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# PHYSICOCHEMICAL PROPERTIES OF FUEL COMPOSITIONS OBTAINED FROM DIESEL FUEL AND DIFFERENT KINDS OF FATTY RAW MATERIAL

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***Abstract***

*Increased interest in development of alternative fuels used to power combustion engines is caused by excessive use of fuels obtained from mineral sources. Depletion of resources, political aspects as well as the negative impact on the environment are commonly discussed issues in relation to fossil fuels. On the other hand, biodegradability, lower toxic components emissions and interchangeability with mineral fuels are commonly described benefits related to biodiesel, interpreted as fatty acid methyl esters obtained from fatty raw material. Also the multiplicity of raw materials that can be used for production promotes popularization of the biodiesel. However the variety of raw materials can have significant impact on the number of physicochemical properties of alternative fuels due to the differences in molecular structures forming given type of raw material.*

*The article presents analysis of properties of different types of biodiesel and its mixtures with diesel according to the outlines presented in the quality standards for mineral and alternative fuels. Alternative fuels were produced in the laboratory setup from swine, poultry, rape and sunflower fatty raw material. Such parameters as: density, kinematic viscosity, flash point, acid value, oxidation stability, cold filter plugging point, sulphur content, water content and total contamination were examined, based on the results, the quality of the biofuels was evaluated. Study confirms that biofuels derived from plant origin fatty raw material present favorable results in the aspect water content, total contamination, acid value and cold flow properties, thus biofuels derived from animal origin raw fatty material presents lower density and sulphur content.*

**Keywords:** *Biodiesel quality examination, biodiesel mixtures, animal fat biodiesel, vegetable oil biodiesel, transesterification*

## 1. Introduction

At the current stage of technological development, the use of combustion engines as the main source of propulsion for numerous vehicles and machines appears to be inevitable. It is therefore important to meet the demand for fuels to power these engines. Due to the development of industry and economic growth, the demand for fuels has been growing steadily. Currently, the transport sector uses more than 20% of the world's extracted energy resources to meet the demand for energy, with diesel engines being dominant in the sector [1]. Diesel engines have established their position inter alia due to the higher efficiency compared to spark-ignition engines. The possibility for powering diesel engines with a wide range of fuels, including those obtained from renewable sources, is also an argument for their continued use.

The main objective of activities related to the use of energy from renewable sources is a decrease in the extraction of mineral fuels, which is equated with a reduction in the amount of carbon dioxide emitted to the atmosphere. The process of switching to alternative fuels is particularly noticeable in the automotive sector [2, 3]. To power spark-ignition engines, alternative gaseous fuels (LPG and CNG) as well as petrol additives in the form of ethyl alcohol are used [4]. Fuels for diesel engines are supplemented with increasing amounts of biocomponents obtained mainly from vegetable oils [3].

The use of renewable fuels to power combustion engines enables a decrease in the use of fossil fuels while expanding the range of energy carriers that can partially or fully replace fuels from non-renewable sources [5, 18]. Since biofuels manufactured from plant or animal fats, obtained by transesterification, have physico-chemical properties similar to those of diesel fuel, their use requires no modification to either fuel systems of power units or the infrastructure associated with fuel logistics. In addition to environmental aspects associated with the use of biofuels, the process of converting fat raw materials into a fuel can stimulate the economy as well as justify this method of processing raw materials where they are regarded as waste.

Physico-chemical properties describing the quality of mineral and renewable components of the currently used fuels for diesel engines are highly convergent; however, even small differences in particular values can have a significant impact on the fuel combustion process, and create barriers in terms of the duration and mode of storage, or the use of fuels. It also appears that the type of fat raw material from which a biofuel has been obtained determines a number of its physico-chemical properties [6, 7, 19]. Therefore, in order to make full use of the potential of the wide range of raw materials that can potentially be converted into a fuel, not only the availability of the raw material but also specific physico-chemical features of a particular fuel need to be taken into account.

## 2. Materials and methods

Currently, since plant raw materials are most commonly used in the production of biofuels, other potential raw materials, including animal fats, are only used to a very small extent [8]. In order to convert a fat raw material into a fuel whose physico-chemical properties meet the requirements concerning the currently used mineral fuels, a number of methods have been developed, of which alcohol transesterification of fatty acids is the most common [9, 10, 20]. Transesterification owes its popularity to the optimal qualitative distinguishing features of the final product, which are similar to the properties of the currently used conventional fuels. Another important feature of esters is the possibility of mixing them with both a mineral fuel and esters of other fatty acids at ratios offering a compromise between the number of renewable components and the properties of the finished fuel.

