

THE PROPERTIES OF MIXTURES OF FAEE, DIESEL AND ETHANOL USED TO POWER COMPRESSION IGNITION ENGINES

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Abstract

Due to the continuous increase in prices of conventional fuels, the production of biofuels on an industrial, as well as small scale, nowadays is becoming more economically efficient. However, the usage of biofuels in its pure form is a problem when one have to supply them with modern injection systems. Due to the difference in parameters of biofuels in comparison with conventional fuels, the attempt to develop a mixture of optimal parameters for use in diesel engines, equipped with modern injection system, was made. Fuels derived from substrates which are produced independently of food production and which can energize CI engines are occupying now stronger market positions. Easier access to know-how and an uncomplicated production process result in technological development, not only in mass-scale plants but also in smaller devices which meet the needs of individual users or in which residues of other processes are neutralized or reused. 13 samples were tested, mixed of diesel, FAEE and ethyl alcohol. The mixtures were prepared and tested in The Department of Mechatronics in University of Warmia and Mazury for the most important parameters in the evaluation of possibility of usage to power modern compression ignition engines.

Keywords: *biodiesel, combustion engines, air pollution, biofuels examination, biofuel mixtures, ethyl esters*

1. Introduction

Nowadays, a lot of campaigns are aimed at protecting the natural environment as well as limiting human influence on the atmosphere, which in consequence leads to using renewable fuels, which do not increase atmospheric levels of carbon dioxide, a compound which is considered to be the main factor causing climate changes on Earth. Fuels derived from substrates which are produced independently of food production and which can energize CI engines are occupying now stronger market positions. Easier access to know-how and an uncomplicated production process result in technological development, not only in mass-scale plants but also in smaller devices which meet the needs of individual users or in which residues of other processes are neutralized or reused. Moreover, production and use of biofuels bring about economic results, such as providing markets for agricultural produce which does not meet standards set for edible products. More workplaces are created in order to design, develop and produce the necessary technological infrastructure as well as fuels themselves. The market offering ready-made plants to produce biodiesel on home scale is also developing rapidly, which leads to an increase in the competitive

value of biofuels as compared with conventional fuels. With price fluctuations of conventional fuels, and high likelihood of their depletion in the near future, the applicability of renewable fuels is far more likely to broaden. Yet, applying pure biofuels is associated with a number of limitations. It is known what effect biofuels have on materials which are used to cast injection elements of CI engine systems [1]. Also, carbon fouling and carbonization of injectors are said to occur in engines energized by biofuels [2]. What is more, some of their properties disqualify them from applying in our climate without using special additives or processing which aims at modifying their primary properties. These properties include the CFPP (determined according to the procedure [3]), which is 10°C for pure methyl esters [4]. When ethyl alcohol is used in the production process of esters, it improves low-temperature properties of the derived biofuel [5, 6].

Taking into consideration the above arguments, it is a potentially good idea to apply mixtures of conventional fuels and products of transesterification of lipids in order to fuel vehicles equipped with CI engines or in stationary plants with such engines. At present, the EU law enforces the use of mixtures of conventional fuels and biofuels with 7% of the latter.

The authors of this study have attempted to compare nine important parameters of mixtures composed of conventional fuels and bioadditives in order to choose a mixture of optimal parameters to be used to fuel CI engines. The standard diesel oil available at Orlen petrol stations (EKODIESEL) was used as a conventional fuel, while biocomponents were represented by fatty acids ethyl esters of rapeseed oil and fatty acids ethyl esters of animal fat (swine fat). Every mixture was enriched with highly dehydrated ethyl alcohol.

2. Ethyl esters of rapeseed oil and swine fat – a description of the plant and production process

Rapeseed esters and swine fat esters produced in the Field Esterification Plant, which is part of the equipment of the Chair of Mechatronics and Technical-IT Education at the University of Warmia and Mazury. The plant, whose properties and operation were shown in [6-8], is schematically presented in Fig. 1. In the process of transesterification the following were used:

- to produce rapeseed ethyl esters: 37.5 dm³ oil, 30 dm³ alcohol, 393.75 g potassium hydroxide as an alkaline catalyst solved in alcohol. The process was performed twice in order to maximize reaction efficiency and retrieve as much extra alcohol as possible from the alcohol added to conduct the reaction well,
- to produce swine fat ethyl esters: 24 dm³ swine fat, 24 dm³ alcohol, 285 g potassium hydroxide. The process was performed once due to an innovative modification of the software which controlled the plant. Thus the time of reaction was lengthened and the alcohol evaporation process was modified so that it was not turbulent. Thanks to the modification the derived ester fraction did not contain considerable amounts of alcohol, hence the process of transesterification did not have to be performed twice and alcohol did not have to be evaporated.

