The Study of Intermolecular Interactions in Bio-Jet Fuel and Substantiation of Its Influence on Fuel Properties

Anna Yakovlieva, Sergii Boichenko, Peter Korba, and Pavol Kurdel

1 Introduction

Modern aviation is one of the main consumers of non-renewable hydrocarbon feedstock in the form of aviation gasoline and jet fuels. Due to the rapid development of the aviation industry, it is important to improve the energy efficiency of fuel and reduce aircraft emissions [1]. Today, in accordance with the state policy of the leading countries of the world in the fuel and energy industry, the organization of alternative motor fuels use, in particular aviation fuel, from renewable feedstock is one of the priority tasks.

It is well known that the aviation industry causes significant damage to the environment because the products of fuel combustion are a source of atmospheric pollution. In addition, the emission of CO_2 and other greenhouse gases makes a significant contribution to global climate change [2]. A set of guiding documents of leading world organizations is devoted to the problem of aircraft emissions. They establish the requirements for continual reduction of CO_2 emissions by 1.5% per year on average with the aim to reduce carbon emissions by 50% by 2050 in comparison with 2005 [1–3].

Among the existing today variety of alternative aviation fuels, preference is given to those derived wholly or partially from renewable feedstock—biofuels. The use of fuels from renewable feedstock has a number of advantages, in particular their natural origin, provision of the closed carbon cycle during the production and use and, therefore, the reduction of CO_2 emissions into the atmosphere, the ease of fuel biodegradation in the environment, availability of the feedstock in different

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A. Yakovlieva (✉) · P. Korba · P. Kurdel
Technical University of Kosice, Kosice, Slovakia
e-mail: anna.yakovlieva@tuke.sk

S. Boichenko
National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute", Kyiv, Ukraine

S. Boichenko et al. (eds.), *Modern Technologies in Energy and Transport*, Studies in Systems, Decision and Control 510, https://doi.org/10.1007/978-3-031-44351-0_11

regions, and minimizing the adverse impact on environment during fuel storage and transportation [2, 3].

One of the types of aviation biofuels, which are actively studied today, is a bio-jet fuel that is a blend of conventional jet fuel and bio-additives produced from plant oils [3, 4]. According to studies by [5, 6] there is a variety of oil feedstock, which can be used for bio-additives production: rapeseed, sunflower, camelina oil, jatropha, used cooking oil, animal fats in the form of food industry waste, etc. The choice of feedstock usually depends on its availability in the certain region or country and physical–chemical properties of oil. Supply of the feedstock for bio-jet fuels production shouldn't compete with the needs of food industry. Bio-additives are usually produced through the process of esterification of oils with various alcohols (methanol, ethanol, butanol, etc.) and further vacuum distillation. These processes are well-described in works [1, 6].

During the previous studies [3, 6–8] the authors fulfilled a series of experimental researches aimed on analysis of the basic physical–chemical properties of the bio-jet fuels Within these studies the bio-jet fuels based on methyl and ethyl esters of rapeseed and camelina oils were analyzed by the parameters of density, viscosity, fractional composition and freezing point of the fuel [6, 7]. The results have shown a good level of compatibility of conventional jet fuel and bio-additives, satisfactory physical–chemical properties of bio-jet fuels, which correspond to requirements of standard specifications and improvement of certain operation properties. The results have also shown a need in further studies, which should be devoted to optimization of some physical–chemical properties of bio-jet fuels [7, 8]. Another important issue, is possibility to use new type of feedstock—including both, oils and alcohols. Using of new types of renewable feedstock for bio-additives production may contribute to improvement of physical–chemical and operation properties of bio-jet fuels and provide more of feedstock availability.

This article is presented as a continuation of previously fulfilled studies. The main purpose of the work is to determine the nature and role of intermolecular interaction in the system "hydrocarbon jet fuel—fatty acid esters" to explain the mechanism of interaction and substantiate the influence of bio-additives on the physical–chemical properties of bio-jet fuels. Within this study the following bio-additives were analyzed: rapeseed oil fatty acid methyl esters (RO FAME), rapeseed oil fatty acid ethyl esters (RO FAEE), camelina oil fatty acid ethyl esters (CamO FAEE), palm-kernel oil fatty acid ethyl esters (PKO FAEE) and coconut oil fatty acid ethyl esters (CocO FAEE).

2 Analysis of Hydrocarbon Composition of Conventional Jet Fuel and Fatty Acid Composition of Bio-Additives

From the studies by [1, 4] and other researchers it is known that conventional jet fuels are derived from crude oil by straight-run distillation. They are kerosene-gasoil fraction, which boils in a range 140–250 (280) °C and is composed mainly of paraffinic, naphthenic and some amount of aromatic hydrocarbons C5–C16 [1, 5], which is explained by the natural composition of crude oil which is used for production. Depending on the origin of crude oil the ratio of hydrocarbons in fuel may vary in some range.

