

Such amount of raw material is not capable of satisfying the demand for renewable fuels, although it can supplement other sources of acquisition, while providing an ecologically justified alternative to the need to utilize fats perceived as waste raw material. Raw materials derived from recycling sometimes require advanced methods of purification and production to obtain a final biofuel of high quality [22]. Nevertheless, despite additional financial expenditure incurred during the production, the final product proves price-competitive due to low costs of obtaining the raw material.

2. Possibilities of obtaining animal raw materials for biofuel production

Development of the biofuel market in Poland is determined by the requirements of the European Union and the need to implement the National Index Target (NIT) to stimulate an increase in the use of biofuels and biocomponents. As results from the audit performed by the Supreme Audit Office related to the „Use of biofuels and biocomponents”, one of the most significant problems preventing popularization of biofuels in Poland are high production costs of biofuels, mostly affected by the costs of raw material purchase [11].

A fundamental feature classifying the usability of a given raw material for production purposes is its stability and predictability of its supply, as well as the fat content in its specific volume. To be profitable, biofuel production must be based on stable sources of raw materials used for production. An average farm animal contains 10-15% fat, which is obtained by rendering bones and fatty tissues.

In Poland, about 5 million tons of livestock intended for slaughter are produced each year, in which the total production of fat amounted to more than 100,000 tons in 2012 [13]. A detailed analysis concerning the production of this raw material is presented in Tab. 1.

Tab. 1. Production of fat of animal origin in Poland in 2012 [13]

Specification	Livestock slaughter (million animals)	Fat mass (kg) per animal	Total amount of fat (million kg)
Cattle	5.52	70	43.62
Swine	26.3	12	17.5
Sheep	0.22	14	3.08
Horses	0.22	51	11.22
Poultry	125.42	0.23	28.85

Fats obtained from animal raw material also include post-slaughter fat waste. The annual production of this raw material is about 120,000-160,000 tons of waste fat of animal origin. The fat of this type is usually used for technical purposes. About 5,000 tons of fat per year can be obtained from fallen farm stock [23].

Despite the growing demand for raw material of animal origin, a decrease in the production of animal fat is forecast. The volume of production, amounting to more than 70,000 tons in 2010, is estimated at about 60,000 tons for 2020. This results from the high requirements of animal farming, low profitability and growing competitiveness of foreign companies [13].

3. Materials and methods

Possibility of using biofuels to power CI engines depends on properties characterizing the final product. Since the operation of injection systems is being optimized in terms of using the CDF, the properties of alternative fuels must be very close to the properties of conventional ones. The properties of renewable fuels depend on many factors related to the type and the quality of the raw material and the production method [19], while the quality of the final product is mainly conditioned by the quality and origin of the fatty raw material intended for production.

3.1. Raw material quality characterization

The biofuels used in this study were obtained from three types of fatty raw materials. They were produced and examined in the Biofuel Quality Research Laboratory located in the Department of Mechatronics and IT Education of the University of Warmia and Mazury. The following fatty materials were used for biodiesel production:

- Swine lard – of food quality. The producer declares 100% content of fatty raw material of pork origin. The raw material at room temperature maintains its solid state of matter and is odourless. After heating in the reactor, its state of matter changes into liquid. Biofuel obtained from lard was marked as SLME,
- Turkey lard – was characterized in a liquid state by a yellow, transparent colour, and in a solid state it was white. The raw material was obtained by rendering peritoneal turkey fat purchased in “Indykpol SA”. The rendering was carried out using the dry method [12]. After rendering, the fatty raw material was drained through a cotton filter to remove larger impurities. Product obtained because of transesterification of turkey lard is labelled in the study as TLME,
- Rapeseed oil – refined, food quality, rapeseed oil was used for RME production. The raw material at room temperature maintained a liquid form and it was characterized by light-yellow transparent colour and natural smell. The raw material was not subject to any technological treatment, except for preliminary heating.

Raw materials intended for biodiesel production were stored in cool, shady place. For rapeseed oil and swine lard, before placing it into the reactor, the raw material was heated to 105°C for 10 minutes, in order to remove any water impurities.

Based on the literature [1, 3, 9] and preliminary studies [6, 14, 15], a single-step reaction of transesterification was proposed for production of biofuels, carried out with the use of a methyl alcohol (99.8% methanol pure p.a. – supplied by Chempur) and a base catalyst – potassium hydroxide of laboratory purity (pure p.a. – supplied by POCH BASIC). The amount of alcohol used for the reaction, specified at the constant level for every type of fatty raw material, was 6:1 in the molar ratio to the amount of the fatty raw material. Depending on the type of the fatty raw material, the share of catalyst used for the reaction was determined based on its acid value. Acid values and the amounts of the catalyst for individual components are presented in Tab. 2.

