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DETERMINATION OF OPTIMAL SHARE OF METHYL ESTERS FROM WASTE FATS IN BIOFUELS WITH QUALITY CONSISTENT WITH THE STANDARDS EN 14214 AND EN 590

Summary

As a result of research it was found that substances such as higher fatty acid methyl esters or vegetable oils may be the substitute of diesel. Biofuels may be produced by using all fats, irrespective of their origin, both vegetable oils and animal fats. The objective of the study was to optimise the share of diesel in biofuels from animal fats and used-cooking oil to ensure that the viscosity of the mixture obtained in all the cases complies with the standards EN 14214 and EN 590. The materials used in the research were fatty acid methyl esters deriving from animal fats (AF), used cooking oil (UCO) and diesel (ON). The scope of research included the measurement of the density of fatty acid methyl esters with an aerometric method and the measurement of the dynamic viscosity of mixtures of diesel and fatty acid methyl esters in six aspect ratios: 5%, 10%, 15%, 20%, 25%, and 30%. The research shows that diesel is only a dilution of biofuels and the optimal share of diesel in biofuels deriving from animal fats and used cooking oil equals to 68%, where the kinematic viscosity complies with the standard EN 14214, while the maximum share of biofuels in diesel, where the kinematic viscosity is consistent with the standard EN 590, equals to 72%.
***Key words**: biofuels, fatty acid esters, dynamic viscosity, kinematic viscosity, waste fats*

OKREŚLENIE OPTYMALNEGO UDZIAŁU ESTRÓW METYLOWYCH Z TŁUSZCZÓW ODPADOWYCH W BIOPALIWACH O JAKOŚCI ZGODNEJ Z NORMĄ EN 14214 I EN 590

Streszczenie

W wyniku realizowanych prac badawczych stwierdzono, że substytutem oleju napędowego mogą być takie substancje, jak estry metylowe wyższych kwasów tłuszczowych, a także oleje roślinne. Do produkcji biopaliw mogą być wykorzystywane wszystkie tłuszcze, niezależnie od ich pochodzenia, zarówno oleje roślinne, jak i tłuszcze zwierzęce. Celem pracy była optymalizacja udziału oleju napędowego w biopaliwach z tłuszczów zwierzęcych i oleju posmażalniczego tak, aby lepkość otrzymanej mieszaniny we wszystkich przypadkach była zgodna z normą EN 14214 i EN 590. Materiałem użytym do badań były estry metylowe kwasów tłuszczowych z tłuszczów zwierzęcych (AF) i oleju posmażalniczego (UCO) oraz olej napędowy (ON). Zakres badań obejmował pomiar gęstości ρ estrów metylowych kwasów tłuszczowych metodą areometryczną oraz pomiar lepkości dynamicznej η mieszanin oleju napędowego z estrami metylowymi kwasów tłuszczowych w sześciu proporcjach: 5, 10, 15, 20, 25, 30%. Na podstawie wykonanych badań stwierdzono, że olej napędowy jest wyłącznie rozcieńczalnikiem biopaliw, a optymalny udział oleju napędowego w biopaliwach z tłuszczów zwierzęcych i olejów posmażalniczych, dla których lepkość kinematyczna jest zgodna z normą EN 14214 wynosi 68%, natomiast maksymalny udział oleju napędowego w biopaliwach spełniających wymagania normy EN 590 odnośnie lepkości wynosi 72%.
***Słowa kluczowe**: biopaliwa, estry kwasów tłuszczowych, lepkość dynamiczna, lepkość kinematyczna, tłuszcze odpadowe*

1. Introduction

As a result, economic development has increased the demand for electricity and thermal energy, which contributed to the development of renewable energy sources (RES) such as solar energy, wind energy, and biomass energy. The biomass can be used directly in combustion, as a substitute for biogas plants and for the production of biofuels [9, 21]. Research upon non-conventional fuels that might become an alternative for diesel is currently conducted. Diesel may be substituted by such liquid fuels as fatty acid methyl esters (FAME) and vegetable oils. However, due to legal restrictions in the Polish market only FAME is used as biocomponents of conventional fuels.

For the production of biofuels all fats may be used, irrespective of their origin, both vegetable oils and animal fats [13].