Fatty Acid Composition of Bio-Additives

Based on the results of the previous authors' researches the comparative analysis of chemical composition (fatty acids composition) of bio-additives used for bio-jet fuel production was developed (Table 1) [6–8].

Data in Table 1 show the content (%, mas.) of each individual fatty acid found in samples of bio-additives. Fatty acid composition of RO FAME, RO FAEE, and CamO FAEE were determined and studied during the previous researches [6–8]. At the same time fatty acid composition of CocO FABE and PKO FAiBE were analyzed for the first time and are also presented in the table for the comparative analysis. The table also contains data about the heat of evaporation ($\Delta H_{\text{evap.}}$) of each of the compounds. Values of the heat of evaporation are individual for each of the compounds and are taken from certain reference literature [9]. Values of $\Delta H_{\text{evap.}}$ will be used for further analysis of intermolecular interactions in the bio-jet fuel.

3 Theoretical Fundamentals of Intermolecular Interactions, Which Can Occur Between Hydrocarbons and Fatty Acids Esters in Bio-Jet Fuel

To study and establish the regularities of the influence of the bio-additives obtained from different plant oils on the physical–chemical properties of petroleum jet fuel, it is necessary to carry out a detailed analysis of the mechanisms of compounding (blending) of jet fuels and bio-additives, as well as the nature of the intermolecular interaction in the system "hydrocarbon fuel—fatty acid esters". Today there is a number of studies is devoted to the questions of fatty acid esters production, analysis, and influence on fuel properties. However, the issue of intermolecular processes and interactions, which take place in blended petroleum fuel, and jet fuel in particular, is insufficiently covered in the modern scientific literature.

Table 1 Fatty acid composition of samples of bio-additives

Fatty acid	Short name	RO FAME		RO FAEE		CO FAEE		PKO FAEE		CocO FAEE	
		Content, %	ΔH_{evap}, kJ/mol	Content, %	ΔH_{evap}, kJ/mol	Content, %	ΔH_{evap}, kJ/mol	Content,	ΔH_{evap}, kJ/mol	Content, %	ΔH_{evap}, kJ/mol
Hexanoic	C6:0	–	–	–	–	–	–	0.8	40.4	–	–
Caprylic	C8:0	–	–	–	–	–	–	19.4	44.4	2.9	44.4
Decanoic	C10:0	–	–	–	–	–	–	7.7	47.9	3.2	47.9
Lauric	C12:0	–	–	–	–	–	–	53.1	50.7	47.1	50.7
Myristic	C14:0	–	–	–	–	–	–	17.4	53.5	16.4	53.5
Palmitic	C16:0	6.0	57.5	6.6	58.6	5.7	58.6	4.7	58.6	8.9	58.6
Stearic	C18:0	1.9	60.1	2.6	60.1	2.5	60.1	1.7	60.1	2.4	60.1
Oleic	C18:1	52.6	59.6	20.0	63.5	48.4	63.5	2.0	63.5	14.3	63.5
Linoleic	C18:2	21.1	62.1	29.6	63.7	30.6	63.7	0.6	63.7	2.5	63.7
Linolenic	C18:3	7.2	61.1	24.5	62.2	9.0	62.2	–	–	–	–
Arachidic	C20:0	0.45	62.2	1.1	61.6	0.4	61.6	–	–	–	–
Eicosenoic	C20:1	1.25	65.3	9.7	67.0	0.8	67.0	–	–	–	–
Heneicosanoic	C21:1	4.2	63.6	–	–	–	–	–	–	–	–
Eicosadienoic	C20:2	–	–	1.3	64.7	–	–	–	–	–	-
Behenic	C22:0	0.23	64.9	–	–	–	–	–	–	–	–
Erucic	C22:1	2.5	67.7	0.9	69.3	0.4	69.3	–	–	–	–
Others		2.57	–	3.7	–	1.2	–	1.6	–	2.3	–

Thus, the works [10, 11] provide data on the solubility of triacylglycerides of vegetable oils in some polar solvents. The works of scientists [12, 13] provide data on the solubility of biodiesel and diesel fuels in various organic solvents. However, information on the mutual solubility of fatty acids esters and hydrocarbons of kerosene-gasoil fractions of oil refining (jet fuels) is not presented in the modern literature. Accordingly, this issue requires study, analysis, and substantiation.

Samples of bio-jet fuels can be considered at the macro level as a two-component system, in which each of the components (petroleum jet fuel and bio-additives) are in the liquid state under normal conditions. At the same time, at the micro level the bio-jet fuel is a multicomponent system, which includes paraffinic, naphthenic, aromatic hydrocarbons, saturated and unsaturated fatty acid esters [14].

In order to study and analyze the processes of compounding (blending) of hydrocarbon fuels and fatty acid esters the fundamentals of physical chemistry: the processes of intermolecular interaction, colloidal chemistry and solution theory were applied [11].

