Chemical, stoichiometric and thermal analysis of fatty acid methyl esters from processed animal fat

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Abstract

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The paper focuses on liquid biofuel raised by transesterification of processed animal fat from rendering plant production suitable for energy use. The objective of the paper is to carry out an element analysis and stoichiometric analysis of selected samples of fuel from rendering plant production and to compare them with classic elements. The results of the analyses prove higher values of nitrogen concentration in the samples from rendering plant fat. In case of the samples of fatty acid methyl esters (FAME) from it a reduction of nitrogen was proved even if the values are still higher than at fatty acid methyl esters rape oil. Concerning the concentration of sulphur and chlorine in the samples of both rendering plant fat and FAME from it their concentration concerning the limiting values do not cause any problem. The net calorific value of the analysed samples is slightly lower. The net calorific value of the samples is particularly reduced by the higher amount of ash and by the oxygen concentration in the sample itself. Higher amount of ash in the fuel increases the amount of solid emissions.

Keywords: biofuel; rendering plant fat; transesterification; net calorific value; emissions

The economic growth in less developed parts of the world (China, India etc.) is attended by increasing consumption of energy materials and energy itself. Energetics is becoming one of the liming factors of further development of the countries. The basic contemporary tasks are to reduce the strategic dependence on oil and natural gas supplies from danger regions and to arrange the reduction of CO_2 emissions worldwide even if the consumption of energy will grow (COM/2007/0723).

The original ideas that the above mentioned objections can be reached by consumption saving and by using renewable resources proved to be unrealistic. The renewable resources have to play a more important role equivalent to their potential and competitiveness according to the world prices.

The research in the USA and Europe aims mainly at the research and development of new technologies of electricity production which meet the requirements of adequate expenses and which do not emit greenhouse gases (or with reduced amount of emissions). Such technologies are firstly nuclear energetics, pure coal utilization with limited CO_2 emissions, the preparation of nuclear fusion and renewable resources in the extent corresponding to their expected potential (COM/2007/0723).

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Recently, the utilization of rendering plant products has been reassessed. One of the possibilities how to use rendering plant products is their energy processing. Except of the processed animal fat it is possible to use also its fatty acid methyl esters (FAME) as so called biodiesel. It is fuel produced from oils, which can be mixed in oil fuel in various dose and so it is a suitable substitute for diesel motors. Its main advantage is that it is a renewable, biodegradable and nontoxic fuel. The increasing usage of such alternative fuels does not only contribute to the effort not to be fully dependent on oil fuels but it also helps to improve environment. Oils and fats cannot be used directly as a fuel for diesel motors because of a range of problems. One of the most serious problems is their high viscosity. It can be removed by so called transesterification. The principle of such a reaction is the conversion of triglycerides of fatty acid into esters of lower alcohols. Another utilizable product of this reaction is glycerol (Antolin et al. 2002).

The objective of the paper is to state other possibilities and limiting values of the energy use of this type of fuel and its comparison to similar fuels including fossil fuels. Therefore it is essential to come out from the chemical composition of the used samples and from stoichiometric calculations. An important task is to determine the stoichiometric analyses and to form model dependences of these combustion processes. The calculation determines the net calorific value of the fuel, the amount of oxygen (air) needed for a perfect combustion of fuel, the amount and composition of combustion products and the specific weight of combustion products.

MATERIAL AND METHODS

To produce FAME derived from fat from rendering plant the method of acid transesterification reaction was used (Prošková et al. 2009). This method was chosen because of high acidity of starting fat (31.14 mg KOH/g of oil). Waste oils and fats with high content of free fatty acids cannot be transesterified only by an alcalic catalysis which is satisfactorily used for plant oils. In the case of waste oils and fats with a high acidity value it comes to saponification at reaction with free fatty acids during alcalic catalysis. Soaps remove the catalyst from the reaction and impede the separation of glycerins and esters. The produced biofuel was tested with chemical analyses and stoichiometric and heat characteristics were identified.

To be able to judge the suitability of the combustion of rendering plant fat sample or biodiesel from rendering plant fat in a specific type of combustion appliance or to evaluate the quality of the samples, it is essential to know its characteristic qualities. In this paper they are:

– content of water in the original fuel W (% wt),
– content of ash in the original fuel A (% wt),
– gross calorific value Q_s and net calorific value Q_i (MJ/kg),
– content of the entire sulphur in fuel S (% wt),
– also the physical-mechanical features which are not mentioned in this paper.

The gross calorific value is determined by measuring in calorimeter (ČSN EN 14 918, 2010). In technical practice the gross calorific value and net calorific value are determined by a calculation (according to ČSN EN 14 918, 2010), where the results of the total (elementary) or technical (immediate) fuel analysis are used.