### 2. 1. Production of biofuels

Biofuels produced for the purposes of tests concerning this study were obtained from a single-step transesterification reaction of a fat raw material and methyl alcohol, performed in the presence of an alkaline catalyst at an atmospheric pressure.

Biofuels used in the tests were obtained from swine lard, poultry fat, rapeseed oil and sunflower oil. The production of biofuels used for the tests was based on fat materials of food quality, as the controlled quality of these raw materials had no adverse effect on the quality of the obtained biofuels.

Biofuels were prepared by reacting 500 g of fat raw material with 100 g methyl alcohol (approximately 6:1 molar ratio) and either 5.3 g of potassium hydroxide (respectively for swine lard and rapeseed oil – 0.9% weight ratio) or 6.5 g of potassium hydroxide (respectively for poultry fat and sunflower oil – 1.1% weight ratio).

Laboratory equipment used during the production as well as the method of conducting reactions were similar to those described in the authors' previous studies devoted to the subject [8, 11-13].

The production process involved the supply of a previously weighed amount of a fat raw material to the reactor to which, after the fat has reached a temperature at a level of 60°C ± 2°C, a mixture of a catalyst dissolved in alcohol was fed. The duration of transesterification was set at 45 minutes.

Further activities related to biofuel production involved the evaporation of excess alcohol, precipitation and removal of the glycerol phase, solid impurities and moisture. The collection of alcohol was carried out in a vacuum distiller through the evaporation of alcohol at a temperature of <60°C with a rate of 1-1.5 $cm^3$/min. The glycerol phase was separated in a separatory funnel in which, following the addition of the post-reaction mixture, the glycerol phase settled to the bottom of the funnel from which it was removed. The ester phase at room temperature was then filtered two times through a filter medium on which a bed of anhydrous sodium sulphate had been placed.

The authors' previous studies demonstrated that mixtures with equal ratios of mineral and renewable components offered the optimal compromise between the fuel quality and the renewable component content [8, 11, 12]. For this reason, quality testing was also carried out on mixtures of the manufactured biofuels containing the above-mentioned ratio of components. Each biofuel was mixed with commercial diesel fuel (DF) in 1:1 volume proportions. Swine lard methyl esters and their mixture with DF were labeled respectively as SL100 and SL50. The same system of labeling was used for the remaining biofuels: poultry fat methyl esters and their mixture with DF were labeled respectively as PL100 and PL50; rapeseed oil methyl esters and their mixture with DF were labeled respectively as RO100 and RO50; sunflower oil methyl esters and their mixture with DF were labeled respectively as SO100 and SO50.

### 2. 2. Analysis of physico-chemical properties of biofuels

The obtained fuels were subjected to tests to determine their physico-chemical properties. All assays were performed on certified equipment being in accordance with the procedures specified in PN-EN 14214 Standard. Each parameter was determined in three replications, and the result presented in this study is the arithmetic mean of the obtained partial results. The analyzed parameters were: density at 15°C [$kg/m^3$], viscosity at 40°C [$mm^2/s$], flash point [°C], sulphur content [mg/kg], water content [mg/kg], total contamination [mg/kg], oxidation stability [h], acid value [mg KOH/g] and cold filter plugging point (CFPP) [°C].

The entire work related to the production and qualitative analysis of biofuels was carried out at laboratory facilities of the Department of Mechatronics and Technical and Information Technology Education of the University of Warmia and Mazury.

## 3. Results and discussion

Physico-chemical properties of fuels are an extremely important factor that determines the possibility for using them as fuels to power combustion engines [14]. The properties for which the limit values are specified in appropriate quality standards are, in a way, a guarantee of the proper operation of the engine and all systems that come into contact with both the fuel and the combustion gas. An analysis of results for physico-chemical properties of biofuels can also identify undesirable features of the raw material or irregularities associated with the method of their production. Finally, the results of tests for physico-chemical properties of biofuels determine the conditions and the manner in which they can be used (in the form of either a pure fuel or a biocomponent). Results of the analyzed physico-chemical properties are listed in Tab. 1.

The density of biofuels fell within the scope specified in standard PN-EN 14214. The biofuel obtained from poultry fat was characterized by the lowest density (874 $kg/m^3$), while that from sunflower oil by the highest density (885 $kg/m^3$). As regards the analysis of density of particular fuels, it was observed that biofuels obtained from plant raw materials are characterized by higher density compared to the biofuels obtained from animal raw materials. Since the density of diesel fuel (824 $kg/m^3$) was lower than that of biofuels, mixtures SL50, PL50, RO50 and SO50 were characterized by lower density compared to pure biofuels, while maintaining the relationship between the density of particular biofuels.