Tab. 2. Acid value and share of a catalyst added to the reaction of fatty raw material transesterification

Fatty raw material	Acid value [mg KOH/g]	Share of catalyst in the reaction [wt.%]
Swine lard	0.61	0.9
Turkey lard	1.14	1.3
Rapeseed oil	065	1.0

3.2. Process of biofuel production and purification

The production of biodiesel was carried in the laboratory setup with a 1.000 cm³ capacity three-neck, round-bottom flask as a transesterification reactor. After adding fatty raw material to the reactor and stabilisation of temperature at the level of 60°C ±2°C, the mixture of a catalyst dissolved in the volume of alcohol was added. The reaction was carried for 60 minutes.

The final product of individual reactions was collected to tightly closed HDPE containers, for each fatty raw material separately, and then subjected to the purification process. Purification consisted in collecting the excess alcohol, separation and removal of the glycerine phase and drainage of the ester phase through a filtration barrier. The alcohol evaporation process was similar to the method developed in the Field Esterification Plant [17]. A detailed description of the apparatus applied with a description of procedures related to production and purification of biodiesel has been presented in detail in earlier publications of the authors [2, 6].

3. 3. Biodiesel blending

The obtained biofuels were used to produce mixtures with CDF purchased at the petrol station. The mixtures subjected to further analyses were prepared in three volume proportions (v/v) 25%, 50% and 75% of the renewable raw material, mixed with an appropriate number of CDF. The mixture obtained from SLME and CDF was labelled, respectively, as S25, S50 and S75, where the number after the S prefix denotes the percentage share of the renewable raw material in the mixture. The same method for sample labelling was used for mixtures obtained from TLME and CDF (T25, T50 and T75), and for RME and CDF (R25, R50 and R75).

4. Results and discussion

The obtained biodiesel was characterized by a transparent, clear colour; the smell of alcohol was not perceptible and no impurities or sediments either on the bottom or in the upper part of containers were visible.

The mixtures and pure fuels used for their production were subject to laboratory tests in order to determine certain physicochemical characteristics. Determinations were made according to procedures specified in the PN-EN 14214 Standard for biofuels and mixtures and the PN-EN 590 Standard for CDF. Table 3 presents the compiled results of the performed analyses for CDF, biofuels and mixtures. Determination of each parameter was made in three replications, and the result presented in the table is the arithmetic mean from the obtained results.

Tab. 3. Characteristics of obtained fuel mixtures

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 stability [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	
	Mineral Diesel limits (according to PN-EN 590)								
	820-845	2-4.5	>55	<10	<200	<24	–	–	
SLME	876	4.45	134	1.44	496	22.5	1.32	0.14	9
S75	858	3.92	80	2.31	420	17.6	6.64	0.13	5
S 50	847	3.59	71	2.74	230	11.0	8.22	0.10	0
S25	835	3.17	63	3.70	170	8.2	>19	0.10	-4
TLME	875	4.12	141	1.86	390	25.7	0.14	0.37	-1
T75	861	3.73	69	3.09	280	22.9	0.57	0.23	-2
T50	849	3.37	61	3.37	250	19.3	0.42	0.22	-7
T25	836	3.08	56	4.39	150	15.6	1.87	0.19	-12
RME	879	4.39	135	3.14	250	21.3	5.75	0.15	-11
R75	863	3.89	79	3.77	200	18.9	13.8	0.14	-12
R50	851	3.52	66	4.09	260	16.8	>20	0.16	-12
R25	839	3.12	57	4.73	120	13.8	>20	0.21	-12
CDF	824	2.78	56	5.58	56	5.8	>20	0.17	-12

Fuel density affects the range of the fuel stream injected to the combustion chamber. Its reduction is correlated with a decrease in the calorific value, resulting in a reduction of engine power or in an increased fuel consumption. High-density fuels are characterized by emission of a larger number of sediments in the combustion chamber [2, 18]. Fuel density is also related to emission of solid particles and nitric oxides, while high-density fuel is characterized by an

increased emission of those compounds [22]. Density of all biofuels analysed in the study satisfies requirements specified in the standard. The biofuel derived from turkey fat demonstrated the lowest density and the biofuel derived from rapeseed demonstrated the highest. The differences between values of these parameters for individual biofuels are not significant and amount to 4 kg/m^3 . An addition of CDF to biofuels results in density reduction of the obtained mixtures proportional to the share of mineral component. Mixtures with a 50% share of the biocomponent only slightly exceeded the acceptable density levels set forth for CDF, which suggests that mixtures with such biocomponent contents will behave like commercial fuels in a combustion chamber.

