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BIOMASS DERIVED MOTOR FUELS WITH HIGHER COMBUSTION HEAT, ECOLOGICAL AND CHEMMOTOLOGICAL CHARACTERISTICS

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High pour point and low combustion heat were defined as the major disadvantages of biodiesel type motor fuels. We have proposed to add wood biomass derived bicyclic compound hydrocarbon (1S,5S)-6,6-dimethyl-2-ethylenebicyclo [3.1.1] heptane ($C_{10}H_{16}$) into fat acids methyl esters (FAME) type biofuel to improve its performance and ecological qualities. A novel blended 100% biofuel is thus obtained. For a comparision we have studied performance properties of the methyl ester of rape oil (MERO) mixture with mineral diesel fuel. It was determined that the optimal performance characteristics of such fuel mixture is near 30% of MERO. Density, kinematic viscosity, pour point and combustion heat of the blends were investigated: measured, calculated, and analyzed.

Key words: *biofuel, diesel fuel, (1S,5S)-6,6-dimethyl-2-ethylenebicyclo[3.1.1] heptane, fuel blends*

Introduction. The alternative and renewable fuels are widely applied in the developed countries, but this tendency only becomes to spread in the developing states. FAME (fat acids methyl esters) type biodiesel is considered to be most perspective in comparison with the traditional fuels produced from petroleum. Nevertheless this alternative fuel has some disadvantages as: lower value of combustion heat versus diesel and also a higher pour point.

Thus an improvement of FAME type biodiesel characteristics is an actual problem and simultaneously an object of research in chemmotology. Therefore removing of mentioned disadvantages gives an opportunity to use such fuel in a wider range of applications, including air transport .

FAME type biodiesel is one of perspective renewable source of energy, it is produced from vegetable-oil and it usually consists of various esters of fatty acids, especially of fat acids methyl esters (FAME).

Advantages of FAME type biodiesel are reviewed in a great number of publications together with its negative sides [1-6].

Thus benefits of the FAME type fuels application are as following:

- Sulphur free;
- Biodegradable fuel;
- Usage of biomass derived renewable raw material;
- Better lubricating properties that increase the Energy Conversion Efficiency (ECE) of an internal combustion engine and correspondingly its operating time;
- More fire safe because of high value of ignition temperature.

The disadvantages of the biodiesel application are as following:

- Short term of storage (less than three months);
- High pour point;
- Lower values of the combustion heat in comparison with traditional diesel;
- Relatively frequent change of the fuel filters.

Methods of FAME type biodiesel characteristics improvement are investigated and examined not completely.

Our investigation is focused on improvement of alternative fuel (biodiesel) quality by means of a high-energy component adding and analysis of its effectiveness.

For comparison of the results obtained with the common practice we have studied also the blends properties of petroleum derived diesel fuel with the most introduced into practice “biodiesel”. Biodiesel is an environmentally friendly type of biofuels; it is produced from vegetable oil or animal fat and is used to replace petroleum diesel fuel. From a chemical point of view it is a mixture of methyl and / or ethyl esters of long chained fatty acids (saturated and unsaturated).

Biodiesel appears as yellow , moderately viscous liquid that almost does not mix with water, it has a high boiling point and low pressure of saturated vapors. Made from uncontaminated raw materials biodiesel is nontoxic. It has relatively high flash temperature near 150 °C, which makes this fuel relatively fire safe.

Biodiesel is characterized with such parameters as viscosity, density, cetane number, cloud point, pour point, flash point, ash content, sulfur content, acid number.

Our studies have been conducted in order to determine also several performance properties of the fuel mixture of methyl esters of rape oil with mineral diesel fuel in different percentages. It was determined that the optimal performance characteristics posesses the fuel mixture B30. So, on the basis of the experimental data it can be offered a state standard for a mixture consisting of 30% vol. MERO and 70% vol. of petroleum diesel fuel.