Vegetable oils may be produced from various raw materials. The most popular vegetable oils that may be used to produce bio-diesel are: rapeseed oil, sunflower oil, soybean oil, palm oil [5, 19] and oils from seeds: *Swietenia mahagoni*, *Pistacia chinensis*, or *Jatropha curcas* L. [6, 12, 14, 22] and oils from oil plants, e.g. *Camelina sativa L.* [20]. After being previously used for food purposes those oils may also be used as, e.g. used cooking oils [5, 15]. For biodiesel production the most frequently used animal fats are animal tallow or waste materials deriving from animal raw material processing [10, 19]. The non-conventional research upon production of bio-diesel from esters obtained from wet coffee grounds was also successful [15].

Due to the high viscosity of waste fats that adversely affects the engine operation, they are subject to the transesterification reaction with simple monohydroxy alcohols, most frequently methanol or ethanol. The efficiency of the esterification process is affected by a kind of the applied alcohol, the nature and concentration of the applied catalyst, and the process conditions (temperature, pressure and mixing intensity) [4].

There are several chemical methods of obtaining biofuels from waste fats. Those methods vary from one another, among others, in terms of a kind of catalyst used in the reaction.

Homogenous catalysts used in the transesterification reaction may be both alkaline and acidic. Among others, H_2SO_4 is the most frequently used acidic catalyst, but due to the high corrosiveness of apparatuses, alkaline catalysts are more frequently used in the industry. Among them, homogeneous catalysts such as NaOH or KOH are the most popular. The research was also conducted with the use of other compounds such as $KOCH_3$, CaFeAl and Sr/ZrO_2 [16, 19]. The reaction with the alkaline catalyst takes place at 60-70°C. By using homogeneous catalysts, it is possible to acquire a highly purified product but the process may only be conducted periodically without the possibility of conducting the continuous production. The transesterification reaction may be conducted by means of homogeneous catalysts. In this reaction CaO is the most frequently used homogeneous catalyst. The reaction takes place at 180-220°C. The particular advantage of this process consists in the possibility of conducting the process on a continuous basis but due to its high costs it is seldom used in the industry [7].

The transesterification reaction may also be carried out with enzyme catalysts such as: *Candidia antarctica*, *Candidia rugosa*, *Mucor meihei* (Lipozyme-IM), *Cryptococcus* sp., *Trichosporon asahii*, *Yarrowia lipolytica* [1, 2, 3,18].
Another conversion methods use reactions in which foreign matter-based catalysts are not applied. In supercritical conditions alcohol is the catalyst and the reaction takes place at 239-385°C and at 10MPa [7].

Since vegetable oils and animal fats adversely affect the engine operation (injection, pumping and spraying fuel in the engine), some actions are taken to decrease the viscosity values of those substances [17]. There are several effective methods of changing viscosity values of fuels: mixing with diesel, pyrolysis, micro-emulsification and transesterification [10].

In the transesterification process the key result is the reduced weight of vegetable oil particles and, consequently, the reduced viscosity of biofuel. Whereas, during the pyrolysis (cracking) reaction chemical bonds are divided to create smaller particles. Those processes may be conducted with the use of vegetable oils, animal fats and used oils [8, 17, 18].
Another method used to reduce the kinetic viscosity of vegetable oils is to create biofuels through mixing diesel with alcohols with a small molecular mass. Alcohols like methanol are characterised by limited solubility in vegetable oils, hence in order to increase their solubility an amphiphilic compound is added to dilute the oil and to reduce its kinetic viscosity. Hybrid diesel may also be produced by using a co-solvent to solve the mixture. A series of variants of those solutions were employed to create hybrid diesel, among others, through mixing a micro-emulsion or a co-solvent mix with diesel. The research upon emulsification of animal fats and vegetable oils has proven that the viscosity of biofuels may be reduced in this way [10, 11].

The mixture of vegetable oil and diesel is the easiest way to change the viscosity value of biofuels and to obtain stable mixtures of various proportions. So far, there have been a lot of research upon the viscosity of mixtures of vegetable oil (e.g. safflower oil and sunflower oil) and diesel with various content of the vegetable oil in the mixture with diesel. However, the research results are not unambiguous [10, 17].

The objective of the study was, therefore, to optimise the share of diesel in biofuels from animal fats and used cooking oil to ensure that the viscosity of the mixture obtained in all the cases complies with the standards EN 14214 and EN 590.

2. Methodology

The objective of the study was to determine the impact of the diesel additive on the viscosity of fatty acid methyl esters of used cooking oil (UCO) and animal fat (AF) for six mixtures containing: 5, 10, 15, 20, 25, 30% of diesel.