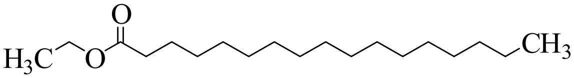
It is well-known that dissolution is a complex physical and chemical process [10, 14]. According to physical theory [14, 15], dissolution is the uniform distribution of dissolved substance particles throughout the solvent volume. According to the chemical theory [14, 15], solutions are systems formed by particles of the solvent, dissolved substance, and unstable chemical compounds formed between them by hydrogen bonds or electrostatic forces of interaction. The modern theory of solutions considers the dissolution process as an interaction between particles of different polarity [15].

It is known from the works [12–14] that the dissolution (mixing) of substances is based on the solvation process—the interaction of solvent particles with the particles of the dissolved substance. In the dissolution process, part of the energy is released as a result of breaking the bonds between the molecules of the dissolved substance, and part is absorbed during the formation of new bonds between the molecules of the solvent and the dissolved substance. That is, the dissolution process is determined by intermolecular interaction of the system components. Van der Waals forces and hydrogen bonds belong to intermolecular interactions [15].

To analyze the process of dissolution of the fatty acid esters in the hydrocarbon fuel it is necessary to establish the presence and role of these forces between the molecules of the esters. As it is known, ester molecule is a fatty acid radical with carbonyl group -C = O, conjugated by hydroxyl oxygen atom with alcohol radical (Fig. 1) [6].

The presence of oxygen atoms indicates the ability of molecules to form hydrogen bonds. Thus, these molecules can be hydrogen bond acceptors. At the same time, hydrogen atoms in ester molecules are bound by strong covalent bonds with carbon atoms in acid and alcohol radicals and can't be hydrogen bond donors [15]. It follows

Fig. 1 Molecule of the typical fatty acid ester



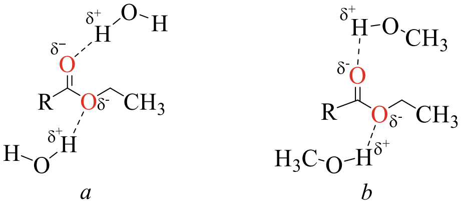


Fig. 2 Intermolecular interaction of esters molecules with low carbon number with water (**a**) and alcohol (**b**) via hydrogen bonds

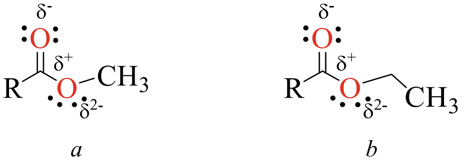


Fig. 3 Induction effect and shift in atoms' charges in a—FAME and b—FAEE

that hydrogen bonds are not formed between the fatty acid esters molecules, and the molecules are not capable of mutual association through hydrogen bonds.

Ester molecules can form hydrogen bonds only with other molecules, being acceptors of such bonds. This explains the solubility of esters with the number of carbon atoms in acyl residues up to 5 in water and alcohols, in polar molecules in which hydrogen atoms interact with electronegative oxygen atoms (Fig. 2). However, as the length of the hydrocarbon chain increases, the solubility of esters in polar solvents decreases.

Hydrogen bonding is a particular case of dipole–dipole or orientational Van der Waals interaction. The basis of the orientational interaction (Kizome forces) is the ability to orient one molecule relative to another with charges opposite in sign [15].

The electronegativity of oxygen atoms (3.5) in a molecule is greater than the electronegativity of carbon (2.5). Undivided pairs of oxygen electrons shift the electron density of neighboring carbon atoms, acquiring partially negative charge (induction effect). In turn, the carbonyl carbon atom acquires a partially positive charge (Fig. 3).

As a result, the ester molecule becomes polar and has a constant electric dipole moment. This peculiarity of the structure of the fatty acid ester molecules explains their ability to orientation interaction.

An ester molecule consists of two parts: a polar hydrophilic part and a nonpolar hydrophobic one. Accordingly, the hydrophilic part of the molecule has the ability to orientation interaction [14]. At the same time, acyl radicals are nonpolar (hydrophobic) and orientation interaction is not typical to them. Dispersive interaction forces (London forces) arise between them. These forces arise due to the appearance of instantaneous dipoles as a result of the shift in the electron density of electron shells that are in constant motion relative to the nuclei [14, 17]. The constant motion of the electrons leads to an asymmetric redistribution of charges in the molecules, and instantaneous dipoles arise in the particles. Thus, nonpolar molecules can become polar for a moment. In general, the dispersion interaction depends on the deformation ability of the molecules and the distance between them.

Fig. 4 Spatial electrostatic model of fatty acid ester molecule

In the spatial electrostatic model of the molecule (Fig. 4) one can see its polar part, where the accumulation of negative charge is shown in red and positive charge in blue. The nonpolar acyl radical is shown in green.