Materials and methods of investigation. The aim of work is assessment of biodiesel quality improvement. The object of investigation are blends of traditional biodiesel and biomass derived hydrocarbon in various proportions.

The research was conducted at the Department of Chemistry and Chemical Technology in the National Aviation University. The used sample of the traditional biodiesel met the country adopted standard DSTU 6081:2009.

Preparation of fuel mixture of diesel mineral fuel with biodiesel was conducted in a laboratory by gradual addition of diesel mineral fuel to a definite volume of biodiesel (methyl esters of rape oil MERO) and subsequent stiring during 1 – 2 min. The volumes of fuel were measured with a burette. As a result of mixing were prepared the fuel mixtures B0, B10, B30, B50, B70, B90, B100 . Results are presented in table 1.

Table 1

Preparation of fuel mixtures of biodiesel (MERO) with a petroleum diesel fuel (DF)

MERO,% / DF, %	0	10	30	50	70	90	100
100	B0	-	-	-	-	-	-
90	-	B10	-	-	-	-	-
70	-	-	B30	-	-	-	-
50	-	-	-	B50	-	-	-
30	-	-	-	-	B70	-	-
10	-	-	-	-	-	B90	-
0	-	-	-	-	-	-	B100

The results of research and discussion

Research of biomass derived biofuel blends

A biomass derived bicyclic compound - hydrocarbon (1*S*,5S)-6,6-dimethyl-2-ethylenebicyclo [3.1.1] heptane ($C_{10}H_{16}$) as a high-energy admixture (HEA) was added to biodiesel as a component of the blends. The biodiesel and HEA were mixed in various proportions:

- mixture 1: 2.5 ml of HEA and 47.5 ml of biodiesel;
- mixture 2: 10.0 ml of HEA and 40.0 ml of biodiesel;
- mixture 3: 20.0 ml of HEA and 30.0 ml of biodiesel;
- mixture 4: 30.0 ml of HEA and 20.0 ml of biodiesel;
- mixture 5: 40.0 ml of HEA and 10.0 ml of biodiesel.

We have measured the following quality parameters of the investigated HEA blends: the density, the kinematic viscosity, pour (chilling) point. The combustion heat was calculated according equation (1):

$$\Delta H_r^0 = \sum (n_i \Delta H_{f_i}^0)_{products} - \sum (n_i \Delta H_{f_i}^0)_{reagents}, \quad (1)$$

where H_r^0 – is value of the combustion heat of a chemical reaction under standard conditions, n_i – is the stoichiometric coefficient of reagent in chemical reaction, $H_{f_i}^0$ – is value of the compounds heat formation under standard conditions in kJ/mol.

The density of the investigated mixtures was measured according to the national standard GOST 3900–85 "Petroleum and petroleum products. Methods for determination of density". The density of prepared mixtures was determined using the hydrometer AHT-2.

The kinematic viscosity was determined according to GOST 33–2000 "Petroleum products. Transparent and opaque liquids. Determination of kinematic viscosity and calculation of dynamic viscosity" by viscometers (VPG–2).

The measurements of density and kinematic viscosity were conducted at conditions 20^0C and pressure 101,3 kPa.

The pour point was measured according to the national standard GOST 5066–91 "Motor fuels. Methods for determination of cloud, chilling and freezing points".

Quality assurance is guaranteed through double measurements of three replications. Statistical proceeding of received data was fulfilled with program *Microsoft Excel*.

The density is considered to be an important fuel characteristic as it determines completeness of combustion process. The density rise causes enlargement of fuel drops and decreasing of fuel combustion effectiveness. Thus the higher value of density leads to increasing of fuel consumption. The results of density measurement are presented in fig.1.