The first research stage consisted in the measurement of the density of diesel and fatty acid methyl esters with an aerometric method at a temperature of 20°C and the measurement of the viscosity of diesel and methyl esters and of each of six mixtures. The viscosity tests were conducted with the RC1 rotational viscosity meter with the measurement system MS-CC48, the Lauda thermometer RE 206, and the software Rheo 3000.

During the tests an appropriate volume of diesel was entered into the measurement cylinder and the test apparatus was set up. Subsequently, when the temperature in the entire measurement system stabilised at 40°C ± 1°C, values of the last fifty measurement points were recorded and methyl esters were injected. The measurement points were recorded at equal intervals of 5.1 seconds. Then, methyl esters were injected each time after recording two hundred measurement points. Consequently, there were obtained the measurements for six mixtures of diesel and methyl esters: 5, 10, 15, 20, 25 and 30%. This procedure was carried out for 21 samples of various methyl esters.

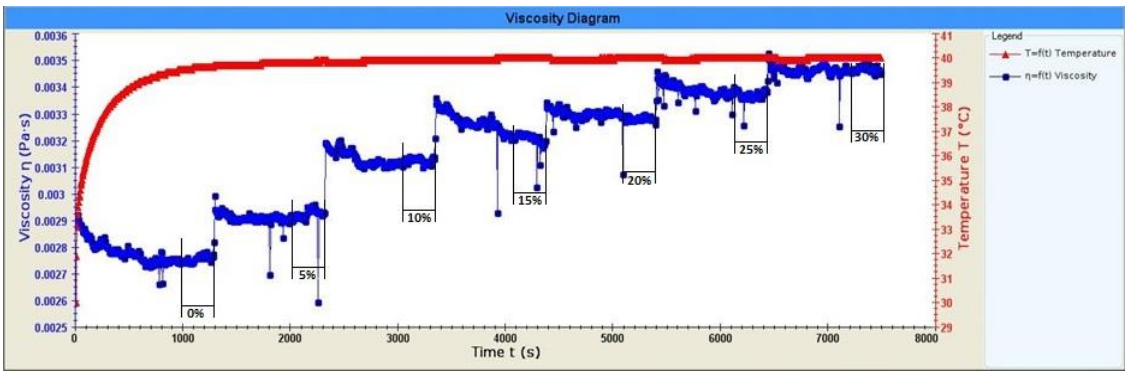

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Fig. 1. Distribution of measurement points of the exemplary measurement
Rys. 1. Rozkład punktów pomiarowych przykładowego pomiaru

The recorded results were used to determine an arithmetical mean, a standard deviation and a coefficient of dynamic viscosity value changeability for diesel and for each of six mixtures of diesel and methyl esters.

The next stage aimed at the determination of the density ρ and kinematic density η_k for each of six mixtures of diesel and methyl esters on the basis of density of both substances according to the following formula:

$$\rho = a \cdot \rho_{ON} + b \cdot \rho_{EM} \quad (1)$$

Where:

ρ – mixture density [kg·m^{-3}],
a – share of diesel in mixture [%],
b – share of fatty acid methyl esters in mixture [%],
ρ_{ON} – density of diesel [kg·m^{-3}],
ρ_{EM} – density of fatty acid methyl ester [kg·m^{-3}].
The density of diesel at 40°C is 810 kg·m^{-3}.

$$\eta_k = \frac{\eta}{\rho} \quad (2)$$

Where:

η_k – kinematic viscosity [mm^2·s^{-1}],
η – dynamic viscosity [Ps·s],
ρ – density [kg·m^{-3}].

The next stage was to determine the minimum and maximum function describing the distribution of viscosity with respect to the share of diesel in methyl esters. The distribution of the function describing the dependency between the kinematic viscosity and the mixture composition is linear as diesel is only a dilution of methyl esters.

3. Results

For the entire group of the tested samples of methyl esters the analysis of the single-factor variation was conducted. The analysis has proven that statistically, at the 5% confidence interval, the test source is irrelevant. It has also been found that any further analyses might be conducted jointly for all the biofuels, irrespective of their origin (Fig. 2).

