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EFFECT OF DOPING DIESEL OIL WITH METHYL ESTERS ON PHYSICOCHEMICAL PROPERTIES OF THE OBTAINED FUEL, IN THE ASPECT OF ITS EXPLOITATION POTENTIAL

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Abstract

Vision of depletion of fossil fuels and associated with the usage negative impact on the environment, resulted in increased interest in finding alternative sources of materials, which may be used to power internal combustion engines. Usage of biofuels to power diesel engines offers a wide range of benefits for the user and also the environment. Biodiesel interpreted as fatty acid methyl esters obtained from renewable resources by transesterification of fatty acids, can be used as an alternative fuel to petro-diesel, as well as pure fuel or as an additive to diesel. Due to its "renewable" origin and characteristics, such as biodegradability or lower emissions of toxic components in the exhaust gases, biodiesel is a highly attractive alternative to fossil fuels.

Although it is possible to feed CI engines with pure biodiesel, many researchers points lot of, operational and related to combustion processes, problems with usage 100% biodiesel in modern engines, equipped with technologically advanced injection systems. In order to maintain best performance properties, a number of standards have been made. These standards clearly define the parameters that biodiesel must met to be used for powering CI engines.

This paper presents comprehensive analysis of properties of pure biodiesel and its mixtures with diesel in terms of usage to feed modern CI engines. Also procedure of obtaining biodiesel, laboratory equipment and procedures were presented. A number of key parameters (density, viscosity, acid value, cold filter plugging point, oxidation stability, sulphur content and flash point) were examined for pure biodiesel and its mixtures. Tests were performed according to procedures outlined in the PN-EN 14214. Based on the results the utility of biofuels and their mixtures was presumed for use in compression ignition engines.

Keywords: *Fuel, Oils & Lubrication, Exhaust Emission & Ecology*

1. Introduction

The constantly rising number of vehicles powered by combustion engines requires the supply of increasing quantities of fuels used to power them. Unfortunately, this phenomenon contrasts with decreasing mineral fuel resources. The deposits of crude oil, which is a non-renewable energy source, will be depleted sooner or later despite speculations about its abundance. Many researchers are searching for alternative methods of feeding combustion engines to reduce the negative effects of using mineral fuels. For CI engines, the history of usage fuels obtained from renewable raw materials is at least as old as the engine itself. When presenting his invention to the world, Rudolf Diesel originally used peanut oil as the fuel. However, over the course of time, products of mineral origin started to be used to feed such engines. As oil-processing technologies developed, diesel fuel was characterized by improving properties and engine injection systems also became

increasingly advanced. Synergic development of combustion engines and fuels for their powering contributed to improved fuel combustion effectiveness in the engines, causing their increased efficiency and reduced fuel consumption, while decreasing the emissions of harmful substances contained in exhaust gasses. When the spectre of oil resource depletion became real, there was a return to the idea of feeding combustion engines with fuels obtained from renewable materials. Due to the high level of sophistication of the injection systems in modern CI engines and the properties of some raw materials, it is not possible to use renewable materials (vegetable oils, animal fats) in their pure, unprocessed form.

2. Methods of obtaining biofuels

The basic properties disqualifying the application of unprocessed raw materials for feeding CI engines are their high viscosity and low temperature properties (fat of animal origin is usually solid at room temperature). A number of methods have been developed and have been successfully applied to improve these and other parameters of raw fatty material. These measures include thermo-and physicochemical processes aimed at the optimization of fat properties to enable their application in CI engines interchangeably with mineral diesel fuel, without the need for far-reaching injection apparatus modifications. These methods are decomposition under the influence of temperature (pyrolysis), the creation of emulsions, mixtures and transesterification.

– Pyrolysis is a thermochemical process through which liquid and gaseous products, which can serve as fuel, are obtained from biomass.

The process occurs at a temperature of around 200-300°C, in a device called a gasifier [1]. When vegetable oils are pyrolyzed, they thermally decompose to such products as alkanes, alkenes and carboxylic acids. The characteristics of the obtained biofuels are close to diesel fuel. Such biofuel, while retaining a calorific value similar to mineral diesel fuel, does not contain above-standard amounts of sulphur or water, but is characterized by a lower cetane number, contains substantial quantities of solid impurities, has high corrosive properties and unfavourable low temperature properties [2].