Viscosity of particular biofuels was 4.43 $mm^2/s$ for SL100, 4.41 $mm^2/s$ for RO100, 4.30 $mm^2/s$

for SO100 and 4.14 mm$^2$/s for PL100, respectively. The addition of DF decreased the viscosity of mixtures while maintaining the relationships between the viscosity of particular renewable components.

*Tab. 1. Physico-chemical properties of the analysed fuels and their mixtures and the permissible limits of these values in relation to PN-EN 14214*

| Sample name | Density at 15°C [kg/m$^3$] | Viscosity at 40°C [mm$^2$/s] | Flash point [°C] | Sulphur content [mg/kg] | Water content [mg/kg] | Total contamination [mg/kg] | Oxidation stablility [h] | Acid value [mg KOH/g] | CFPP [°C] |
|---|---|---|---|---|---|---|---|---|---|
| | *Biodiesel limits (according to PN-EN 14214)* | | | | | | | | |
| | *860-900* | *3.5-5* | *> 101* | *<10* | *<500* | *<24* | *>6* | *<0.5* | |
| SL100 | 876 | 4.43 | 139 | 1.52 | 296 | 19 | 3.4 | 0.21 | 8 |
| SL50 | 853 | 3.55 | 73 | 4.48 | 188 | 13.1 | 9 | 0.18 | -1 |
| PL100 | 874 | 4.14 | 140 | 1.9 | 290 | 19.3 | 3.1 | 0.28 | -1 |
| PL50 | 850 | 3.38 | 73 | 4.69 | 189 | 13.5 | 8.5 | 0.22 | -6 |
| RO100 | 881 | 4.41 | 134 | 3.22 | 190 | 17.4 | 5.8 | 0.16 | -11 |
| RO50 | 852 | 3.49 | 71 | 5.33 | 131 | 12.5 | >11 | 0.16 | -10 |
| SO100 | 885 | 4.30 | 139 | 4.22 | 200 | 17.9 | 2.9 | 0.13 | -11 |
| SO50 | 858 | 3.46 | 74 | 5.9 | 144 | 12.6 | 7.8 | 0.15 | -10 |
| DF | 828 | 2.63 | 59 | 7.4 | 90 | 7 | >11 | 0.16 | -10 |

The analyzed biofuels were characterized by flash point at similar levels, higher by over 30°C than the minimum permissible value. Given that the flash point of DF was lower in relation to biofuels, the addition of this fuel significantly decreased the flash point of all mixtures, of which RO50 was characterized by the lowest flash point (71°C), and SO50 by the highest flash point (74°C), flash point of both mixtures containing biofuels obtained from animal fats was 73°C respectively.

In all analyzed biofuel samples, the determined sulphur content was below the permissible limits, and below the value determined for DF. An analysis of this parameter revealed differences in sulphur content compared to biofuels obtained from plant and animal raw materials. Biofuels obtained from animal raw materials were characterized by a lower sulphur content than biofuels obtained from vegetable raw materials.

Water content determined in a sample of diesel fuel was significantly lower than the values determined for fuels obtained from renewable raw materials. The highest water content was determined for the biofuel obtained from swine lard (296 mg/kg); the high water content of this biofuel was probably due to the method of packing the fat raw material used to produce this biofuel (swine lard used in biofuel production was packed in a wrap, while other fats were purchased in air-tight containers limiting moisture penetration into the raw material). The water content of the biofuel obtained from poultry fat was also high (290 mg/kg). Biofuels obtained from plant raw materials were characterized by a lower water content than the biofuels obtained from animal raw materials by almost 100 mg/kg. Compared to the results concerning water content of biofuels presented in the author's previous study [8, 11, 12], significant differences were observed between the currently and previously presented results. It appears that this fact was affected the most by the performance of the process of water removal involving the filtration of biofuels through a bed of anhydrous sodium sulphate.

The total contamination of biofuels obtained from plant raw materials (17.4 mg/kg and 17.9 mg/kg, respectively for RO100 and SO100) was lower than that for biofuels obtained from animal raw materials (19.0 mg/kg and 19.3 mg/kg respectively for SL100 and PL100).

Nevertheless, results for all analyzed fuels met the requirements as regards the permitted amount of solid contaminants in biofuels. Similarly to water content, the determined amounts of solid impurities in the studies described in this article were lower compared to the previously obtained results [8, 11 12] which suggests that complementing the biofuel production process to include processes related to the removal of solid impurities and moisture contributed to a considerable improvement in the quality of the final product.