The dependence between the gross calorific value Q_s^r and the net calorific value Q_i^r can be expressed by the relation according to ČSN EN 14 918 (2010):

$$Q_i = Q_s - (0.02442 \times 1{,}000) \times (W + 8.94 \times H) \quad \text{(kJ/kg, kJ/m}^3_N\text{)} \quad (1)$$

where:

W	– content of water in analytic sample (%)
8.94	– coefficient for conversion of oxygen into water
H	– content of oxygen in analytic sample (%)
0.02442	– value corresponding to energy used for heating of 1% water at the temperature 25°C

The base of each calculation of heat work of combustion appliance is the element analysis of burned biofuel. The element composition of the biofuel influences all stoichiometric calculations, the calculations of thermal efficiency, losses of combustion appliance and their heat work. In case of fuels an elementary (elemental) analysis is used to find out the element composition, which helps to determine the percentage mass share of carbon, hydrogen, oxygen, sulphur, nitrogen and of water in the original fuel. Non-combustible substances of fuels, e.g. the content of ash and water, are determined by combustion or drying of the sample. The element analyses of the fuels are specified for normal conditions (temperature t = 0°C and pressure p = 101,325 kPa) (Gürdíl et al. 2009).

In addition to the basic classification and characterization of selected samples the following chemical features were stated:

– the content of water in the original sample W (% wt) – method of drying in a drier – the content of water in the analytic sample (ČSN EN 14 774-3, 2010);
– the content of ash in the original sample A (% wt) (ČSN EN 14 775, 2010);
– determination of the gross calorific value Q_s (MJ/kg) (ČSN EN 14 918, 2010);
– the content of carbon, hydrogen and nitrogen – instrumental methods (ČSN CEN/TS 15 104, 2006);
– the content of oxygen, sulphur and chlorine (% wt) (ČSN P CEN/TS 15 289, 2006);
– physical-mechanical features which are not mentioned in this paper.

The element analysis of the samples was determined with respect to the basic parameters of the fuels. Primarily the content of water (% wt), ash (% wt), gross calorific value (MJ/kg), carbon (% wt), hydrogen (% wt), nitrogen (% wt), sulphur (% wt), oxygen (% wt) and chlorine (% wt) were observed. The element analyses were done in an accredited laboratory of the Institute for Research and Use of Fuels, Prague-Běchovice, Czech Republic. The element analyses are an essential part of the fuel analysis to determine the stoichiometric and heat characteristics of the used samples.

The chemical characteristics are important for the stoichiometric analysis of combustion motors, which supplements the characteristics of the fuel and is a base for any heat calculation. This analysis is very important when solving many problems from the practice or when checking the work of current combustion appliances (Malaťák et. al. 2008). This analysis determines:
– net calorific value of the sample Q_i (MJ/kg);
– content of oxygen (air) needed for a perfect combustion of the sample (kg/kg, m^3_N/kg);
– amount and composition of combustion products (kg/kg, m^3_N/kg);
– specific weight of combustion products (% wt, % v).

The stoichiometric analysis is converted to normal conditions and the reference content of oxygen in combustion products.

All resulting values of the element and stoichiometric analysis are specified both in tables and in graphs in the following order, which is repeated for each type of the original sample:
(1) Element analysis of the original sample. To compare with reference fuels an element analysis for three reference fuels in the original state is determined.
(2) The stoichiometric analysis of the original sample under normal conditions and of the reference content of oxygen in combustion products.
(3) Determination of the net calorific value in dependence on converted water in fuel under normal conditions. To express the net calorific value in various states of converted water in fuel the original sample is converted into dry substance and is subsequently converted up to 50% of the content of entire water.
(4) Graphic representation of carbon dioxide in the amount of oxygen in combustion products showing the coefficient of surplus of air in the original sample under normal conditions.

To draw the graphic dependence it is essential to know the element constitution of the given fuel sample. The element constitution of the samples is set into the stoichiometric analysis. The stoichiometric analysis is given for the coefficient of air surplus in the extent 1 to 6. The resulting values are in Figs 1–3. The content of oxygen in combustion products is plotted on the axis x, the content of carbon dioxide (CO_2) is plotted on the axis y. The final curve represents the coefficient of air surplus.

A dependence stated in Figs 1–3 shows how many per cent of carbon dioxide the combustion products content and how big the coefficient of air surplus is. For practical use it is necessary to know the real value of oxygen content (O_2) in combustion products in the measured combustion appliance. A vertical line of the measured oxygen content (O_2) in combustion products in per cent by volume is plotted on the horizontal axis x, which intersects the line of the air surplus coefficient. In the place of the intersection of the air surplus coefficient line a horizontal line is drawn, which intersects the axis y with marked concentration of carbon dioxide in combustion products.

