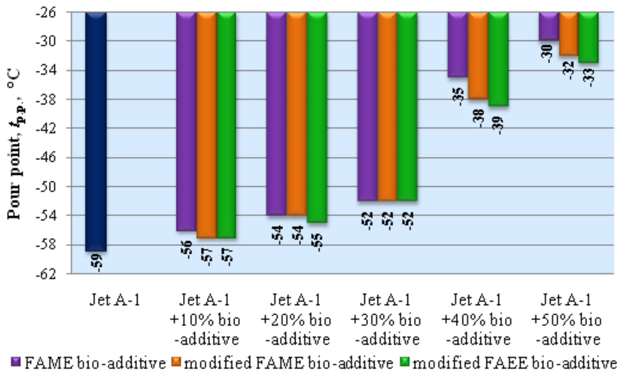

Fig. 1. PP of tested fuel samples

When content of bio-additives in JF exceeds 30 % the amount of comparatively large esters molecules is sufficient for their associations. Thus, associated esters' molecules initiate formation of structure within blended JFs. The other explanation of PP of blended JFs rise may be proposed: during temperature decrease small molecules of JF bond with single molecules or group of associated esters molecules. This promotes association of hydrocarbons and freezing of blended JFs.

We have also assumed that with temperature decrease there is a certain phenomenon in modified fuels: small-sized molecules of hydrocarbon fuel are combined with individual molecules or a set of associated esters molecules, which promotes the association of hydrocarbons and its hardening (Yanovskii *et al.* 2005).

After mathematical processing of experimental data the dependence of fuels' PP on bio-additive concentration was built (Fig. 2).

The polynomial equations were derived and mathematical models (1)–(3), which describe dependence of the FP t_{FP} of jet fuels on concentration of bio-additives, were proposed:

– for FAME bio-additive

$$t_{FP\,1} = -58{,}5 - 0{,}025c + 0{,}013c^2; \qquad (1)$$

– for modified FAME bio-additive

$$t_{FP\,2} = -58{,}714 - 0{,}017c + 0{,}011c^2; \qquad (2)$$

– for modified FAEE bio-additive

$$t_{FP\,3} = -58{,}714 - 0{,}037c + 0{,}011c^2. \qquad (3)$$

where: t_{FP} – freezing point, ºC; c – concentration of bio-additive in jet fuel samples.

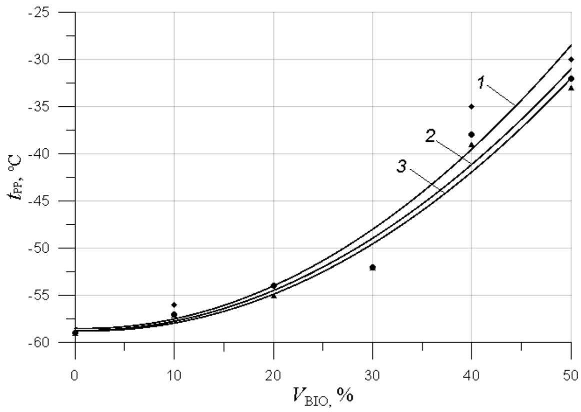

Fig. 2. Dependence of fuels' PP on bio-additive concentration: 1 – jet fuel + FAME, 2 – jet fuel + modified FAME, 3 – jet fuel + modified FAEE

It is known that the reason for the decreasing of fuel pumpability at low temperatures is a significant increase in fuels' viscosity (Kulik *et al.* 2015). In order to evaluate viscosity of blended JFs we have determined fuels viscosity in temperature range from -20 to 100 ºC. Then we have studied the mutual influence of temperature and concentration of bio-additives on its viscosity (Fig. 3–5.). This was done by the method of linear regressive analysis.

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

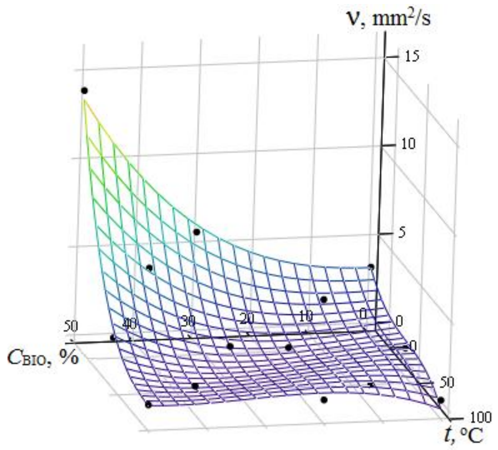

Fig. 3. Kinematic viscosity of tested fuel samples as a function of temperature and FAME bio-additive concentration