3. Physical and chemical determinations of rapeseed esters and swine fat esters

The produced rapeseed esters and swine fat esters were characterized with reference to the basic qualitative properties, i.e. density at 15°C, kinematic viscosity at 40°C, water content, sulfur content, contamination level, and acid value. These determinations were performed according to the standards which present appropriate procedures of such determinations.

4. Preparation of mixtures derived from rapeseed esters and swine fat esters and methods of their analysis

Taking into consideration results for both rapeseed as well as swine fat esters which were produced (Tab. 1), 12 mixtures were composed and they contained such biocomponents as: rapeseed oil esters, swine fat esters and 99.95% ethyl alcohol. Appropriate amounts of these

components were mixed with diesel oil which was bought at a petrol station and analysed with reference to its density, kinematic viscosity, and the content of water, sulphur and contaminations (Tab. 1).

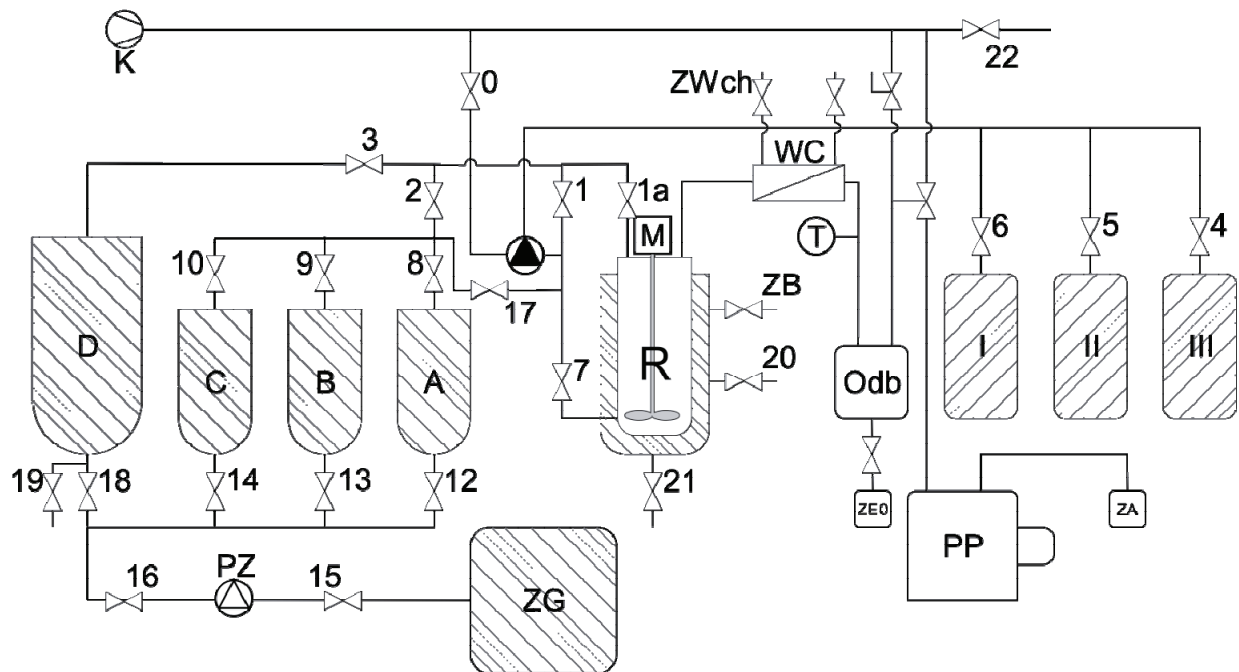


Fig. 1. System diagram. R – reactor, I – catalytic mixture tank, II – ethanol tank, III – oil tank, A, B, C – post-reaction mixture separators, D – 24-hour tank, K – compressor, M – electric engine, Odb – ethanol receiver, PP – vacuum pump, PT – Tapflo pump, PZ – gear pump, T – thermometer, WC – heat exchanger, ZA – alcohol tank, ZB – safety valve, ZE0 – ethanol tank, ZWch – cooling water tank, 1, 2, 3 – four-terminal network valves, 1a – reactor valve, 4, 5, 6 – reactor tank valves, 7 – reactor valve, 8, 9, 10 – separator inlet valves, 11 – ethanol receiver valve, 12, 13, 14 – glycerol separator outlet valve, 15, 16 – glycerol gear pump valve, 17 – tank filling valve, 18 – glycerol draining from the D tank valve, 19 – D tank draining valve, 20 – reactor coat filling valve, 21 – coat draining valve, 22 – compressed air valve

Tab. 1. Parameters of diesel oil

Parameter	ON
Density at 15°C [g/ cm ³]	0.826
Kinematic viscosity at. 40°C [mm ² /s]	2.64
Water content [mg/kg]	20.0
Sulphur content [mg/kg]	5.9
Total contamination [mg/kg]	5.0

The qualitative choice of components for all the mixtures was made on the basis of the expertise of the authors and empirical studies of samples of particular components.

The mixtures were prepared and analyzed in the Biofuels Quality Laboratory in the Chair of Mechatronics and Technical-IT Education at the University of Warmia and Mazury. The composition of the analysed mixtures was presented in Tab. 2.