All volumes and weights of combustion air and combustion products are stated under so called normal conditions, that is at the temperature t = 0°C and pressure p = 101,325 kPa and for the reference content of oxygen in combustion products for liquid biomass O_r = 3%.

RESULTS

The resulting values of the element and stoichiometric analysis are introduced in the following synopsis:
– Chemical analysis of the original, waterless combustible samples in comparison to the reference

fuels such as rape oil, heat petrol and light fuel oil (Table 1).
– The stoichiometric analysis of the original samples under normal conditions and the reference content of oxygen in combustion products (Table 2).
– The dependence of the net calorific value (MJ/kg) on converted water in fuel (% wt) under normal conditions (Table 3).
– The dependence of carbon dioxide on the amount of oxygen in combustion products expressing the coefficient of air surplus in the original sample under normal conditions (Figs 1–4).

DISCUSSION AND CONCLUSION

From the results of element analysis on selected samples the amount of sulphur, chlorine and nitrogen is the most determining concerning the concentrations of emissions. In case of given fuels a high increase in nitrogen emissions is apparent, for the samples themselves show higher values of nitrogen in original state (Fig. 4) in contrast to liquid fossil fuels. The raised content of nitrogen can limit further usage of the liquid biofuels.

During combustion chlorine passes largely in gas phase. In selected samples the analysis of chlorine amount in original fuel was done. The chlorine concentration in analyzed liquid samples is on a very low level.

The importance of chlorine lies in HCI emissions on one side – in their possible influence on the creation of polychlorinated dibenzo/dioxins and furans (PCDD/F) and on the other side in corrosive effect of these elements in case of their further compounds (Olsson et al. 2003).

During combustion chlorine also sulphur passes largely in gas phase as SO_2 or SO_3. Sulphur emissions on heat appliances for the use of fuels from renewable energy sources are no problem concerning the limited values, which was also confirmed by the samples, see Fig. 5.

The crucial factor of sulphur concentration in fuel can be presence of corrosive agents. Other values of the element analysis fulfil the optimal parameters for the use of the biofuel samples for combustion appliances.

The most significant for the thermic use of fuels is the content of water and ash. The content of entire water present in the samples is rather low, which has a positive benefit to the fuel net calorific value. The content of ash is also very low as the element analyses of selected samples show. The amount of water and ash influences significantly heat characteristics of the analysed samples and it affects subsequently both the choice of water and the adjustment of the combustion appliance.

The net calorific value of the samples is shown in Fig. 6. The net calorific value for the comparison of the samples is stated in waterless state and converted subsequently in 10% of water content in the sample.

The resulting values from the stoichiometric analysis indicate very good heat-emission parameters of the analysed samples. The stoichiometric analysis of the analysed samples implies that the net calorific value parameters, water content and

Table 1. Chemical analysis of original samples

Sample	H_2O	Ash	Calorific value (MJ/kg)		C	H	N	S	O	Cl
	(% wt)		gross	net	(% wt)					
Rendering plant fat (original)	0.19	0.08	39.30	36.74	74.90	11.64	0.45	0.06	12.68	0.0000145
Rendering plant fat (RPF) (waterless)	–	0.08	39.37	36.81	75.04	11.66	0.45	0.06	12.71	0.0000145
Rendering plant fat (combustible)	–	–	39.40	36.84	75.10	11.67	0.45	0.06	12.72	0.0000145
Biodiesel from RPF (original)	0.01	0.10	39.48	36.82	75.37	12.11	0.18	0.06	12.17	0.0000071
Biodiesel from RPF (waterless)	–	0.10	39.48	36.82	75.38	12.11	0.18	0.06	12.17	0.0000071
Biodiesel from RPF (combustible)	–	–	39.52	36.86	75.46	12.12	0.18	0.06	12.18	0.0000071
Rape oil (original)	–	0.01	39.24	37.05	77.70	11.60	–	0.001	10.60	0.06
Heat petrol (original)	0.15	0.002	44.26	41.16	85.37	14.20	0.007	0.006	0.16	0.0
Light fuel oil (original)	0.01	0.05	42.90	40.30	86.00	11.90	0.05	1.40	0.10	0.08

Table 2. Stoichiometric analysis of original samples under normal conditions and the reference content of oxygen in combustion products, O_r = 3%