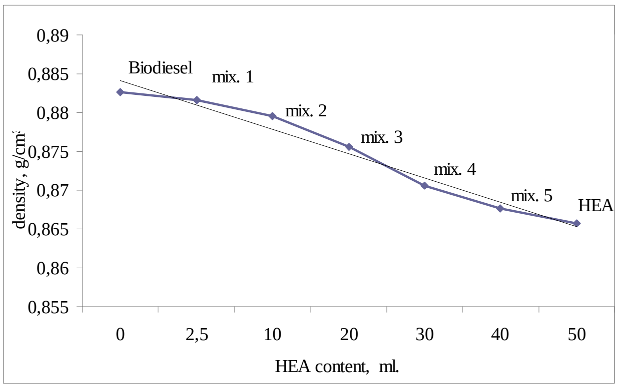

Fig. 1. The density of the investigated mixtures under standard conditions

The results concerning the blends density have shown that its values decrease proportionally to the increase of the HEA content. In comparison: the density of the original biodiesel is 0.883 g cm^{-3} and that of natural bicyclic compound 0.866 g cm^{-3}.

The fuel viscosity also influences combustion process by hindering fuel spraying.

The results of kinematic viscosity measurement are presented in fig. 2.

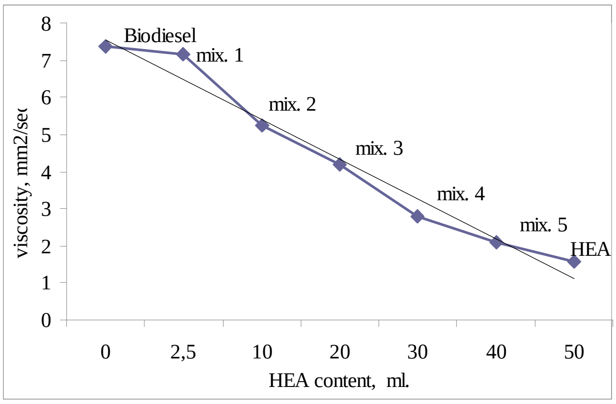

Fig. 2. The kinematic viscosity of the investigated mixtures under standard conditions

The blends kinematic viscosity measurement has shown that it decreases with increasing of HEA part similarly to density. Starting biodiesel has 8.342 mm^2/s and the original hydrocarbon admixture near 1.804 mm^2/s viscosity.

It was observed that increasing of natural bicyclic compound fraction in blends leads to decrease of dynamic viscosity value. The dynamic viscosity of petroleum diesel equals to some 7.363 mPa sec, while the same parameter of pure HEA is only1.562 mPa sec. The results of the dynamic viscosity measurement are presented in fig. 3.

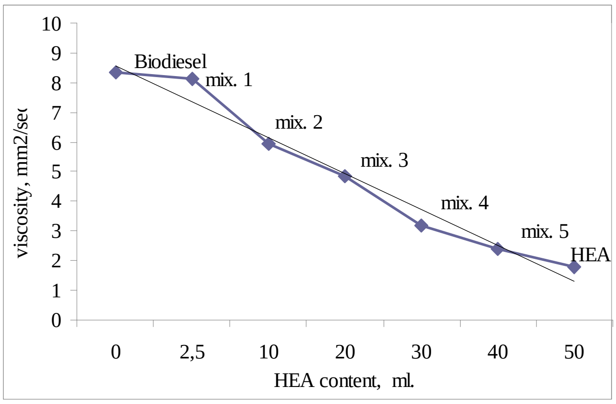

Fig. 3. The dynamic viscosity of the investigated mixtures under standard conditions

The pour point belongs also to the determinant quality characteristics of fuels. The low value of pour point gives an opportunity to apply biodiesel at low temperatures that can lead to its usage in a wider range, particularly in aviation. The results of pour point measurement are presented in fig. 4.

The values of pour point of the investigated mixtures decreased with increasing of HEA content, but in case of mixtures № 2 and № 3 it does not change and is relatively the same. The value of pour point for a starting biodiesel is minus 10 ^{0}C.

