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BIODIESEL FUELS BASED ON VEGETABLE OILS: ENVIRONMENTAL SOLUTION IN THE OPERATION OF VEHICLES

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Abstract: The worldwide increasing demand for energy prompts scientists to focusing their research fields at developing sustainable processes for using renewable source of energy. Recently, the depletion of fossil reservoirs become really dramatic for European Countries due to geo-political crises and the high concern for global warming, caused by greenhouse gas emissions from the combustion of
fossil fuels, render the use of waste biomass as energy feedstock very interesting from an economic and environmental point of view. Although the EU banned the production of petrol and diesel automotives by 2035, the employing of biodiesel from waste biomass seems a very interesting alternative, solving problems connected to both fossil depletion and waste disposal.
The purpose of this article is to study the operational and lubricating properties of methyl esters of rapeseed oil, methyl esters of hemp oil, isopropyl esters of rapeseed oil.

Keywords: biodiesel, rapeseed oil, hemp oil, soybean oil, waste cooking oil, methyl esters, ethyl esters, operational properties, lubricating properties.

1. INTRODUCTION

Environmental and sustainability experts agree: The world needs to take quick action on climate change and accelerate our transition to clean energy. And with rising costs and fuel shortages, in part driven by the war in Ukraine, the urgency around securing a reliable, affordable energy source is of the utmost importance to all planet now.
The growth of the world's population and industries has caused the serious demand for energy supply and also the decline in energy reserve, especially in fossil fuel [1]. Owing to this, there is a need to find alternative renewable energy sources such as wind energy, solar energy, geothermal energy, hydro power, and biofuels. Among these, biodiesel from biofuels seems to be the best alternative to compensate diesel as it has almost the same performance as diesel fuel in engines and brings about fewer pollutants compared to fossil fuel. Biodiesel refers to fatty acid methyl esters (FAMEs) or mono-alkyl esters of long-chain fatty acids obtained from vegetable oil and animal fats through transesterification process [2]. Natural oil or fat varies with the chemical composition and structure of fatty acids. As described in ASTM D6751, the properties of biodiesel depend greatly on the various FAMEs [3]. Biodiesel has numerous advantages over petroldiesel, some of which are reduced exhaust emissions [4], better lubricity which is as a result of the capacity of long-chain FAMEs to conform to a firm lubricating layers on metal surfaces [5,6], high flash point, improved biodegradability and reduced toxicity [7] and also can be blended with other biofuels without the inclusion of fossil diesel for GHG benefit [8]. However, the challenge of low oxidation stability (OS) and poor cold flow properties has limited the applications of biodiesel. Low oxidation stability is caused by the presence of polyunsaturated FAME which can produce undesirable aldehydes, ketones, peroxides and acids that alter biodiesel properties. It is reported that oxidation of biodiesel can lead to undesirable saponification and then cause an increase in the total acid number (TAN) and kinematic viscosity [9,10]. As a result, it is difficult to store unsaturated FAMEs for a longer period [11]. As a crucial

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parameter of fuel quality, OS is specified in standards such as ASTM D6751 and the European biodiesel standard EN 14214 [3].
Achievements of the tasks outlined in the article are realized with the use of standard, generally accepted in the oil refining industry, as well as special physical, physicochemical and other methods. Standard methods are based on current national standards (DSTU), harmonized with international (ISO) and European (EN). The basis of experimental studies of performance indicators is based on known standardized techniques using modern devices.

2. RESULTS AND DISCUSSIONS

The Euro 6 environmental standard, which came into force in 2015, provides for a halving of nitrogen dioxide emissions for diesel vehicles produced later than this deadline. One of the methods to solve this problem is to add a certain amount of environmentally friendly bio-components to diesel fuels.
Diesel biofuels have become increasingly widespread abroad in recent years. An increase in diesel fuel production from vegetable raw materials is observed in a number of Western European countries, primarily in Germany and France, as well as in the United States, Brazil, and Malaysia [13]. In European countries, the production of diesel biofuels focuses on the use of rapeseed oil, including from rapeseed grown in Ukraine. In the United States and Brazil, they prefer the production of biodiesel from soybean oil, and in Southeast Asian countries - from palm oil [14]. A mixture of complex methyl esters obtained based on rapeseed oil (MERO) is used as 100% diesel fuel in tractors that are operated in Austria. In France, a mixture of diesel fuel with 5% MERO was used. In the United States, soybean oil-based methyl esters are used as a 100% non-fuel or as a 20% supplement to petroleum fuel. Unfortunately, in Ukraine, this problem is more theoretical in nature in the absence of data on the results of a study of the mass use of bio-components for diesel fuel.
The quality of diesel fuels made from vegetable raw materials differs from oil, which is due to the difference in chemical composition. The methyl and isopropyl esters of rapeseed and soybean oils closest to diesel fuel, and methyl esters based on palm oil differ significantly in their properties [15 16].
Standards for biodiesel mixtures are constantly being revised by ASTM International (American society for testing and materials) for adopting biodiesel mixtures by manufacturers of components for cars (Original Equipment manufacturer – OEM). The EU regulates the requirements for biodiesel EN 14214:2003 «Automotive fuels – Fatty acid methyl esters (FAME) for diesel engines – Requirements and test methods», in the USA – ASTM D 6751 «Standard Specification for Biodiesel Fuel Blend Stock (B100) for middle Distillate Fuels».
The process of obtaining rapeseed oil esters is based on the reaction of transesterification of rapeseed oil with isopropyl or methyl alcohols using an alkaline catalyst – potassium alcoholate. The transesterification reaction consists of adding alcohol to triglyceride in the presence of an alkaline catalyst, and esters and glycerol are formed. The latter practically does not mix with esters.
Transesterification was performed in a glass reactor with the separation of the glycerol fraction from below. The reaction mixture was stirred at a temperature of 60 °C with a glass agitator using an electric motor. The temperature was maintained by a temperature-controlled water bath. At the end of the reaction, the mixture is gravitationally separated into two layers: biodiesel and glycerol, which settles on the bottom of the flask. By chemical composition, the new biodiesel fuel is isopropyl esters of rapeseed oil and is a yellow-lemon-collared liquid with a pungent alcohol smell [17, 18].
At the next stage of the work, the physical and chemical properties of methyl esters of rapeseed oil, methyl esters of hemp oil, isopropyl esters of rapeseed oil were studied. Table 1 shows the characteristics that are most important for oil acid esters and are determined according to standard methods [11, 12].
Table 1 also shows the main features of methyl esters obtained by transesterification reaction in methanol of soybean oil (SO) and domestic waste cooking oil (WCO), which is a promising source of biofuel, solving at the same time problems related to waste disposal of hexausted oils [19].