It appeared that the reduction in duration of transesterification reaction tangibly contributed to an improvement in the biofuels' resistance to oxidation, compared to the previously obtained results [8, 11, 12]; nevertheless, the obtained results for the biofuels' oxidative stability still failed to meet the requirements specified in the standard. The least favorable results were obtained for the biofuel manufactured from sunflower oil (2.9 h for SO100). The biofuel obtained from swine lard (3.4 h for SL100) was slightly better than the biofuel obtained from a competitive animal raw material (3.1 h for PL100). RO100 was characterized by the highest resistance to oxidation, which amounted to 5.75 h. The results for fuels containing renewable and mineral components were at an acceptable level (7.8 h for SO50, 8.5 h for PL50, 9 h for SL50 and >11 h for RO50, respectively).

All analyzed fuels met the requirements as regards the acceptable acid value. A clear difference was observed in the results between the group of biofuels obtained from animal raw materials (0.21 mg KOH/g and 0.28 mg KOH/g for SL100 and PL100, respectively) and plant raw materials (0.16 mg KOH/g and 0.13 mg KOH/g for RO100 and SO100, respectively). As the acid value for DF was 0.16 mg KOH/g in mixtures of SL50 and PL50, a decrease was observed in the acid value to a level of 0.18 mg KOH/g and 0.22 mg KOH/g, respectively.

Low-temperature properties of fuels are an extremely significant criterion in terms of the possibilities and methods of their use. The classification of alternative fuels in terms of low-temperature properties is presented in Tab. 2 [15, 16].

*Tab. 2. Requirements for biofuels used as pure fuels or as components of diesel fuel*

| Biofuel used as fuel | | | | Biofuel used as biocomponent | |
|---|---|---|---|---|---|
| Temperate climate | | Arctic climate | | | |
| Type | CFPP max [°C] | Class | CFPP max [°C] | Type | CFPP max [°C] |
| A | 5 | 0 | -20 | A | 13 |
| B | 0 | 1 | -26 | B | 10 |
| C | -5 | 2 | -32 | C | 5 |
| D | -10 | 3 | -38 | D | 0 |
| E | -15 | 4 | -44 | - | - |
| F | -20 | - | - | - | - |

Biofuels obtained from plant raw materials were characterized by significantly better low-temperature properties (-11°C for RO100 and SO100), compared to the results obtained for biofuels manufactured from animal raw materials (-1°C and 8°C for PL100 and SL100, respectively). According to the information provided in Tab. 2, RO100 and SO100 can be classified as type D, while PL100 as type B, where biofuels are intended to be used to power engines in a pure form in temperate climates.

Biofuel obtained from swine lard, whose cold filter plugging point was determined at a level of +8°C, exhibited the least favorable low-temperature properties, which excludes the SL100 from the possibility for using it as a pure fuel; however, it classifies the fuel as type B where it is used as a biocomponent. Low-temperature properties of biofuels are significantly affected by the percentage content of particular fatty acids forming molecules of particular fats; in this context, the used plant raw materials had a more favorable composition compared to fats obtained from animal raw materials [17].

## 5. Conclusions

During the course of the study it was confirmed that biofuels manufactured from fat materials belonging to various groups (plant and animal raw materials) are characterized by high convergence of obtained results. However, biofuels obtained from animal raw materials were characterized by significantly lower density and sulphur content. In turn, such biofuel parameters as water content, total contamination, acid value and cold flow properties favored biofuels obtained from plant raw materials.

The reduction in the duration of transesterification and the decrease in temperature in the process of post-reaction alcohol removal resulted in an improvement in the resistance to oxidation of biofuels, compared to the results presented in the authors' previous studies [8, 11, 12]. Nevertheless, none of the analyzed biofuels met the requirements as regards the minimum resistance to oxidation. However, the addition of diesel fuel (a mineral fuel containing 7% biocomponents and antioxidant substances) significantly improved this parameter.

As regards the cold flow properties, both biofuels obtained from plant raw materials and that obtained from poultry fat were suitable for powering a compression ignition engine in a pure form. The fuel obtained from swine lard can only be used as an admixture to diesel fuel. However, it should be noted that the share of this biocomponent will significantly affect the cold filter plugging point of the obtained fuel mixture.