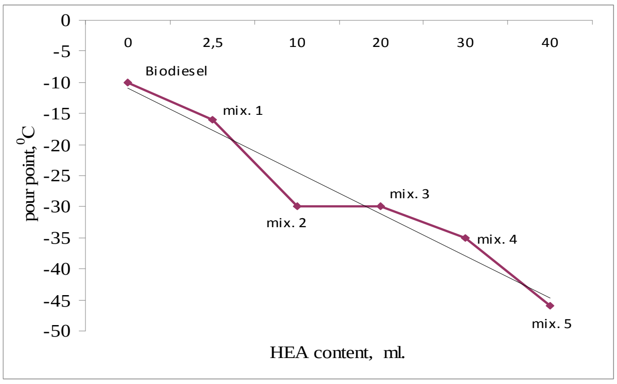

Fig. 4. The pour point of the investigated mixtures

The combustion heat of a fuel is the amount of energy that is released at its combustion (in our case for 1 m^3 of fuel), it corresponds to the useful energy output.

The results of combustion heat calculation are presented in fig. 5.

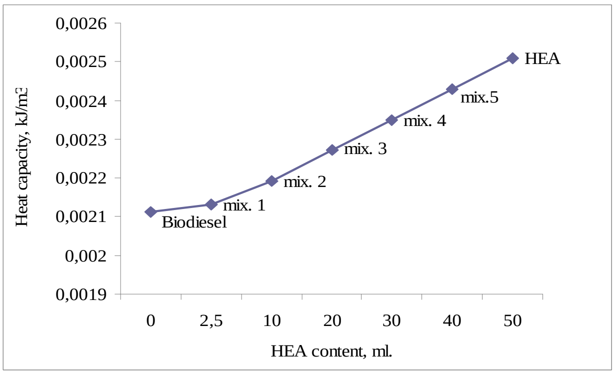

Fig. 5. The combustion heat for the investigated mixtures

Therefore addition of natural bicyclic compound changes the value of the combustion heat: increase of HEA part in blends leads to growth of combustion heat. The combustion heat minimal value for the mixtures is 0,00215 kJ/cm^3, while the used petroleum diesel component had some lower – 0,00210 kJ/cm^3. The maximal calculated value of combustion heat was equal to 0,00245 kJ/cm^3 (mixture № 5).

Research of biomass-petrochemical fuel blends

Measuring of viscosity of the prepared fuel mixtures was made with Ostwald viscosimeter, diameter of capillary tube 0,62 mm. The time of effluence of fuel through the capillary onto viscosity recalculation was carried out according equation, and the passport of viscosimeter:

$$\nu = \frac{g}{980.7} \cdot \tau,$$

ν – Kinematic viscosity, sSt;

τ – time of effluence, s;

g – acceleration, м/s^2.

Experimental data of recalculation the τ onto viscosity are given in tabl. 2.

Table 2

Viscosity of MERO mixtures with a mineral diesel fuel in different ratios for temperature 20 °C

Content of MERO in blend with mineral DF , %	Viscosity m,sSt	Time of effluence of fuel τ, min.
0	3,71 ± 0,15	6,19 ±0,10
10	3,82 ± 0,16	6,3 ±0,11
30	4,51 ±0,11	7,43 ±0,12
50	5,42 ±0,10	9,04 ±0,15
70	6,81 ±0,17	11,37 ±0,16
90	8,52 ±0,12	14,10 ±0,17
100	9,30 ±0,19	15,56 ±0,12