The mixtures were characterized with reference to their: kinematic viscosity at 40°C (PN-EN ISO 3104), sufur content (PN-EN ISO 20884), water content (PN-EN ISO 12937), density at 15°C (PN-EN ISO 12185), acid value (PN-EN 14104), oxidation stability at 110°C (PN-EN 14112), flash point (PN-EN ISO 3679), CFPP (PN-EN 116), solid contamination content (PN-EN 12662).

Tab. 2. The composition of the produced mixtures

Sample	Diesel [g]	REE [g]	SFEE [g]	Ethyl alcohol [g]
M ₁	742	158	0	100
M ₂	530	370	0	100
M ₃	212	688	0	100
M ₄	106	794	0	100
M ₅	742	0	158	100
M ₆	530	0	370	100
M ₇	212	0	688	100
M ₈	106	0	794	100
M ₉	0	500	400	100
M ₁₀	0	200	700	100
M ₁₁	0	900	0	100
M ₁₂	0	0	900	100
M ₁₃	0	100	800	100
M ₁₄	530	185	185	100

5. Statistical analysis

The results of the studies were analyzed statistically with the use of Statistica 9.0 PL (StatSoft Poland). One-way analysis of variance (ANOVA) with Tukey's test (at $p=0.05$) were used to show the significance of differences between the samples of oils.

6. Results

The results of the studies pointed to significant variation of the determinations analyzed for the produced rapeseed esters and swine fat esters (Tab. 3). Yet, it was found that the analyzed samples met most of the standards for physical and chemical determinations. One exception was the content of contaminations, which was higher than the acceptable limits (max. 24 mg/kg) by 65.6 mg/kg in rapeseed esters, and by 138.4 mg/kg in swine fat esters. Overall, it was proved that values of such determinations as density at 15°C, viscosity at 40°C, and acid value were considerably higher for the rapeseed esters sample, while water content and sulphur content were lower for this sample.

Mixtures of rapeseed esters and swine fat esters with diesel oil considerably differed statistically with reference to the analyzed qualitative determinations (Tab. 3).

Density of the received mixtures significantly varied and ranged between 832.6 kg/m³ for M5 sample and 872.8 kg/m³ for M11 sample (Tab. 4). According to the PN-EN 14214 standard, the level of this determination should remain within the range of 860-900 kg/m³. Among the analyzed samples, eight (mixtures M1-M2, M5-M8 and M13-M14) did not meet this requirement, with density lower than the standards (Tab. 4). Viscosity of the enumerated samples, apart from M14, was also lower than the standard (3.5-5.0 mm²/s). The results of the study unambiguously show that diesel mixtures with rapeseed esters in 4.70:1 and 1.43:1 proportions (samples M1 and M2) as well as all mixtures of diesel oil and swine fat esters (samples from M5 to M8) with lowered density and viscosity would not ensure enough lubrication for pressure systems in injection pumps, which in turn would contribute to their faster wear.