		Description	Biodiesel from RPF	Rendering plant fat (RPF)	Light fuel oil
Weight combustion	O_{min}	theoretical oxygen content for perfect combustion (kg/kg)	2.86	2.80	3.24
	L_{min}	theoretical air content for perfect combustion (kg/kg)	12.32	12.08	13.98
	L_{real}	real air content for perfect combustion (kg/kg)	14.41	14.13	16.36
	n	air surplus coefficient (–)	1.17	1.17	1.17
	m^v_{sp}	weight amount of damp combustion products (kg/kg)	15.82	15.53	17.81
	m^s_{sp}	weight amount of solid combustion products (kg/kg)	14.15	13.92	16.08
	m^s_{spmin}	theoretical weight amount of damp combustion products (kg/kg)	14.06	13.87	15.71
	m_{CO_2}	weight amount of CO_2 (kg/kg)	2.77	2.75	3.16
	m_{SO_2}	weight amount of SO_2 (kg/kg)	0.00	0.00	0.00
	m_{H_2O}	weight amount of H_2O (kg/kg)	1.67	1.61	1.73
	m_{N_2}	weight amount of N_2 (kg/kg)	10.88	10.67	12.35
	m_{O_2}	weight amount of O_2 (kg/kg)	0.49	0.48	0.55
	Single combustion product components in weight percent				
	CO_{2max}	theoretical weight concentration of carbon dioxide in solid combustion products (% wt)	19.65	19.80	20.07
	CO_2	carbon dioxide (% wt)	17.51	17.72	17.75
	SO_2	sulphur dioxide (% wt)	0.01	0.01	0.00
	H_2O	water (% wt)	10.53	10.40	9.69
	N_2	nitrogen (% wt)	68.76	68.69	69.35
	O_2	oxygen (% wt)	3.07	3.07	3.10
Volume combustion	O_{min}	theoretical oxygen content for perfect combustion (m^3_N/kg)	1.99	1.95	2.26
	L_{min}	theoretical air content for perfect combustion (m^3_N/kg)	9.49	9.31	10.78
	L_{real}	real air content for perfect combustion (m^3_N/kg)	11.10	10.89	12.61
	n	air surplus coefficient (–)	1.17	1.17	1.17
	v^v_{sp}	weight amount of damp combustion products (m^3_N/kg)	12.30	12.06	13.77
	v^s_{sp}	weight amount of solid combustion products (m^3_N/kg)	10.51	10.33	11.94
	v^s_{spmin}	theoretical weight amount of damp combustion products (m^3_N/kg)	8.81	8.66	10.01
	v_{CO_2}	weight amount of CO_2 (m^3_N/kg)	1.40	1.39	1.60
	v_{SO_2}	weight amount of SO_2 (m^3_N/kg)	0.00	0.00	0.00
	v_{H_2O}	weight amount of H_2O (m^3_N/kg)	1.79	1.73	1.83
	v_{N_2}	weight amount of N_2 (m^3_N/kg)	8.67	8.50	9.84
	v_{O_2}	weight amount of O_2 (m^3_N/kg)	0.34	0.33	0.38
	Single combustion product components in volume percent				
	CO_{2max}	theoretical volume concentration of CO_2 in solid combustion products	15.87	16.04	15.94
	CO_2	carbon dioxide	11.39	11.54	11.61
	SO_2	sulphur dioxide	0.00	0.00	0.00
	H_2O	water	14.55	14.36	13.27
	N_2	nitrogen	70.47	70.51	71.48
	O_2	oxygen	2.75	2.76	2.79

O_r = 3% (reference content of oxygen in combustion products)

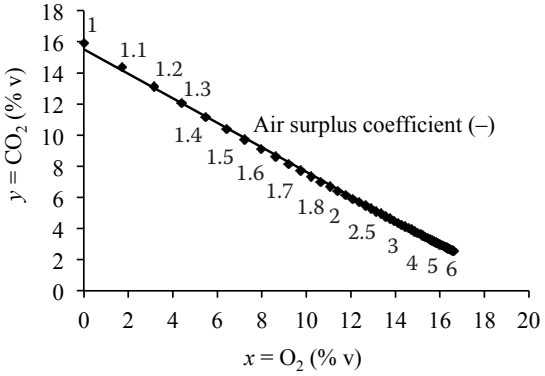

Fig. 1. Dependence of carbon dioxide on the amount of oxygen in combustion products expressing the coefficient of air surplus in the original sample under normal conditions for RPF