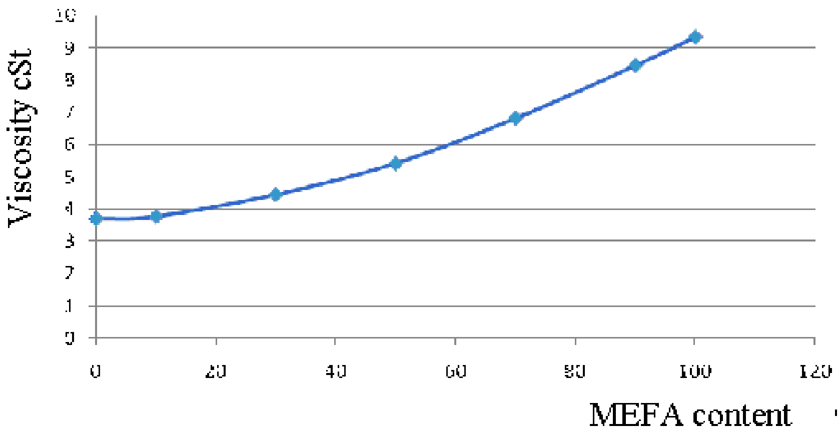

Fig. 6. Viscosity of MERO mixtures with DF at different content of MERO (0, 10, 30, 50, 70, 90, 100 % at.)

The curve of dependence of viscosity of MERO content is shown on fig.6. Linearity was observed starting from B30. Viscosity appropriately grows with the increase of content of biodiesel fuel. Until addition of biodiesel up to 10 %, substantial influence on the change of viscosity was not observed.

Research of density of mixtures B0, B10, B30, B50, B70, B90, B100

Measuring of density was carried out by an areometric method (oil densimeter). The results of experiment are presented in tabl. 3.

Table 3

Dependence of density of mixture of mineral DF with MERO from content of MERO for temperatures 20,5 °C

Content of MEROs in mineral DF, %	Density ρ, g/cm^3
0	0,825 ± 0,025
10	0,830 ± 0,031
30	0,842 ± 0,035
50	0,855 ± 0,025
70	0,867 ± 0,035
90	0,878 ± 0,023
100	0,886 ± 0,033

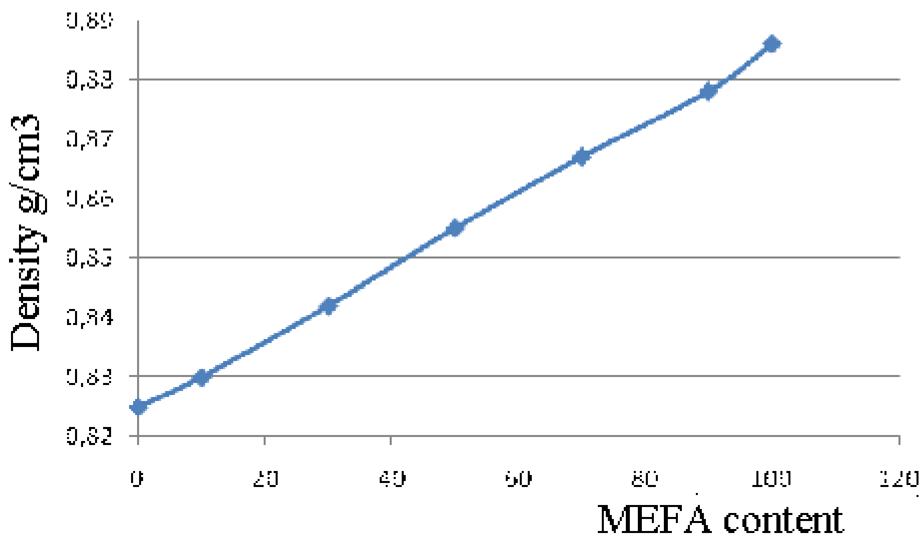

Fig. 7. Dependence of density of mixture of mineral DF with MERO from content of MERO at temperature 20,5 °C

Dependence of density on content MERO in the mineral diesel fuel is shown on Fig. 7. It is linear dependence. Density is an important index in fuel industry.

According density measurement (in relation to fuel mixtures) it is possible to define the percentage of biodiesel fuel in a mineral diesel fuel as by an express-method .