Tab. 3. Properties of rapeseed ethyl esters (REE) and swine fat ethyl esters (SFEE)

Requirements	samples	
	REE	SFEE
density at 15°C [kg/m ³]	872.6 ^b	862.7 ^a
kinematic viscosity at 40°C [mm ² /s]	4.407 ^b	4.288 ^a
water content [%]	0.066 ^b	0.106 ^a
sulphur content [mg/kg]	7.29 ^b	2.15 ^a
particulate matter content [mg/kg]	89.6 ^b	162.4 ^a
acid number [mg KOH/g]	0.44 ^b	0.23 ^a
% FFA	0.22	0.12

a,b... - mean values in rows marked with the same letter are not significantly different ($p \leq 0.05$)

The flash point can be seen as a determination which illustrates safety of using, storing and transporting a fuel. The flash point is a specific property of a given plant oil and its value results from the composition of fatty acids and depends on the contamination level [10]. The flash point determined in this study for the analysed mixtures, i.e. a temperature lower than 23°C, disqualifies them as a potential fuel in CI engines (Tab. 4).

The lowest temperature at which fuel passes through a filtering device in standardized conditions is defined as a cold filter plugging point [10]. Three of the analyzed samples - M3, M11 and M14 - showed considerably lower, negative values of this parameter, respectively: -13°C, -11°C and -10°C (Tab. 6.2). Three mixtures of diesel oil and rapeseed esters (M1, M2, M3) and one mixture of diesel oil and swine fat esters (M5) had the same CFPP (-9°C). Positive values were determined for three out of fourteen samples, namely: M7, M8 and M12 (Tab. 4).

According to the Regulation of the Minister of Economy of 22 January 2009, water content in esters applied as fuel can maximally amount to 500 mg/kg. All the prepared mixtures met this requirement (<0.5%). Similarly, sulfur content in the analyzed mixtures of diesel oil and rapeseed esters and swine fat esters did not exceed the allowed norm of 10 mg/kg. The content of this element in the analyzed samples ranged from 1.97 mg/kg (M12 and M13) to 6.48 mg/kg (M4).

As determined in the PN-EN 14214 standard, a contaminations level in esters should be lower than 24 mg/kg. Given the contents of the prepared mixtures, only eight of them could have this determination assessed (M1-M7 and M14). It was unambiguously stated that in these samples contaminations content (>37 mg/kg) was considerably higher than the standard limit (Tab. 4). The remaining mixtures dissolved filters used during analyses, which precluded determination of their CFPP.

The acid value, which determines the content of free fatty acids, ranged from 0.19 mg KOH/g (M5) to 0.54 mg KOH/g (M11), which meant from 0.095% to 0.270% of free fatty acids in these samples. According to the PN-EN 14214 standard, the acid value should not be higher than 0.5 mg KOH/g of oil. Among 14 mixtures, only in the case of M11 this value was higher than that. It can be suspected that it was due to the fact that transesterification reaction was not completed and the esters purification was insufficient.

Performing the accelerated oxidation test, oxidation stability was determined for the analyzed samples. It was found that all of the mixtures were highly susceptible to oxidation due to their short induction period (from 33 minutes to 2h 15 minutes), which suggested their life would be short in storage. The minimum induction period set in the PN-EN 14214 standard is 6 hours, thus none of the prepared mixtures qualified as fuel acceptable for CI engines when it comes to this determination.