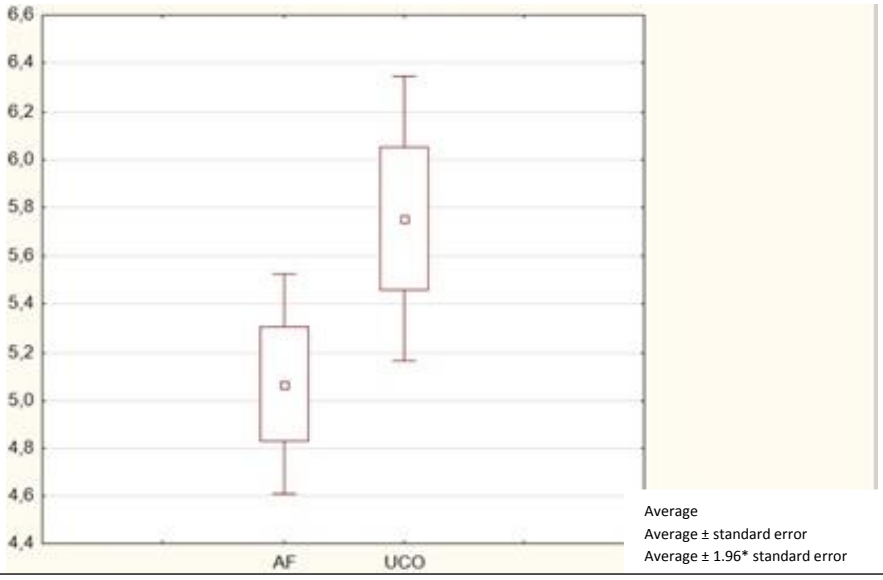
Table 1. Viscosity of biofuels with AF and UCO at 40°C
Tab. 1. Lepkość biopaliw z AF i UCO w temperaturze 40°C

Test number	Type of fat	Viscosity [mm^2·s^{-1}]	Test number	Type of fat	Viscosity [mm^2·s^{-1}]
1	UCO	5.0820	12	UCO	5.6597
2	UCO	5.3123	13	AF	5.8391
3	UCO	5.3512	14	AF	5.0002
4	UCO	5.1878	15	AF	4.7570
5	UCO	5.6658	16	AF	5.0745
6	UCO	7.3555	17	AF	5.1618
7	UCO	5.9713	18	AF	6.5757
8	UCO	5.0897	19	AF	5.1361
9	UCO	7.5689	20	AF	4.6847
10	UCO	4.9621	21	AF	4.6321
11	UCO	5.1984			

Source: own work / Źródło: opracowanie własne

The diagram of the maximum function and the minimum kinematic viscosity limited by the standard EN 14214 has the maximum value of 5 mm^{2}s^{-1} for 79% share of diesel in methyl esters and the minimum value of 3.5 mm^{2}s^{-1} for 56% share of diesel in methyl esters. The optimal share of diesel in methyl esters equals to 68%. In all the cases the matching of trend lines to experimental data was very good, which is proven by the obtained values of the determination coefficient $R^2 \geq 0.99$ (Fig. 3).

The diagram of the function of the maximum and minimum kinematic viscosity according to the standard EN590, i.e. 4.5 mm^{2}s^{-1}, shows the maximum value of the share of diesel in methyl esters, which is 70% (Fig. 4).



T test for dependent tests (Weronika Gracz)
Marked differences are significant with p < 0.05000

Variable	Average	Standard deviation	Significant	Difference	Standard deviation Difference	T	Df	p
AF	5.066036	0.740072						
UCO	5.754663	0.949348	10	-0.688627	1.177539	-1.84931	9	0.097458

ource: own work / Źródło: opracowanie własne

Fig. 2. Analysis of dependency of viscosity of biofuels with AF and UCO
Rys. 2. Analiza zależności lepkości biopaliw z AF i UCO