– The creation of emulsions is a number of measures aimed at obtaining a homogeneous component mixture, which is in the state of thermodynamic equilibrium and does not separate into phases.

Emulsions are most often created by combining fatty material with alcohols (methanol, hexanol), mineral diesel and compounds improving performance characteristics of obtained emulsion (e.g. the cetane number) [2]. Biofuels thus obtained are characterized by lower viscosity compared to unprocessed fats and when the alcohol used to create the emulsion was obtained from renewable sources, they are valuable ecologically. However, since the alcohol content in fuel for CI engines is not always desirable, despite their advantages, emulsions are not the most widespread method for obtaining biofuels.

– To optimize the properties of vegetable oils with regard to their application as fuels for CI engines, their mixtures with mineral diesel fuel can be used.

Mineral diesel and vegetable oil mix in any proportions forming a homogeneous mixture [3]. Research indicates [4] that mixtures containing under 25% fatty material are characterized by optimal properties in the context of their use as fuel for CI engines. Mixing reduces the viscosity of the biofuels without bearing additional costs for their creation because the method does not require any additional measures or energy inputs. The disadvantages of this method include the use of fuels from non-renewable sources.

– Transesterification – this is the most common method for converting fatty material to biofuel.

Transesterification, the reaction of fat with alcohol in the presence of a catalyst, is widely used both on an industrial scale and by individual producers. The reaction product is commonly called biodiesel. Transesterification owes its popularity to the good quality characteristics of the reaction product, which are close to the properties of currently used mineral diesel. Many types of

conducting transesterification are known and used, which are applied depending on the used fatty material, its quality or the scale of production [5]. Transesterification process is also easy to automation, making the process easy to conduct even by unprofessional personnel [6].
As a result of the reaction, 3 molecules of fatty acid esters and one glycerol molecule are obtained from one triacylglycerol molecule and 3 alcohol molecules.

Since the most popular transesterification reaction (using basic catalysts) proceeds until a state of equilibrium is established in the ratio of the compounds participating in the reaction, an excess of alcohol needed for the reaction is used to attain higher efficiency or the reaction is carried out in stages, collecting the by-product (glycerol) after each of them. Depending on the reaction conditions, total conversion can reach a value of 99%, but the products of intermediate stages can be found in the final product, which is not desirable because of the deteriorated properties of the obtained esters.

A very important property of biodiesel obtained in the transesterification reaction is the possibility of its mixing with mineral fuel or other biodiesel in any proportions. A mixture of mineral diesel and biodiesel is homogeneous and can be successfully used to fuel CI engines. The percentage of individual components should be a compromise between the users' expectations as to the use of renewable materials and the quality of the obtained fuel.

The use of biofuels in a pure form or as mixtures should depend, above all, on product quality because the injection apparatus of modern CI engines is very advanced and the use of low-quality fuel can cause permanent damage to its components or the entire engine. To prevent this, biodiesel used as an autonomous fuel or its mixture with mineral diesel must meet a number of requirements and individual physicochemical properties, which are defined by appropriate standards [7].

The potential use of biodiesel mainly depends on the physical and chemical properties determining its usefulness for feeding CI engines. Biodiesel properties are affected by many factors, from the type of components used for its production, through the method of conducting transesterification process to the storage of the finished product. Pure biodiesel is built of fatty acids with different saturation levels – double bonds between carbon atoms in the molecule and a different content of individual fatty acids in the raw material from which the biodiesel was obtained. In Poland, the most popular raw material for biodiesel production is rapeseed oil; the methyl esters of this oil are sold and admixed to mineral diesel available at gas stations around the country. This results from high rape production [8], uncomplicated transesterification and a suitable percentage of fatty acids in this oil, which results in optimal properties of rapeseed oil esters in applications for feeding CI engines. The authors of this paper have examined the quality of biodiesels obtained from this raw material many times [9-11]. Since it was found based on performed analyses that the prepared mixtures of methyl and ethyl rapeseed oil esters with DF met the requirements of the PN-EN 14214 standard, except for oxidation stability, it is supposed that they would be a suitable fuel for CI engines. For diversification of raw materials used to obtain biodiesel, they undertook the task of obtaining and analysis of the key characteristics of esters obtained from swine lard and methyl alcohol in a transesterification reaction using a basic catalyst. An important aspect of the study is also the fact that the use of swine raw material will enable the management of raw material unfit for food purposes, thus allowing the neutralization of waste from the meat industry. The authors believe that a similar composition of fatty acids in rapeseed oil and swine lard (Tab. 1) will produce biodiesel characterized by good properties for potential use [12].