Placed in space, ester molecules are oriented by opposite charge signs, and dipole–dipole bonds are formed between the polar parts of the molecule. Dispersive interaction forces arise between hydrophobic acyl radicals. The longer the radical, the larger the area of its contact and, consequently, the area for the formation of dispersion interaction forces. It follows that as the length of the hydrocarbon chain increases, the force of intermolecular interaction increases. Importantly, as the length of the hydrocarbon chain increases, dispersion interaction forces begin to dominate over orientation forces, and the ester molecule acquires hydrophobic properties. This is revealed by loose of ability to dissolve in polar solvents [16, 18].

The presence of double bonds in acyl radicals of esters has a significant effect on their intermolecular interactions and, accordingly, on the physical–chemical properties of esters. The angle of the valent double bond between the carbon atoms is 120° compared to the angle of a single bond (110°), which makes the shape of the molecule more curved. The distance between the "curved" acyl radicals with one or several double bonds is greater than in the case of straight (saturated) ones. This contribute to weakening of the forces of dispersion interaction between the molecules [12, 14, 16].

In addition to the orientation and dispersion interactions between ester molecules, an inductive interaction can occur: the non-polar parts of the molecule are polarized under the action of the electric field of the polar part of the molecule and acquire an induced dipole moment.

Summarizing the above mentioned it can be concluded that the forces of dispersion interaction between ester molecules prevail. The dispersion interaction energy can be expressed by the London formula [14, 15]:

$$E_{disp} = -\frac{3I}{4}\frac{\alpha^2}{d^6}, \tag{1}$$

where I—ionization energy of the molecule; α—coefficient representing the polarization ability of molecules; d—distance between the moment dipoles.

Formula (1) shows that as the polarization ability α increases, i.e. as their size of the molecules increases, their dispersion interaction energy also increases. At the same time, the ionization energy *I* of ester molecules changes insignificantly with the increase of their linear size [14, 17] and, in general, does not affect the disperse interaction energy. Quantitative values of size of the molecules [9] for fatty acids methyl and ethyl esters are given in Table 2. Therefore, we may expect the rise of polarization ability and energy of dispersion interaction with the increasing of molecules size.

Hydrocarbons of jet fuels can be conditionally divided into two groups: non-polar and non-polar, but capable of polarization—paraffin-naphthenic and aromatic hydrocarbons respectively. Some paraffins as well as naphthenes can give an insignificant reduced dipole moment [10, 17].

The spatial electrostatic models of typical molecules of hydrocarbon jet fuel and fatty acids esters of rapeseed oil are shown in Table 3. Hydrocarbon molecules have smaller sizes compared to ester molecules, correspondingly smaller polarization ability and dispersion interaction energy.

Basing on the analyzed literature and data it has been established that during the process of blending of hydrocarbon jet fuel and fatty acids esters the mutual mixing of components takes place. This mixing occurs under the influence of induction and dispersion forces of Van der Waals interaction, among which the dispersion component prevails. As the proportion of esters in the system 'hydrocarbon jet fuel—fatty acid esters' increases, an increase in intermolecular interaction is observed. This is evidenced by an increase in the evaporation heat of its components [9] (Table 4).

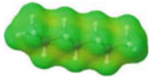
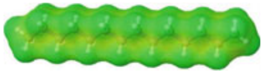
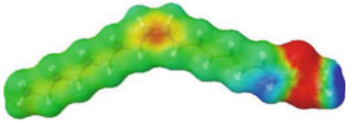
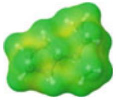
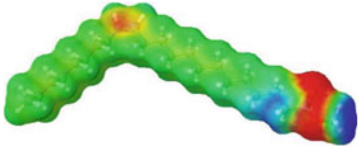
This is explained by an increase in the proportion of the dispersion component in the total intermolecular interaction as a result of an increase in the polarizability of the system molecules. Induction interaction in the system occurs due to polarization by carboxyl groups of naphthenic and aromatic hydrocarbons esters of jet fuels.

The energy of the system decreases by 31–69.3 kJ/mol as the proportion of esters in the hydrocarbon fuel—fatty acid esters system increases. Reduction of the total energy in the system has a direct influence on the physical–chemical properties of bio-jet fuels blended with fatty acids esters.