Viscosity depends on the type of fatty raw material used for biodiesel production and presence of unreacted fat particles. It grows proportionally to the increase in the length of the carbon chain and decreases with the number of unsaturated bonds in the particle. Fuel viscosity affects its lubricating properties, as well as the quality of spraying. Low viscosity fuel sprays better, but particles formed have low weight and quickly reduce their speed, which results in congestion near the injector nozzle. Excessive fuel density prevents complete combustion of the fuel mixture in some areas of the combustion chamber. In turn, excessively high viscosity contributes to a reduction of the fuel stream spraying degree, which may result in delayed combustion of the fuel mixture, as well as contribute to incomplete combustion, creating formation of carbon deposits [10, 22]. Viscosity of all biofuels under analysis satisfies the requirements specified both in the standard specified for biofuels and for mineral fuels. The fuels containing biocomponents obtained from turkey fat are characterized by the lowest viscosity. This relation can be observed both for pure biofuels and for mixtures with CDF. The highest viscosity is demonstrated by mixtures obtained from swine raw material. An additive of CDF reduces the viscosity of fuel mixtures in proportion to the share of the commercial fuel - this relation is observable for all mixtures under analysis.

Flash point is a parameter specifying fire safety for storage and transport of biofuels. Additionally, it is used to determine the accuracy and correctness of removing alcohol used at the production stage. Flash point for biofuels is lower than for unprocessed fatty raw material, although it is significantly higher than for CDF. Impurities – particularly alcohol residues – affect the reduction of the flash point for biofuels [2, 18]. The biofuels investigated in the study satisfy requirements for the minimum flash point temperature. For all biofuels under analysis, this temperature was above 130°C , which proves the correct removal of any alcohol residues. Since the flash point determined for CDF was 56°C (which was consistent with the PN-EN 590 standard), mixtures of renewable and mineral fuels are characterized by a lower value of this parameter, proportionally to the CDF share. An addition of CDF most significantly reduces the flash point in mixtures with biofuel obtained from turkey fat. Among the mixtures containing the highest CDF share, mixtures obtained from swine raw material demonstrate the highest flash point.

Sulphur content present in mineral fuels has a positive effect on lubricating elements of injection systems. Biodiesel, although it is characterized by a clearly lower share of this element, demonstrates very good lubricating properties. In all samples under analysis, sulphur content was significantly lower than value specified in normative requirements. In none of the mixtures under analysis did the content of this element reach half of the acceptable limit. Since the highest content of this element was determined for CDF, its greater share in the mixture resulted in a higher measurement. Among the renewables, the highest content of sulphur was determined for RME, while biofuels produced from animal raw materials demonstrated the sulphur content at the level of 1.44 mg/kg and 1.86 mg/kg for SLME and TLME, respectively (Tab. 3).

Water in fuel results in corrosion of fuel system elements, enables the development of microorganisms and reduces fuel's calorific value [5]. Water dissolved in fuel can contain various types of impurities or rust leading to tribological degradation of engine elements. Water in biofuel can occur in two forms: as particles dissolved in the volume or in the form of the so-called "bound

water”, the content of which can reach up to 1500 ppm. For diesel fuel, this value usually does not exceed 50 ppm. A high amount of water also contributes to biofuel hydrolysis to free fatty acids [8, 21]. Water content determined for CDF was significantly lower than for renewable fuels. In mixtures, an increase in water content was observed, proportionally to the share of the biocomponent. SLME demonstrated the highest water content (496 mg/kg – Tab. 3), with determination results slightly lower than the maximum permitted value – 500 mg/kg. Biofuel obtained from rapeseed oil is characterized by the lowest water content. A high content of water in biofuels obtained from animal raw material certainly results from the need to keep this material refrigerated which. Absence of appropriate protection, leads to moisture absorption from the environment. A low water content in rapeseed biofuel is a consequence of producing this raw material in an industrial plant where it was deprived of water and put into tightly-sealed packages. A high water content in biofuel samples obtained from animal raw materials suggests the need to carry out procedures aimed at reducing its amount in case of their longer storage or production in conditions other than in the laboratory.

Impurities in biofuels emerge at the production or transport stage and are formed as a result of oxidation or a contact with materials susceptible to their effects. The content of impurities in biofuel obtained from turkey fat exceeds the permitted limits. Very high amounts of impurities were also determined for other biofuels, although they did not exceed the limits specified by the standard. Rapeseed-derived biofuel demonstrated the lowest content of impurities among all renewable fuels under analysis. Since CDF was characterized by a very low level of impurities, the content of impurities in mixtures decreased along with an increase of the commercial fuel share. All mixtures of renewables and CDF demonstrated the content of impurities at a level permitted by the standard. The lowest level of impurities was observed for mixtures with the highest percentage of commercial fuel, among which the S25 mixture was characterized by the lowest content of impurities.