Determination and research of cetane number for fuel mixtures B0-B100

In the given work the cetane number of fuel was determined by an empiric method. There is dependence between density and viscosity of petroleum product and cetane number. This dependence is presented by equation:

$$CN = \frac{(V_{20} + 17{,}8) \cdot 1{,}5879}{\rho_4^{20}}$$

where ρ_4^{20} - relative density of fuel at 20 °C, that is determined experimentally;

ν - kinematic viscosity of diesel fuel at 20 °C, determined experimentally with viscosimeter.

The calculated values of cetane number are presented in table 4. It is seen that at addition of biodiesel fuel MERO it is possible promote the cetane number.

Table 4

Cetane number of fuel mixtures, calculated in relation to ρ and μ

Content of MERO in mineral DF, %	Density ρ, g/cm^3	Viscosity μ, cSt	CN
0	0,825 ±0,005	3,71 ±0,05	41,38 ±0,45
10	0,830 ±0,006	3,83 ±0,06	41,32 ±0,44
30	0,842 ±0,007	4,54 ±0,07	42,05 ±0,42
50	0,855 ±0,015	5,49 ±0,03	43,08 ±0,39
70	0,867 ±0,004	6,81 ±0,04	45,05 ±0,43
90	0,878 ±0,035	8,52 ±0,09	47,56 ±0,42
100	0,886 ±0,025	9,31 ±0,08	48,56 ±0,41

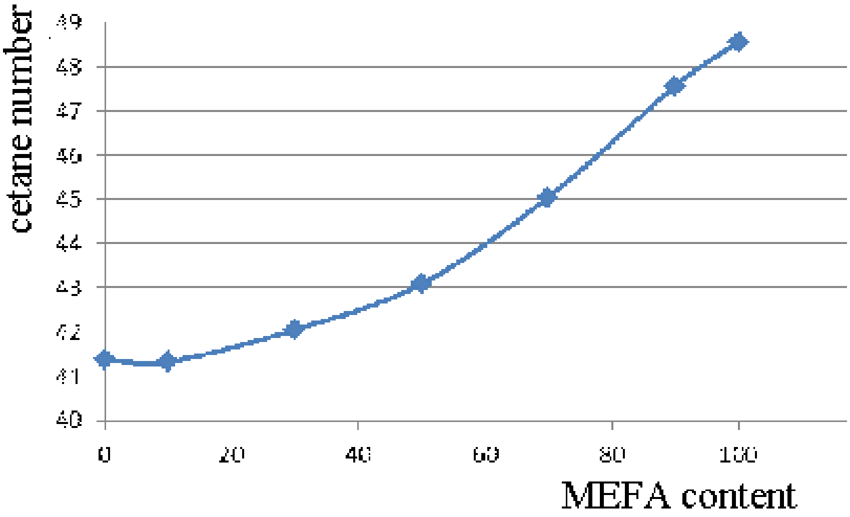

Fig. 8. Growth of cetane number at increase of content of biodiesel in a fuel mixture

From the curves position it is seen, that biodiesel addition in a quantity 10 % does not affect cetane number. The rise of cetane number is observed in mixtures with greater content of biodiesel.

Research of temperature of freezing (pour point) of fuel mixtures

Freezing properties are of major value from the point of view of any fuel user as they determine such vital for an engine chemmotological property as pumpability.

Table 5

Temperature of freezing of MERO mixtures with a mineral diesel fuel at different ratios of components

Content of MERO in mineral DF %	Temperature of freezing (pour point) ^{o}C
0	-15 ±0,90
10	-13 ±0,80
30	-15 ±0,80
50	-15 ±0,75
70	-10 ±0.68
90	-8 ±0,70
100	-8 ±0,81