Very low sulphur content determined in biofuels obtained from animal raw materials may effectively translate into an extension of the duration of the failure-free operation of parts of exhaust systems used in modern engines (which are very sensitive to the presence of sulphur compounds in exhaust gasses) and may also result in lower emissions of sulphur compounds to the atmosphere.

## References

[1] BP p.l.c. 2017, *BP Statistical Review of World Energy*, London, United Kingdom 2017.

[2] Information about the audit results „*Stosowanie biopaliw i biokomponentów w transporcie*", NIK, KGP-4101-01-00/2013, 192/2013/P/13/054/KGP, 2014.

[3] Polska Organizacja Przemysłu i Handlu Naftowego, *Annual Report – Oil industry and trade*, 2016.

[4] Nowak, M., Rymaniak, Ł., *CNG and LPG as fuels for combustion engines*, Combustion Engines, 1 (148), 2012.

[5] Aransiola, E. F., Ojumu, T. V., Oyekola, O. O., Madzimbamuto, T. F., Ikhu-Omoregbe, D. I. O., *A review of current technology for biodiesel production: State of the art*, Biomass and Bioenergy. 61, pp. 276-297, 2014.

[6] Aninidita, K., Subrata, K., Souti, M., P*roperties of various plants and animals feedstocks for biodiesel production*, Bioresource Technology, 101, pp. 7201-7210, 2017.

[7] Wan Nor Maawa Wan Ghazali, Rizalman, M., Masjuki, H. H., Gholamhassan, N., *Effects of biodiesel from different feedstocks on engine performance and emissions: A review*, Renewable and Sustainable Energy Reviews, 51, pp. 585-602, 2015.

[8] Duda, K., Mikulski, M., Krajewski, M., *Biofuels from animal fatty raw material – availability and quality assessment,* Journal of KONES, 23/4, 2016.

[9] Van Gerpen, J. H., Hammond, E. G., Johnson, L. A., Marley, S. J., Yu, L., Lee, I., Monyem, A,. *Biodiesel processing and production*, Fuel Processing Technology, 86, pp. 1097-1107, 2005.

[10] Fukuda, H., Kondo, A., Noda, H., *Biodiesel fuel production by transesterification of oils*, Journal of Bioscience and Bioengineering, 92, pp. 405-416, 2001.

[11] Mikulski, M., Duda, K., Wierzbicki, S., *Performance and emissions of a CRDI diesel engine fuelled with swine lard methyl esters-diesel mixture*, Fuel 164, pp. 206-219, 2016.

[12] Duda, K., Wierzbicki, S., Śmieja, M., Mikulski, M., *Comparison of performance and emissions of a CRDI diesel engine fuelled with biodiesel of different origin*, Fuel 212, pp. 202-222, 2018.
[13] Mikulski, M., Duda, K., Piętak, A., Wierzbicki, S., *Influence of contribution of biofuels derived from renewable materials in the fuel on the combustion process and toxic compounds emission of compression ignition engine*, Journal of KONES, 21/4, 2014.
[14] Atabani, A. E., Silitonga, A. S., Badruddin, I. A., Mahlia, T. M. I., Masjuki, H. H., Mekhilef, S., *A comprehensive review on biodiesel as an alternative energy resource and its characteristics*, Renewable and Sustainable Energy Reviews 16, pp. 2070- 2093, 2012.
[15] www.auto-swiat.pl/eksploatacja/paliwa-letnie-przejsciowe-i-zimowe-czym-zatankowac-auto/tderft, access 25.01.2018.
[16] www.pachemtech.eu/index.php/pl/oferta-uslugowa/badania-laboratoryjne/74-oznaczanie-temperatury-zablokowania-zimnego-filtra-wg-pn-en-116, access 02.09.2016.
[17] Sandhya, K. V., Mary, N. V., Abinandan, S., Velappan, K. C., Vedaraman, N., *Winterization studies of different vegetable oil biodiesel*, Bioresource Technology Reports, 1, pp. 50-55, 2018.
[18] Rostek, E., *Biofuels of first and second generation*, Journal of KONES, 23(4), pp. 413-420, 2016.
[19] Abdelfattah, O. Y., Allam, S., Youssef, I., Mourad, M., El-Tawwab, A., *Influence Of Biodiesel From Egyptian Used Cooking Oil On Performance And Emissions Of Small Diesel Engine*, Journal of KONES, 24(1), pp. 7-22, 2017.
[20] Ambrosewicz-Walacik, M., Tańska, M., Jankowski, K., *The effect of oils quality and transestrification method on the degree of conversion of the fatty acids methyl esters*, Journal of KONES, 23(2), pp. 17-24, 2016.

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