Table 2 Ability to polarization of fatty acid esters expressed as a molecule size [9]

The ability to polarization, α						
Methyl	–	–	$C_{17}H_{34}O_2$	$C_{19}H_{38}O_2$	$C_{21}H_{40}O_2$	$C_{23}H_{44}O_2$
esters	–	–	$32.7 \cdot 10^{-24}$cm^3	$36.4 \cdot 10^{-24}$cm^3	$40.1 \cdot 10^{-24}$cm^3	$43.8 \cdot 10^{-24}$cm^3
Ethyl	$C_{14}H_{30}O_2$	$C_{16}H_{32}O_2$	$C_{18}H_{36}O_2$	$C_{20}H_{40}O_2$	$C_{22}H_{42}O_2$	$C_{24}H_{46}O_2$
esters	27.2 10^{-24}cm^3	30.9 10^{-24}cm^3	$34.6 \cdot 10^{-24}$cm^3	$38.2 \cdot 10^{-24}$cm^3	$41.9 \cdot 10^{-24}$cм^3	$45.6 \cdot 10^{-24}$cm^3

Table 3 Comparative view of spatial electrostatic models of molecules of jet fuel and fatty acid esters

Hydrocarbon jet fuel		Fatty acid esters	
Compound	Spatial electrostatic models of the compound	Compound	Spatial electrostatic models of the compound
Paraffins		Saturated esters	
Heptane		Methyl-palmitate	
Tetradecane		Ethyl-stearate	
Naphthenes		Non-saturated esters with one double bond	
Trimethylcyclopentane		Methyl-oleate	
Secbuthylcyclopentane		Methyl-erucate	

(continued)

Table 3 (continued)

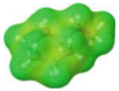
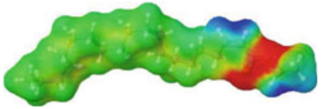
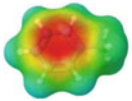
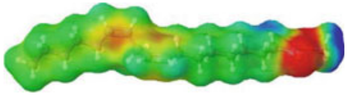
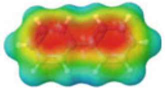
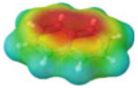
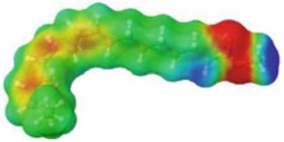
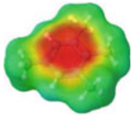
Hydrocarbon jet fuel		Fatty acid esters	
Compound	Spatial electrostatic models of the compound	Compound	Spatial electrostatic models of the compound
Ethylcyclohexane		Ethyl-eicosenoate	
Aromatics		Non-saturated esters with two double bonds	
Toluene		Methyl-linolate	
Biphenyl		Non-saturated esters with three double bonds	
Naphthalene		Methyl-linolenate	
Tetramethylbenzene			

Table 4 Heat of evaporation, ΔH of components of bio-jet fuels [9]

Type of molecules	Heat of evaporation, ΔH		
	Jet fuel hydrocarbons	Methyl esters	Ethyl esters
Heat of evaporation, ΔH, kJ/mol	31.0–47.0	57.5–67.7	40.4–69.3

Table 5 Physical–chemical properties of conventional jet fuel and bio-additives

Property	Jet fuel	Bio-additives				
		RO FAME	RO FAEE	CO FAEE	PKO FAEE	CocO FAEE
Density at 20 °C, kg/m^3	792.0–794.0	880.38	873.22	871.13	860.4	866.92
Viscosity at 20 °C, mm^2/s	1.50–1.58	6.734	7.355	6.422	4.546	4.041
Freezing point, °C	Minus 59–minus 60	Minus 19	Minus 18.5	Minus 7	Minus 13	Minus 12

4 Experimental Analysis of the Influence of Intermolecular Interactions on Some Physical–Chemical Properties of Bio-Jet Fuels

In order to substantiate the influence of intermolecular interactions on properties of bio-jet fuels the experimental study of some of the basic physical–chemical properties has been done. For the study the set of sample of bio-jet fuels were prepared. Each of the bio-additives (RO FAME, RO FAEE, CO FAEE, PKO FAEE and CocO FAEE) were blended with conventional jet fuel in quantity 10%, 20%, 30%, 40% and 50%. Conventional jet fuels of grade Jet A-1 with no bio-additives content was studied as a reference fuel. Such properties as density, kinematic viscosity and freezing point were chosen for the investigation. These properties are determined and substantiated by the chemical composition of fuel and structure of fuel's molecules. Therefore, research and analysis of these of bio-jet fuel properties allows understanding the degree of influence of intermolecular interactions and processes, which take place in fuels.

Table 5 summarizes the values of basic physical–chemical properties of bio-additives samples and conventional jet fuel used during the experiment. These data allow analyzing and understanding the differences in properties basing on research of their structure and composition.

Data in Table 5 shows that quantitative values of density, viscosity and freezing point of bio-additives significantly differ from conventional jet fuel. Typically, density of the fuel depends on its chemical and fractional composition. All the studied bio-additives possess much higher density values comparing to the density of conventional JF.

It is explained by its chemical structure. Unlike hydrocarbons of conventional JFs, which contain 5–16 carbon atoms, acyl radicals of ester molecules contain a wider range of molecules, usually with 8–22 carbon atoms or even more, depending on the feedstock. This is the reason of a strong dispersion interaction forces between them and, consequently, higher density compared to jet fuel.