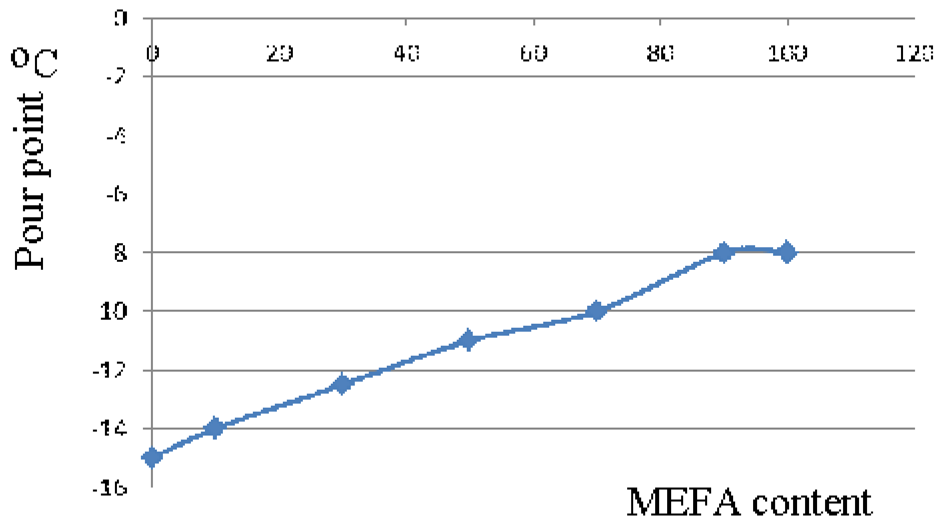

Fig. 9. Temperature of freezing of MERO mixtures with DF at different content of MERO (0, 10, 30, 50, 70, 90, 100 %)

Research of relationship between viscosity and density for the mixtures of DF with MERO at different ratios

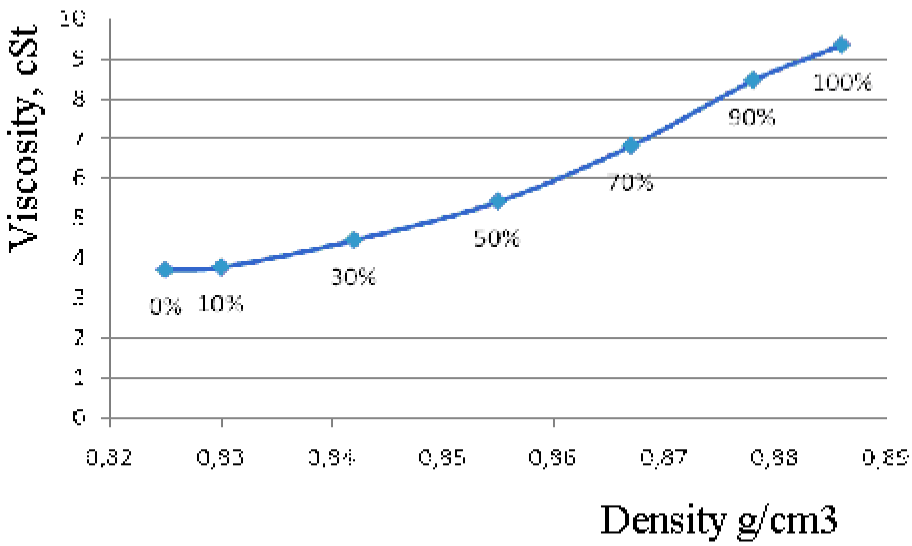

Fig. 10. Relationship between viscosity and density for the mixtures of DF with MERO at different ratios

CONCLUSION

1. The FAME type biodiesel is considered to be a perspective alternative fuel, but it has significant disadvantages which demands removing, among which are low combustion heat and high pour point.

2. Adding the offered natural bicyclic compound has positively influenced FAME type biofuel characteristics: it causes decreasing of density and kinematic viscosity, consequently increasing fuel combustion effectiveness

3. It was found that the value of pour point for a pure petrodiesel equals to minus 10 ^{0}C, while the minimal received value for investigated blends is minus 16 ^{0}C and the best is minus 46 ^{0}C. Thus adding natural bicyclic compound leads to the pour point lowering and widening the offered fuel application range.