3. Description of esters production process

Swine lard methyl esters were obtained at the Biofuel Quality Research Laboratory located in the Department of Mechatronics and IT Education of the University of Warmia and Mazury, where the mixtures were also prepared and the key characteristics of the raw materials, the pure esters and their mixtures with mineral diesel were examined.

– Materials and equipment.

The raw materials used in the production of swine lard methyl esters were: edible lard, laboratory-grade purity methyl alcohol and potassium hydroxide with a purity of 85%.

Tab. 1. Comparison of fatty acids in rapeseed oil and swine lard

Material	Fatty acid profile						
	Myristic (Tetradecanoic) C14	Palmitic (Hexadecanoic) C16	Stearic (n-Octadecanoic) C18	Oleic (C18:1)	Linolenic (C18:3)	Linoleic (C18:2)	Any special fatty acid
Rapeseed oil		4.9	1.6	33	7.4	20.4	Erucic 23.0
Lard	1-2	28-30	12-18	40-50	0-1	7-13	

A transesterification reactor built based on a round-bottomed three-neck flask with a capacity of 1000 cm^3 was used during methyl ester production. The flask was placed in a heating device, fitted with magnetic stirrer with the possibility of heating power and stirring speed adjustment. A ball cooler for cooling and returning alcohol vapours to the reaction flask was mounted on the flask; the cooler was continuously cooled by water flowing through it. A certified thermometer indicating the current temperature of the reaction mixture was in the flask during the reaction. The unit is shown schematically in Fig. 1. The transesterification reaction was carried out parallel in two identical units.

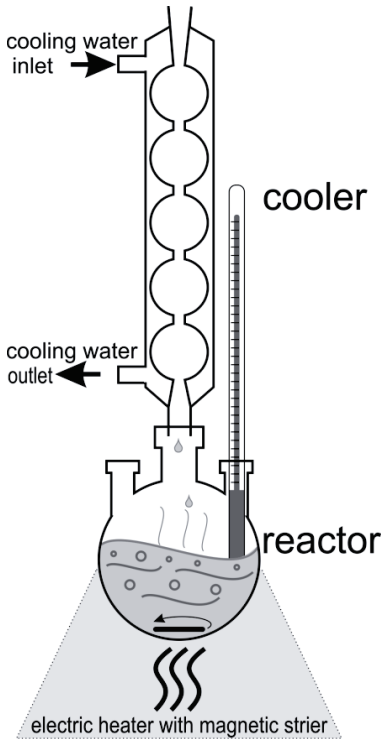

Fig. 1. Experimental set-up used for the transesterification process

A vacuum distillation unit built based on a round-bottomed flask with a capacity of 500 cm^3, placed in a heating jacket with adjusted heating power, was used during the collection of excess alcohol. A distillation column fitted with a water jacket enabled alcohol vapour condensation and the reduction of pressure in the system was possible by using a vacuum pump. The condensed alcohol was collected in a dedicated cylinder. The vacuum control system was additionally fitted

with a pressure gauge indicating the current pressure in the system and a vacuum control valve. Fig. 2 shows a diagram of the excess alcohol collection unit.

A separation funnel was used to separate the glycerol phase from the ester phase. The ester phase was then passed through a car fuel filter through which it flowed freely from the tank placed over the filter to the tank under the filter.