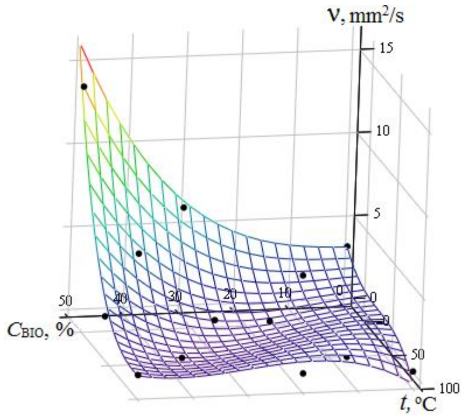

Fig. 4. Kinematic viscosity of tested fuel samples as a function of temperature and modified FAME bio-additive concentration

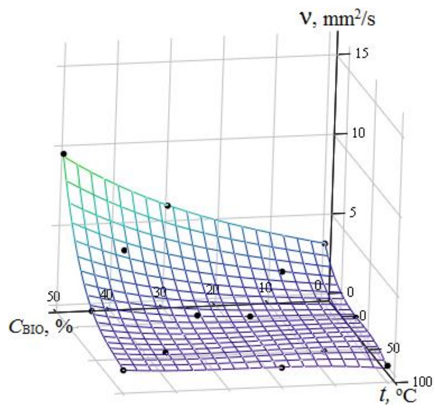

Fig. 5. Kinematic viscosity of tested fuel samples as a function of temperature and modified FAEE bio-additive concentration

The third-order polynomial equations, which describe the mutual influence of the temperature *t* and the concentration *c* of bio-additives on the viscosity *ν* of blended JFs, were derived:

– FAME bio-additive

$$\nu_1 = 2{,}361 \cdot 10^{-5} - 6{,}095 \cdot 10^{-6} t + 7{,}708 \cdot 10^{-4} c - 0{,}037\, t\, c - 7{,}784 \cdot\cdot 10^{-4} t^2 - 5{,}334 \cdot 10^{-5} c^2 + 2{,}179\, t^2 c^2 - 0{,}024 t^3 + 5{,}85 \cdot 10^{-4} c^3 + +4{,}817 \cdot 10^{-5} t^3 c^3; \quad (4)$$

– modified FAME bio-additive

$$\nu_2 = 3.178 \cdot 10^{-5} - 7{,}146 \cdot 10^{-6} t + 8{,}053 \cdot 10^{-4} c - 0{,}033\, t\, c - 8{,}835 \cdot\cdot 10^{-4} t^2 - 7{,}269 \cdot 10^{-5} c^2 + 2{,}228\, t^2 c^2 - 0{,}021 t^3 - 1{,}031 \cdot 10^{3} c^3 + +9{,}149 \cdot 10^{-5} t^3 c^3; \quad (5)$$

– modified FAEE bio-additive

$$\nu_3 = 1.252 \cdot 10^{-5} - 6{,}075 \cdot 10^{-6} t + 9{,}171 \cdot 10^{-4} c - 0{,}046\, t\, c - 1{,}312 \cdot\cdot 10^{-3} t^2 - 1{,}24 \cdot 10^{-5} c^2 + 1{,}967\, t^2 c^2 + 0{,}044 t^3 - 1{,}272 \cdot 10^{-4} c^3 + +1{,}662 \cdot 10^{-5} t^3 c^3; \quad (6)$$

where: *ν* – viscosity, mm^2/s; *t* – temperature, °C; *c* – concentration of bio-additive in jet fuel samples.

The coefficients of the equations (4)–(6) clearly show both the influence of individual factors (temperature and bio-additives concentration) and also their mutual influence.

It is known that the dependence curves of the viscosity of JFs on its temperature change in the low temperature zone rather rapidly. These 3D models show that even insignificant increase of temperature causes a significant decrease in fuels’ viscosity. To avoid potential problems with blended JFs spraying at low temperatures it is possible to increase fuel pressure before the nozzles. This technical solution is well-known for a long time and has been successfully used during JEs exploitation (Yanovskii *et al.* 2005).

Conclusion

In a result of the work the complex of low-temperature properties of the new alternative jet fuels were studied. Experimental results have shown that rising the content of bio-additives in conventional JF leads to general worsening of low-temperature properties of JFs that is revealed by rising of FP. This factor limits using of bio-additives in JFs’ blends: thus maximal content of bio-additives may be 30 % (v/v). JFs’ blends of such composition completely satisfy requirements of specifications to conventional JFs. According to modern specifications maximal FP of jet fuels shouldn’t be higher that minus 47 °C.

It was concluded that maximal content of bio-additives in alternative JFs is 30 % (v/v). Taking into account insignificant difference in characteristics of JFs blended with methyl and ethyl esters it is more rational to use rather FAEE than FAME. The use of ethanol provides production of bio-additives of completely renewable feedstock.

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