Table 1. Physico-chemical parameters of esters of vegetable oils

Indicator	ASTM D 6751	EN 14214	Actual data					
			methyl esters of hemp oil	isopropyl ester of rapeseed oil	methyl esters of rapeseed oil	ethyl esters of rapeseed oil	methyl esters of soybean oil	Methyl esters of waste cooking oil
Cetane number, minimum	47	51	44	53	54	50	44	45
Density, g/cm^3 at 15 ºC	0.870-0.900	0.860-0.900	0.872	0.875	0.880	0.881	0.881	0.880
Flash point, ºC	130	120	131	130	131	110	102	-
Pour point, ºC	-15 to -16	-	-15	-22	-12	-14	-6.6	-6.0
Lubricity, m	520	-	430	420	430	425	-	-
Kinematic viscosity at 40 ºC, mm^2/s	2,5-6,0	3,5-5,0	4,31	12,1	5,6	5,5	3.65	3.67

As can be seen from the table, all the properties of biocomponents are slightly different from fuels of petroleum origin. Cetane number is the main indicator of flammability of diesel fuel. It determines the start of the engine, the rigidity of the working process (rate of increase of pressure), fuel consumption and smoky exhaust gases. The higher the cetane number of the fuel, the lower the rate of pressure rise and the less hard the engine runs. As can be seen from the table, the cetane number of rapeseed oil esters is slightly higher than the cetane number of diesel fuel of petroleum origin. On the contrary, the cetane number values of biodiesel coming from SO and WCO sources are lower than the minimum level required, due to the presence of high degree of unsaturation. Viscosity and density determine the processes of evaporation and mixing in diesel. Lower density and viscosity provide better fuel spraying; with the increase of these quality indicators the diameter of the droplets increases and their complete combustion decreases, as a result the specific fuel consumption increases, the smoke of the exhaust gases increases. Samples of biodiesel fuels differ slightly from diesel fuel of petroleum origin in these indicators. They have a higher density at 15 ˚C. This is due to their chemical structure. Unlike hydrocarbons of petroleum fuels, which contain from 5 to 16 carbon atoms, hydrocarbon chains of ester molecules contain an average of 14-26 carbon atoms, This causes greater values of molecular weight and, consequently, higher density. However, the presence of several C=C double bonds in biodiesel has beneficial effects on its density, which would be even higher if the alkyl chain were totally saturated. Also, due to the longer length of the hydrocarbon chain, the viscosity of biocomponents increases compared to the viscosity of petroleum fuels. As the viscosity of the fuel increases, the resistance of the fuel system increases, the filling of the pump decreases, which can lead to interruptions in its operation. As the viscosity of diesel fuel decreases, the amount of oil that seeps between the plunger and the bushing increases compared to operation on a more viscous fuel, resulting in reduced pump performance. Another important property of diesel fuel is the flash point. For diesel engines (especially direct injection) it is very important at what temperature the fuel mixture ignites. Selection of the optimum temperature promotes complete combustion of diesel fuel. If the temperature

is too low (or vice versa), then some components - mostly unsaturated hydrocarbons - do not burn completely, forming on the surface of the cylinders, spark plugs and other elements of the engine soot. In terms of lubricity, a sample of rapeseed oil methyl ester is the best, although wear features of SO FAMEs have been recently investigated [20].

3. CONCLUSIONS

On the basis of the conducted experimental researches, a comparative analysis of indicators of quality of samples of biodiesel of methyl esters of hemp, rapeseed, soybean and waste cooking oil, ethyl esters of rapeseed and hemp oil, isopropyl esters of rapeseed oil and the European requirements to quality of biodiesel fuel is investigated. It is shown that the properties of the samples of the studied biofuels meet the requirements of the standards for biodiesel.

However, research has shown that the set of quality indicators of rapeseed oil ester samples is slightly different from that of petroleum diesel fuel (they have a high cetane number, high density and viscosity, high pour point). With a high viscosity (the highest value of isopropyl esters of rapeseed oil), biodiesel fuels are recommended to be used, including as a lubricant of environmentally friendly origin and appropriate performance properties for use in vehicles.

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