Oxidation stability specifies biofuel resistance to oxidation. When the process of degradation starts, it progresses very rapidly, resulting in formation of aldehydes, alcohols or carboxylic acids. Products of oxidation form insoluble sediments, which are deposited in the fuel system. Biofuel degradation products specially affect the acceleration of deposit formation in its mixtures with mineral fuels, causing determination of this parameter so important [5, 20]. Unfortunately, none of the biofuels under analysis satisfied requirements for oxidation stability. The lowest value of this parameter was determined for TLME, for which neither the pure biofuel nor any of the mixtures satisfied requirements specified by the standard. SLME also did not meet the requirements specified in the standard, but all of its mixtures did. Low oxidation stability of biofuels obtained from animal raw materials is the result of the need to render the raw material at high temperature, which causes deterioration of its properties and formation of free fatty acids. The fatty acid content forming animal fat particles can also affect the reduction of oxidation stability of biofuels obtained from them. RME only slightly differs from the requirements, and even a 25% addition of CDF resulted in a significant improvement in this parameter. R50 and R75 mixtures were characterized by a definitely longer induction time and measurement for those samples ended after 20 hours. At this point, it should be mentioned that obtained biofuels were not admixed with any substances of antioxidative effect and no remains of a catalysts were removed, the presence of which could affect deterioration antioxidative properties. If analysed biofuels were intended for commercial applications, residues of the catalysts would have to be removed and, at the same time, admixtures improving their antioxidative properties should be used. In addition, the process of fat rendering from animal tissues should be optimized in order to reduce the unfavourable effect of high temperature.

A high acid value may be an indication of the corrosive properties of biofuels [2, 18]. The acid value did not exceed the specified limits for any sample under analysis. The highest number of this parameter was found for the biofuel obtained from turkey fat, while values determined for SLME

and RME were almost the same. The fact that biofuels were not purified to remove the residue of the catalyst may affect the measurement results. Nevertheless, the large discrepancy between measured and the acceptable value indicates that even though the residues of the catalyst affect the result, the permitted acid value was not exceeded in any case.

The behaviour of biodiesel at low temperatures provides a very significant criterion for evaluating its operational potential, particularly in the climatic zone of Poland. Among the biofuels under analysis, definitely the best low temperature properties were demonstrated by biofuel obtained from rapeseed. RME can be qualified as type D (in moderate climate) when used to power engines in its pure form [7]. The least favourable low-temperature properties are demonstrated by SLME, whose CFPP value was determined at the level of +9°C (Tab. 3). Such a high value of CFPP disqualifies this fuel from its use in a pure form. None of the biofuels satisfies the requirements specified for an arctic climate specified in PN-EN 14214 standard. All biofuels under analysis can be used for preparing mixtures with mineral diesel fuel. The CFPP of biofuels is affected by the content of fatty acids forming its particles. In this case, vegetable fat demonstrates an advantage over fat of animal origin. CFPP for CDF was determined at the level of –12°C, which suggests type D of fuel used in moderate climate [7].

5. Conclusions

It was confirmed that the animal fat biodiesel-diesel mixtures meet most of the examined quality standards. Therefore, animal fatty raw material can compete in terms of quality with the most popular vegetable raw material currently used to produce biofuel. Additionally, the use of animal raw material may provide a perfect method of its utilization when it is not suitable for consumption. Production of biofuels from animal raw materials permits to see this type of material as a promising source in terms of diversification of raw materials used for biofuel production.

Due to the relatively low resources, fatty raw material of animal origin will not play a significant role on the national scale. However, it could be useful on a local scale. The production of biofuels from animal raw materials may provide an interesting complement of the product offer of meat processing plants, increasing their competitiveness and reducing waste raw material utilization costs.

Issues concerning a high level of contamination or water content in the biofuel samples under analyses require continuation of studies related to their production and subsequent purification.

Low resistance to oxidation and unfavourable low temperature properties require the application of antioxidants and depressants, which will permit safe storage and the use of biofuels, without affecting their possibility to power CI engines. Antioxidants and depressants are widely available and commonly added to biofuels produced on an industrial scale.

When using analysed biofuels to power engines, authors suggest using mixtures with at least a 25% share of CDF. Mixtures with a 50% biocomponent share provide an optimum compromise and are characterized by very good values of the properties analysed, while preserving a high share of biocomponents.

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