Influence of Intermolecular Interactions on Density of Bio-Jet Fuels

From Table 5 it may be seen that density of different bio-additives significantly varies (860.4–880.38 kg/m^3). This is explained by the fatty acid composition and content of each of the bio-additive. From Table 1 it is seen that RO FAME and FAEE contain molecules with 16–22 carbon atoms in fatty acids radicals. Moreover, about 90% of all molecules are esters of fatty acids with 16, 18 and 20 carbon atoms (palmitic, oleic, linoleic, linolenic, and eicosenic acids). CO FAEE contains mostly esters of palmitic, oleic, linoleic and linolenic acids (C16–C18). Such content of high-molecular esters results in high values of density. At the same time PKO FAEE and CocO FAEE are composed of molecules with lower carbon number (C8–C18), additionally, PKO FAEE contains some amount of C6 molecules. The weaker intermolecular interaction may be supposed in this case and this results in lower density values (860.4–866.92 kg/m^3).

Next, the density of bio-jet fuels with different content of bio-additives was studied (Fig. 5). The density of the bio-jet fuel samples increases with the increase in the content of bio-additives. For all the samples the change of density has an additive character, and is represented by a straight line. The rise in density values is explained by the increased effect of the forces of dispersion interaction between hydrocarbon molecules and acyl radicals of esters, on the one hand, and the emergence of forces of induction interaction between hydrocarbons of the jet fuel and carboxyl groups of esters, on the other. As it was mentioned, acyl radicals of ester molecules contain higher number of carbon atoms, which leads to high values of the interaction energy between ester molecules and, accordingly, their density. At the same time, samples of bio-jet fuels with PKO FAEE and CocO FAEE have lower density values compared to bio-jet fuels with RO FAME, RO FAEE and CO FAEE, are closer to values typical to jet fuels.

Influence of Intermolecular Interactions on Kinematic Viscosity of Bio-Jet Fuels

The viscosity of fuels is the average value of the viscosities of all its components. The viscosity of hydrocarbon jet fuels depends on the structure of the molecules,

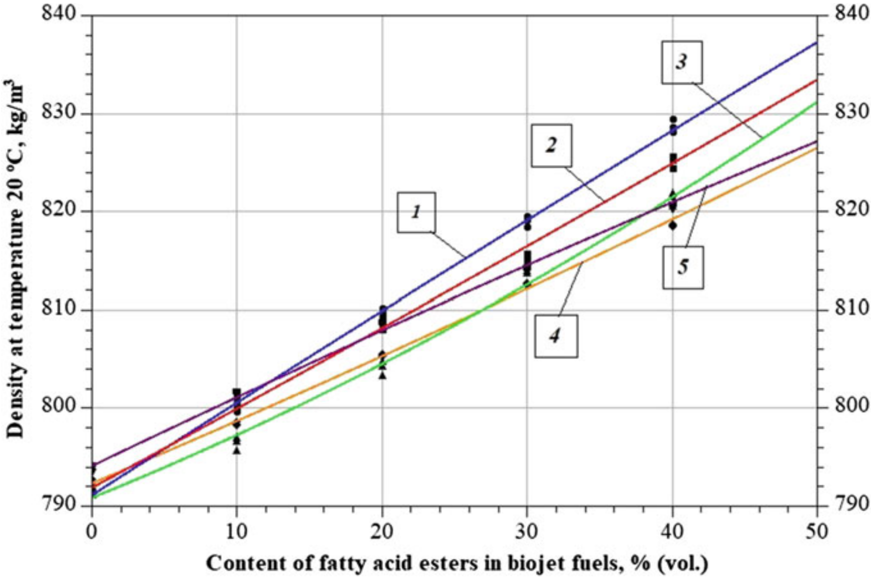


Fig. 5 Dependence of density of bio-jet fuel on the content of bio-additives: *1*—RO FAME, *2*—RO FAEE, *3*—CO FAEE, *4*—PKO FAEE, *5*—CocO FAEE

their interaction and, to a small extent, on their molecular weight. From Table 5 it may be seen that viscosity values of bio-additives (4.041–6.734 mm^2/s) significantly differ from the viscosity of conventional jet fuel (1.50–1.58 mm^2/s).

The reason for this, as mentioned above, is chemical structure of fatty acid esters. The length of the fatty acid radicals determines the large size of the compounds, which leads to a higher energy of their intermolecular interaction. Viscosity, like density, is a property that can be used to characterise the forces of intermolecular interaction in a liquid quite accurately. The higher the energy of intermolecular interaction of fuels, the higher their viscosity. Hydrocarbon molecules do not contain carboxyl groups in their composition and are characterised by much smaller sizes, as a result only dispersion forces act between them, the energy of which is much lower than that of ester molecules.