4. For investigated HEA/MERO blends was observed increase of combustion heat .

5. Adding the proposed natural bicyclic compound improves the quality of FAME type biofuel and may help to extend its application range onto aviation.

6. As a result of the studies, were characterised changes in parameters such as viscosity, density, cetane number and the freezing point for fuel mixtures B0, of 10, B30, B50, B70, B90, B100

7.Addition of MERO increases viscosity of diesel fuels; but up to 10% it does not affect the viscosity. Linearity is observed starting from 30%.

8. Dependence the density of the fuel mixture on the MERO content in diesel fuels is described by linear equations. The density is growing in the range B0 - B100 biodiesel addititions - With increasing the MERO content cetane number of fuel blends increases.

9. Biodiesel addition up to 10% MERO does not increase the cetane number – its increase was observed for the mixtures B12 - B100.

10. Pour point increases with MERO content in blends. Pour point B90-B100 is in the same range.

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МОТОРНІ ПАЛИВА З БІОМАСИ З ПІДВИЩЕНОЮ ТЕПЛОТОЮ ЗГОРЯННЯ, ЕКОЛОГІЧНИМИ ТА ХИММОТОЛОГИЧНИМИ ХАРАКТЕРИСТИКАМИ

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Високі точки замерзання і низька теплотворна властивість є головними недоліками біопалив типу біодизеля. Ми запропонували додавати природний компонент деревної біомаси – біциклічний вуглеводень (1S,5S)-6,6-диметил-2-этиленбицикло[3.1.1]гептан ($C_{10}H_{16}$) в біопалива типу метилових естерів жирних кислот (МЕЖК) для поліпшення їх эксплуатационных властивостей і екологичних характеристик. Таким чином було отримано 100%-ное сумішеве біопаливо. Для порівняння ми вивчили експлуатаційні властивості сумішей метилового ефіру рапсового масла (МЕРО) з мінеральним дизельним паливом.

Було встановлене що оптимальні концентрації такої суміші палив знаходяться поблизу 30% МЕРО. Нами досліджені, виміряні, розраховани, і проаналізовани густина, кінематична в'язкість, точка замерзання і теплота сгоряння вказаних біопалив.

***Ключові слова**: біопаливо, дизельне паливо, (1S,5S)-6,6-диметил-2-етіленбіцікло [3.1.1] гептан, паливні суміші*

МОТОРНЫЕ ТОПЛИВА ИЗ БИОМАССЫ С ПОВЫШЕННОЙ ТЕПЛОТОЙ СГОРАНИЯ, ЭНЕРГЕТИЧЕСКИМИ, ЭКОЛОГИЧЕСКИМИ И ХИММОТОЛОГИЧЕСКИМИ ХАРАКТЕРИСТИКАМИ

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Высокие точки замерзания и низкая теплотворная способность являются главными недостатками биотоплив типа биодизеля. Мы предложили добавлять природный компонент древесной биомассы – бициклический углеводород (1S,5S)-6,6-диметил-2-этиленбицикло[3.1.1]гептан ($C_{10}H_{16}$) в биотоплива типа МЭЖК для улучшения их эксплуатационных свойств и екологических характеристик. Таким образом было получено смесевое 100%-ное биотопливо. Для сравнения мы изучили эксплуатационные свойства смесей метилового эфира рапсового масла (МЭРО) с минеральным дизельным топливом. Было установлено что оптимальные параметры такой смеси горючих находятся вблизи 30% МЭРО. Нами иссследованы, измерены, расчитаны, и проанализированы плотность, кинематическая вязкость, точка замерзания и теплоемкость указанных смесей биотоплив и их смесей.

***Ключевые слова**: биотопливо, дизельное топливо, (1S, 5S)-6,6-диметил-2-этиленбицикло [3.1.1] гептан, топливные смеси*