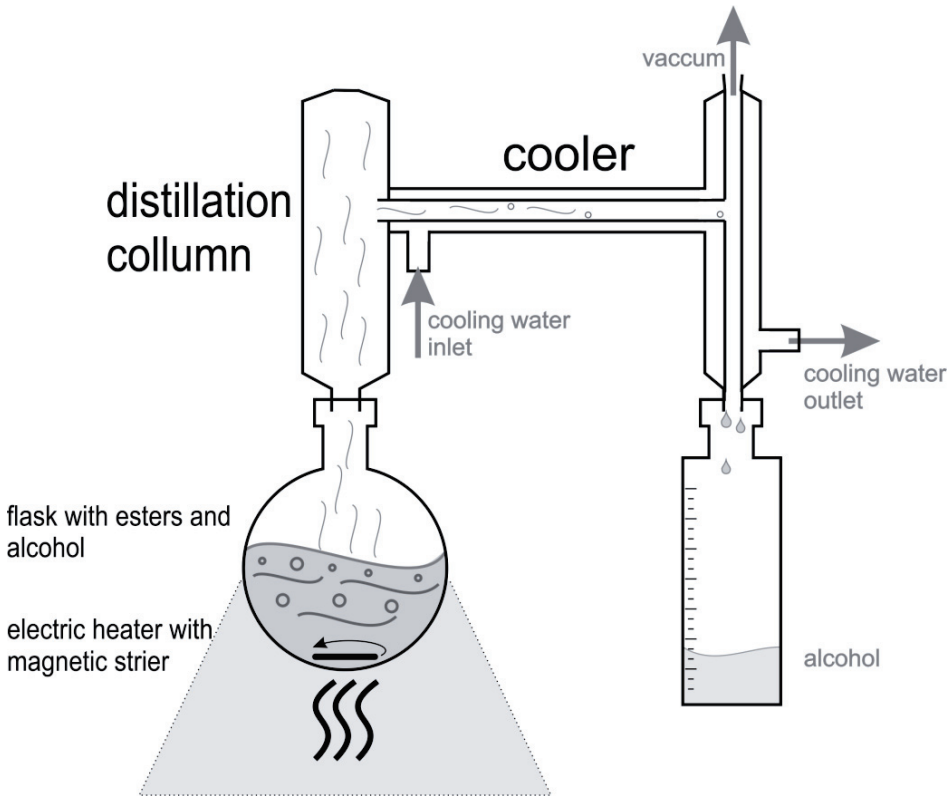

Fig. 2. Experimental set-up used for alcohol removal process

– Procedures

Based on the literature [13] and preliminary research, the authors proposed the following shares of the components participating in the transesterification reaction: fatty material in the amount of ca. 600 g, alcohol in a molar ratio of 6:1 to the fatty material and the catalyst in the amount of 0.9% by weight relative to the weight of the fatty material participating in the reaction. The transesterification reaction was carried out as follows: The fatty material was fed to the flask and then heated to a temperature of 105°C for 10 minutes, to get rid of possible moisture impurities, which could disturb the course of the reaction. After cooling the fat to a temperature of 60°C, the catalysing mixture consisting of the catalyst dissolved in alcohol was added to it. After adding all the components, the temperature of the reactor was maintained at 60°C. Although the change in the mixture's colour (showing that the reaction had occurred) could be observed even after ca. 20 min, the time of conducting the transesterification reaction was set at 60 minutes. Such a long time produced a high degree of component conversion. Starting from the moment that the fatty material dissolved to liquid form, mixing with the magnetic stirrer was continuous, initially of the fat itself, later the reaction mixture. The stirrer was set at the highest attainable revolutions. To produce the amount of the esters necessary for the research, the transesterification reaction was carried out 18 times – 9 times in each reactor, processing ca. 10 kg of pure lard.

The whole obtained post-reaction mixture was subjected to the collection of excess alcohol, used for proper reaction occurrence. To collect the alcohol, the post-reaction mixture was introduced into the flask and then heated to a temperature of ca. 65°C, at which the alcohol collection started. After the formation of alcohol condensate in the cooler was observed, the pressure was gradually

reduced to accelerate alcohol evaporation. The pressure was reduced until the alcohol condensate visible in the distillation column cooler ceased to form.
After the end of alcohol collection, the post-reaction mixture was poured over into the phase separation funnel, in which glycerol was separated from the ester phase. Then the ester phase, at room temperature, was passed through the car fuel filter to remove solid impurities dangerous for the engine's injection apparatus.

The resulting biodiesel based on swine lard was used to create mixtures with mineral diesel. The mixtures were obtained by mixing mineral diesel purchased at a petrol station with swine lard methyl esters in the proportions presented in Tab. 2.

After adding the components to one another, they were thoroughly mixed to make the mixture as homogeneous as possible.