In addition, from Table 5 it may be seen that PKO FAEE and CocO FAEE have lower values of viscosity compared to RO FAME, RO FAEE, and CO FAEE. Referring to the Table 1 it is seen that RO and CO esters are composed of long-chain esters with 16–22 carbon atoms, while PKO and CocO contain molecules with 8–18 carbon atoms. Due to this, forces of intermolecular interactions in PKO and CocO bio-additives are weaker, and, consequently, viscosity is lower. Moreover, RO and CO bio-additives with approximately 80% composed of esters of unsaturated fatty acids with one and two double bonds, which additionally increases their viscosity. On the contrary, PKO bio-additive contains only about 3% of unsaturated fatty acids

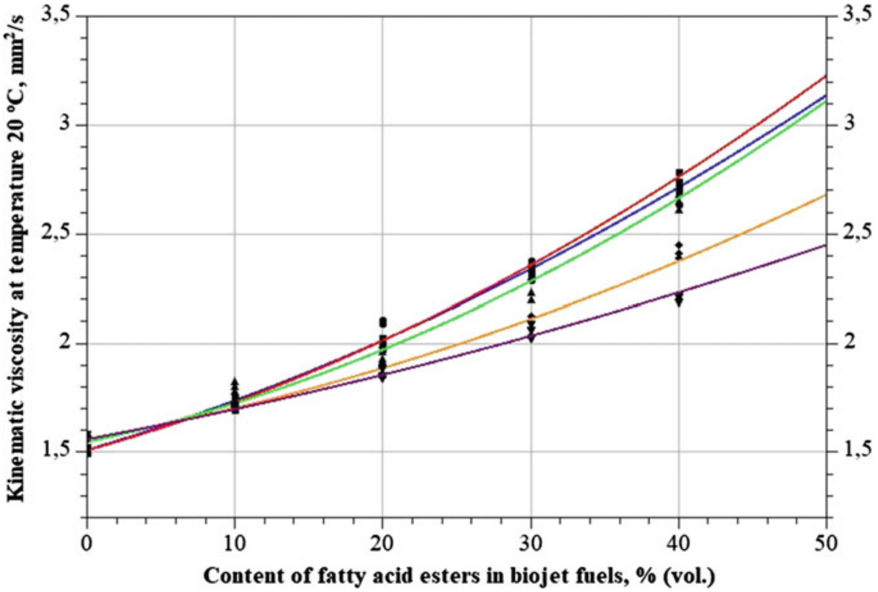


Fig. 6 Dependence of kinematic viscosity of bio-jet fuel on the content of bio-additives: *1*—RO FAME, *2*—RO FAEE, *3*—CO FAEE, *4*—PKO FAEE, *5*—CocO FAEE

and CocO bio-additive—about 17%, which much lower compared to RO and CO esters.

Next, the kinematic viscosity of bio-jet fuels with different content of bio-additives was studied (Fig. 6). It was found that increasing of content of bio-additives in bio-jet fuels results in rising of kinematic viscosity. This phenomenon may be explained by the strengthening of intermolecular interaction forces between hydrocarbon molecules and ester molecules.

It is also seen from Fig. 7 that samples of bio-jet fuels with PKO FAEE and CocO FAEE have lower kinematic values compared to bio-jet fuels with RO FAME, RO FAEE and CO FAEE, and are closer to values typical to conventional jet fuels.

Influence of Intermolecular Interactions on Freezing Point of Bio-Jet Fuels

All of the studied bio-additives based on RO, CO, PKO and CocO have significantly higher values of freezing point compared to conventional jet fuel (Table 5). Such high freezing points of bio-additives are explained by the chemical structure of the molecules and the van der Waals forces that exist between them. The length of the hydrocarbon chain (C8–C22) determines the large size of the compounds, due to