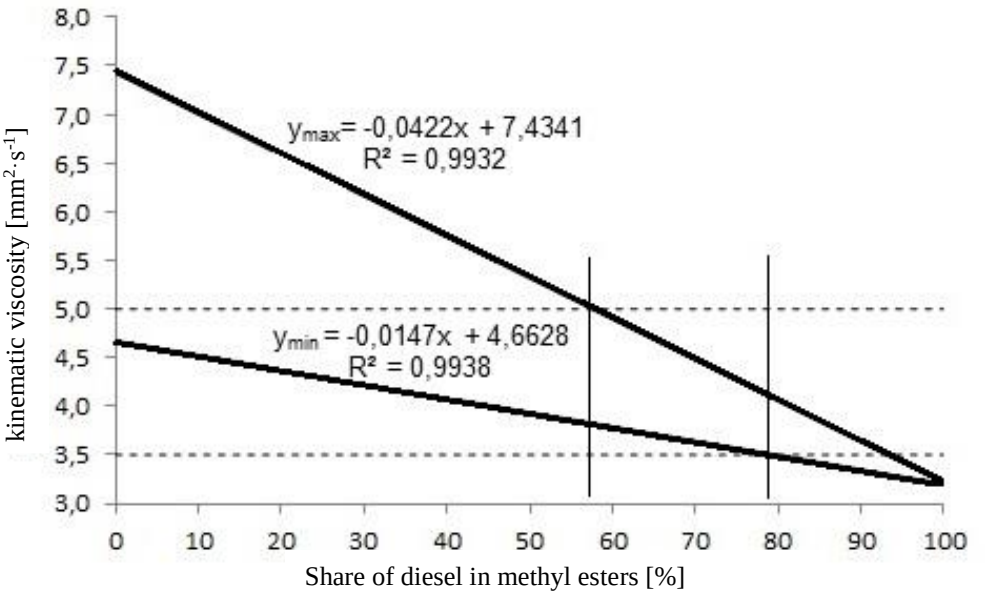


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Fig. 3. Graphic presentation of maximum and minimum kinematic viscosity of mixtures of Diesel fuel and methyl esters according to the standard EN 14214
Rys. 3. Graficzne przestawienie maksymalnych i minimalnych lepkości kinematycznych mieszanin ON z EM zgodnych z normą EN 14214

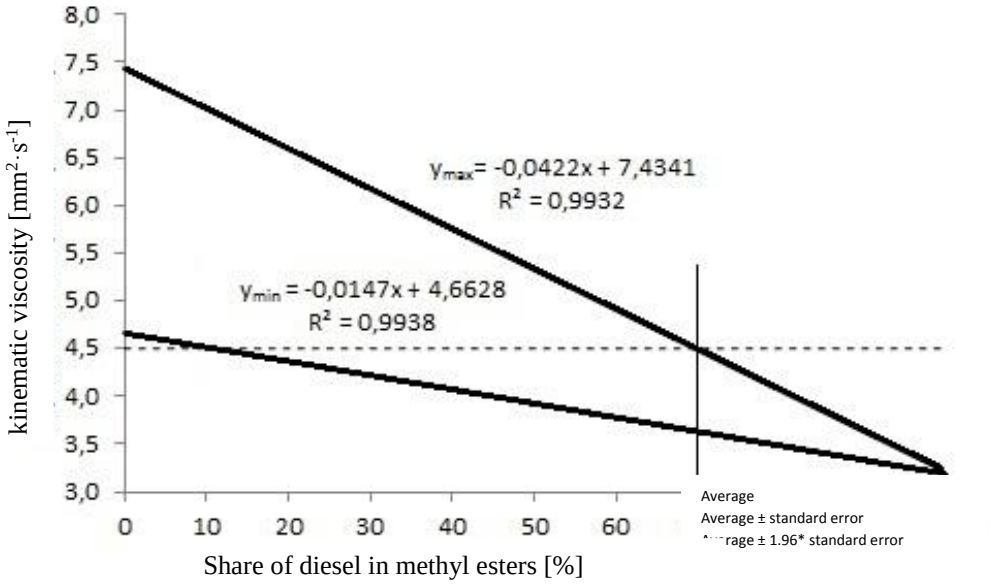

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Fig. 4**.** Graphic presentation of maximum and minimum kinematic viscosity of mixtures of Diesel fuel and methyl esters according to the standard EN 590
Rys. 4. Graficzne przestawienie maksymalnych i minimalnych lepkości kinematycznych mieszanin ON z EM zgodnych z normą EN 590

4. Conclusions

In order to obtain the mixtures of methyl esters and diesel according to the requirements of the standard EN 14214 with respect to their kinematic viscosity, the optimal solution is to apply additives of biofuels from animal fats and used cooking oils at 32%.

Similarly, to obtain the mixtures of methyl esters and diesel according to the requirements of the standard EN 590, it is required to apply the share of biofuels from animal fats and used cooking oils not exceeding 30% of the mixture volume.

Notwithstanding the origin of fats used to produce biofuels (used cooking oils / animal fats), the kinematic viscosity of the obtained esters measured at a temperature of 40°C does not show any significant differences.

Diesel is only a dilution of biofuels. The distribution of the function describing the dependency between the kinematic viscosity and the mixture composition is linear and for all the analysed cases the determination coefficient equals to $R^2 \geq 0.99$.

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