Tab. 2. Volume ratio of mineral diesel (MD) and swine lard methyl esters (SLME) in mixtures

	Content	
	MD	SLME
M1	1	3
M2	1	1
M3	3	1

4. Research methodology and results

The obtained mixtures and the pure esters and mineral diesel fuel were tested to determine the following characteristics: Density (PN-EN ISO 12185), Kinematic viscosity (PN-EN ISO 3104), Flash point (PN-EN ISO 3679), Sulphur content (PN-EN ISO 20884), Total contamination (PN-EN 12662), Oxidation stability (PN-EN 14112), Acid number (PN-EN 14104), Cold filter plug point (PN-EN 116). All the tests were performed according to the procedures described in the PN-EN 14214 standard for esters and mixtures with mineral diesel and in PN-EN 590 for pure mineral diesel fuel. The characteristics were analysed at the Biofuel Quality Research Laboratory belonging to the Department of Mechatronics and IT Education of the University of Warmia and Mazury. Moreover, the acid number was determined for the lard from which the esters were produced to optimize transesterification process. Tab. 3 presents the compiled results of the performed analyses for mineral diesel, esters and their mixtures.

Tab. 3. Characteristics of pure SLME, MD, and their mixtures

Sample	Density at 15°C [kg/m^3]	Viscosity at 40°C [mm^2/s]	Flash point [°C]	Sulphur content [mg/kg]	Total contamination [mg/kg]	Oxidation stability [h]	Acid number [mg KOH/g]	CFPP [°C]
SLME	895.49	4.4528	134	1.44	22.5	1.32	0.14	13
M1	879.79	3.924	80	2.31	17.6	6.64	0.13	8
M2	869.59	3.5937	71	2.74	11.0	8.22	0.10	4
M3	857.09	3.168	63	3.70	8.2	>19	0.10	1
MD	844.49	2.8798	58	4.09	5.0	>19	0.11	-1

The data presented in Tab. 3 show that the obtained esters do not meet only the requirement set by the PN-EN 14112 standard concerning oxidation stability, which should be min. 6 hours.
Objections can also be raised by the cold filter plug point at 13°C for the pure esters, which is a very high value (even when esters are used) in our climate for the summertime. For commercial fuel purchased at a filling station, this temperature was – 1°C.

Such parameters as density and viscosity for the pure ester, though within the normal range, are very high and it is possible that if the esters had not been prepared under laboratory conditions, they might not have met these requirements.

Despite procedures aimed at cleaning impurities from the esters, by sedimentation and filtration, the content of impurities in the pure ester sample was very high, which forces the authors of the paper to seek more efficient methods for the purification of both fatty material and the finished product.

The low sulphur content indicates a lack of inclusion of this element in the fatty raw material used for ester production. The sulphur content in the mixtures gradually rose with an increasing mineral diesel ratio, but it did not exceed the maximum value recommended for the content of this element.

The flash point for the pure esters of 134°C indicates correctly conducted excess alcohol collection process, the flash point decreases with an increasing mineral diesel ratio, for pure mineral diesel it is 58 °C, which is consistent with the PN-EN 590 standard setting out the research methodology and the values of characteristics for mineral diesel.

The very low acid number value, both for pure lard at 0.61 mg KOH/g and for the esters, deserves attention, as this may indicate a low degree of fatty material hydrolysis, because of its high quality. The esters did not undergo thorough purification from catalyst residues after production, which could distort the acid number test result, but because of the low value of this parameter for pure lard, the authors suppose that its value would not have been exceeded for the pure esters, even after allowing for possible distortions of the results caused by catalyst residue in the final product.

5. Conclusions

For the analysis of the use potential of the pure esters and the obtained mixtures, the authors suggest that all the mixtures of the esters with mineral diesel are characterized by optimal values of the analysed characteristics. They all qualify for engine applications and are an interesting subject of study. The used fatty material is an interesting raw material for biodiesel production, diversification of raw materials to obtain a final product and can be an excellent method for the utilization of waste material from the meat industry or the management of raw material unfit for food purposes. Meeting all the characteristics included in the PN-EN 14214 standard by the mixtures suggests that they are the optimal fuel for feeding CI engines. The above-mentioned issues of a high cold-filter plug point, content of impurities or density also give the possibility of further work on the improvement of obtaining esters from this fatty material and post-production measures aimed at improving these characteristics.

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