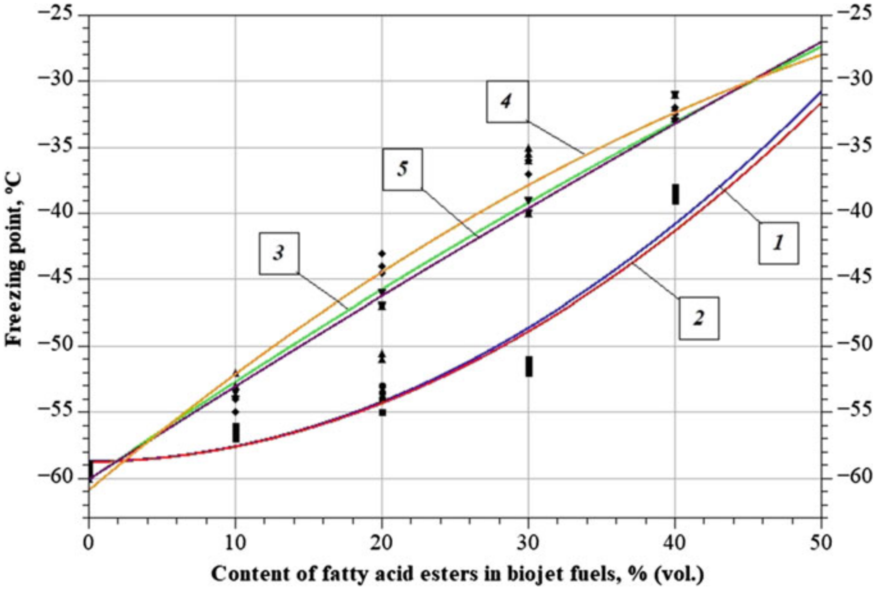


Fig. 7 Dependence of freezing point of bio-jet fuel on the content of bio-additives: *1*—RO FAME, *2*—RO FAEE, *3*—CO FAEE, *4*—PKO FAEE, *5*—CocO FAEE

which the energy of the bonds between the molecules is much higher compared to the conventional jet fuels.

Due to the existence of intermolecular interaction forces, the rate of chaotic movement of fatty acids esters molecules is negligible. As the temperature decreases, their association increases rapidly: on the one hand, due to a decrease in the thermal motion of the molecules, which weakens the bonds between them, and on the other hand, due to a decrease in the mobility of the esters molecules that “interconnect” with each other. With a further decrease in temperature, the viscosity becomes so high that the esters solidify and lose their mobility.

The structure of the bio-additive molecules has a certain influence on the pour point. The presence of double bonds in ester molecules makes their shape curved, which makes it difficult to place them tightly together. The results of the study showed that blending jet fuels with bio-additives increases its freezing point (Fig. 7). At a concentration of bio-additives up to 30% (by volume), their effect on the freezing point is relatively insignificant. At low concentrations of bio-additives, they are evenly distributed in the volume of conventional jet fuel and are at distances insufficient for their interaction. With a further increase in the ester content, the solidification temperature increases and gradually approaches the values typical for pure fatty acid esters.

To explain this effect, the works on the analysis of intermolecular interaction and properties of petroleum products [10, 14] were used. As the content of bio-additives in the bio-jet fuel increases above 30%, the content of relatively large ester molecules becomes sufficient for their association: on the one hand, due to the action of physical forces of attraction, and on the other hand, due to the "adhesion" or "engagement" of molecular chains. A special role in the process of "engagement" is played by unsaturated ester of curved shape. Thus, the associated ester molecules initiate the formation of a structure in the system hydrocarbon jet fuel—fatty acid esters.

From Fig. 7 it may be seen that bio-jet fuels with PKO FAEE and CocO FAEE have higher values of the freezing point compared to RO FAME, RO FAEE, and CO FAEE. The reason for such effect may be explained by the differences in structure of fatty acids radicals. From one side PKO FAEE and CocO FAEE are composed of smaller molecules and weaker forces of interaction should appear between them. However, from the other side, both of these bio-additives are composed mostly of saturated non-curved ester molecules (PKO FAEE—about 93% and CocO FAEE—about 87%). Similar to *n*-paraffins in conventional jet fuels short-chain saturated esters turn into crystals at comparatively high temperatures.

5 Conclusions

The analysis of the nature of intermolecular interactions of fatty acid esters, hydrocarbons of conventional jet fuel and their mixtures allowed to state that during compounding (mixing) of hydrocarbon jet fuel and bio-additives based on fatty acid esters o plant oils, a homogeneous system is formed, in which each of the components is ground to the size of molecules. Interaction between the system components occurs under the action of electrostatic forces of intermolecular interaction (van der Waals forces). In this case, chemical interaction between the system components does not occur. Due to this, hydrocarbon jet fuel is mixed with bio-additives in any ratio and unlimitedly. During the process of storage the absence of stratification of the system is ensured, i.e. the aggregative stability of the fuel is ensured.

Differences in chemical structure of hydrocarbon jet fuel and bio-additives and, therefore, intermolecular interactions appearing between them determine properties of bio-jet fuels. Increasing content of bio-additives in bio-jet fuel leads to rise of the dispersion component in the total intermolecular interaction and graduate reduction of internal energy of the system. This has a direct influence on the physical–chemical properties of bio-jet fuels blended with fatty acids esters. Increasing the content of bio-additives results in rising of fuel density, viscosity and freezing point. Bio-additives based on PKO FAEE and CocO FAEE have molecular composition and weigh, which is closer to composition of conventional jet fuel. Therefore, bio-jet fuels blended with these bio-additives possess properties, which are more similar to properties of hydrocarbon jet fuels.

Acknowledgements This work was supported by the Fellowship for excellent researchers threatened by the conflict in Ukraine (Project code: 09I03-03-V01-00060) within the Slovakia's Recovery and resilience plan Funded by the European Union NextGenerationEU.

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