Tab. 4. Characteristic of analyzed mixtures

Requirements	samples													
	M ₁	M ₂	M ₃	M ₄	M ₅	M ₆	M ₇	M ₈	M ₉	M ₁₀	M ₁₁	M ₁₂	M ₁₃	M ₁₄
density at 15°C [kg/m ³]	835.9 ^b	846.6 ^d	863.1 ^h	868.4 ⁱ	832.6 ^a	840.9 ^c	853.6 ^e	857.6 ^f	868.5 ⁱ	864.5 ^h	872.8 ^j	862.7 ^g	857.7 ^f	835.9 ^b
kinematic viscosity at 40°C [mm ² /s]	2.69 ^a	2.94 ^c	3.50 ^g	3.68 ^j	2.70 ^a	3.01 ^d	3.22 ^e	3.36 ^f	3.67 ^j	3.59 ⁱ	3.73 ^j	3.55 ^{hi}	3.37 ^f	2.81 ^b
ignition temperature [°C]	under 23 ¹	under 23 ¹	under 23 ¹	under 23 ¹	under 23 ¹	under 23 ¹	under 23 ¹	under 23 ¹	under 23 ¹	under 23 ¹	under 23 ¹	under 23 ¹	under 23 ¹	under 23 ¹
cold filter plugging point [°C]	-9.0 ^{cd}	-9.0 ^{cd}	-13.0 ^a	-9.0 ^{cd}	-9.0 ^d	-6.0 ^e	2.0 ^h	2.0 ^h	-2.0 ^f	0.0 ^g	-11.0 ^b	5.0 ⁱ	-1.0 ^{fg}	-10.0 ^{bc}
water content [%]	0.049 ^{ab}	0.070 ^{cd}	0.106 ^g	0.129 ⁱ	0.044 ^a	0.051 ^b	0.077 ^d	0.070 ^{cd}	0.107 ^{ah}	0.088 ^e	0.113 ^h	0.066 ^c	0.097 ^f	0.065 ^c
sulphur content [mg/kg]	4.38 ^g	5.03 ⁱ	5.82 ^j	6.48 ^k	3.91 ^e	2.85 ^d	2.40 ^c	2.15 ^b	4.48 ^h	2.94 ^d	2.92 ^d	1.97 ^a	1.97 ^a	4.05 ^f
particulate matter content [mg/kg]	54.49 ^c	54.82 ^c	42.56 ^c	130.70 ^g	30.58 ^a	37.21 ^b	83.23 ^f	– ²	– ²	– ²	– ²	– ²	– ²	47.74 ^d
acid number [mg KOH/g]	0.31 ^{cde}	0.32 ^{def}	0.39 ^{fg}	0.41 ^g	0.19 ^a	0.20 ^{ab}	0.20 ^{ab}	0.21 ^{ab}	0.38 ^{efg}	0.27 ^{bcd}	0.54 ^h	0.26 ^{abcd}	0.26 ^{abcd}	0.24 ^{abc}
% FFA	0.155	0.160	0.195	0.205	0.095	0.100	0.100	0.105	0.190	0.135	0.270	0.130	0.130	0.120
oxidative stability [h]	~ 1h	~ 0.5h	<0.5 h	~ 0.5h	2h 15min	1h 20 min	~1h	~1h	~ 0.5 h	~ 1h	<0.5 h	1h	59 min	33 min

a, b, ... - mean values in rows marked with the same letter are not significantly different ($p \leq 0.05$)

¹ Not possible to analyze because of the device possibilities (not possible to determine the parameters below ambient temperature)

² Not possible to analyze because of the nature of the mixture which causes the dissolution of the filter used for the test

7. Conclusions

Qualitative determinations which were checked in the study for the majority of the analyzed rapeseed esters and swine fat esters were within norms. An exception referred to the contaminations level, which was considerably higher than the acceptable limit of 24 mg/kg. Yet, in order to unambiguously determine whether the samples could be an appropriate fuel for CI engines, it would be necessary to widen the range of research including all the remaining determinations defined in the PN-EN 14214 standard, such as: monoacylglycerols content, diacylglycerols content, triacylglycerols content, fraction composition, carbon residue, ash residue, etc. Having analyzed the prepared mixtures of diesel oil with rapeseed esters and swine pig esters, it was found that most of their determinations did not meet the requirements established in the Polish standard. This forces the authors to attempt at defining problems posed by transesterification of animal fats in the plant where the process was performed and discussing possible changes in the proportions of particular components, or the method of production. It is also essential to determine qualitative features of lipids used in transesterification process. Summarizing, it can be said that the results of the presented study constitute a basis for further research referring to production processes of both pure plant and animal esters as well as their mixtures.

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