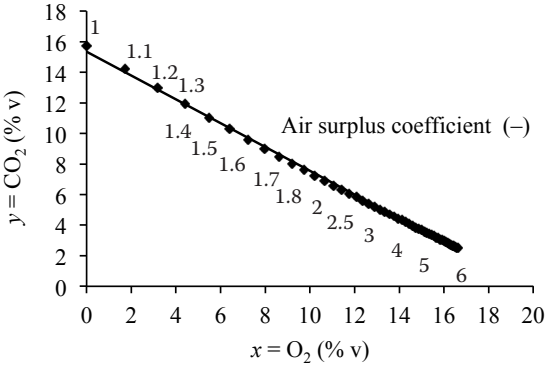

Fig. 2. Dependence of carbon dioxide on the amount of oxygen in combustion products expressing the coefficient of air surplus in the original sample under normal conditions for biodiesel from RPF

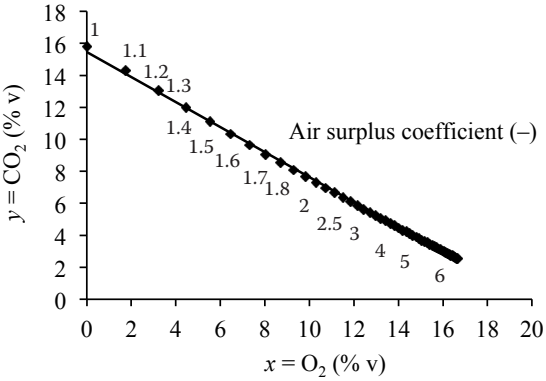

Fig. 3. Dependence of carbon dioxide on the amount of oxygen in combustion products expressing the coefficient of air surplus in the original sample under normal conditions for light fuel oil

energy concentration influence the choice and the design of the combustion appliance. The concentration of N (nitrogen), S (sulphur) a Cl (chlorine) in the samples is rather extensive, as the sample analyses proved.

Oxygen is a problematic component of fuel because it binds hydrogen and partly carbon to water hydroxide and oxides of nitrogen (N – in the form of amines and proteins in fuel) and chlorine. The problem lies in their interaction with conversion appliance, especially thermal one. The values of the stoichiometric analysis serve for further necessary calculations of net calorific values and heat losses of combustion appliances and especially for the control and optimization of combustion appliances (Nordin 1994).

For each used sample the graphic dependences of carbon dioxide are determined on the basis of known, expected or planned changes of oxygen in combustion products. For such determined dependences of carbon dioxide on the amount of oxygen brought into the combustion space expressing the air surplus coefficient in the original sample under normal conditions the following linear regression equation stands:

$$y_{CO_2} = A \times x_{O_2} + B \quad (2)$$

where:

y_{CO_2} – carbon dioxide in combustion products

x_{O_2} – measured oxygen concentration in combustion products

A – table value for the selected sample (Table 4)

B – table value for the selected sample (Table 4)

Table 3. Dependence of the net calorific value on converted water in fuel under normal conditions

	Converted water in fuel (% wt)	0	5	10	15	20	25	30	35	40	45	50
Net calorific value of fuel (MJ/kg)	rendering plant fat (original)	36.82	34.98	33.14	31.30	29.46	27.61	25.77	23.93	22.09	20.25	18.41
	biodiesel from RPF (original)	36.84	34.99	33.15	31.31	29.47	27.63	25.79	23.94	22.10	20.26	18.42
	light fuel oil (original)	40.30	38.29	36.27	34.59	32.24	30.23	28.21	26.19	24.18	22.17	20.15

RPF – rendering plant fat

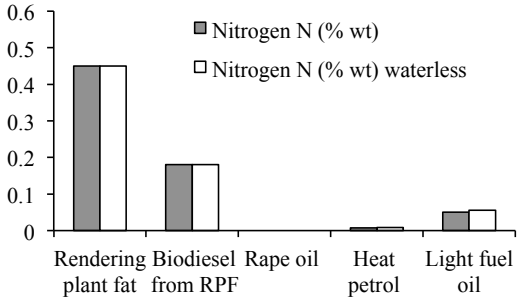

Fig. 4. Content of nitrogen in the original state of sample in weight % and content of nitrogen in waterless state in weight %

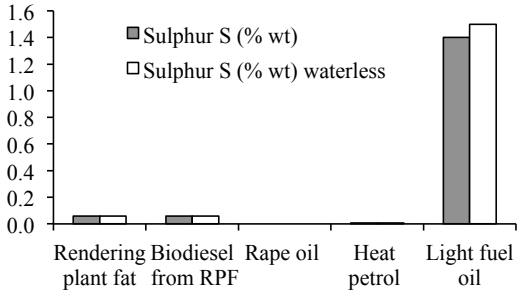

Fig. 5. The content of sulphur in the original state of sample in weight % and the content of sulfur in waterless state in weight %

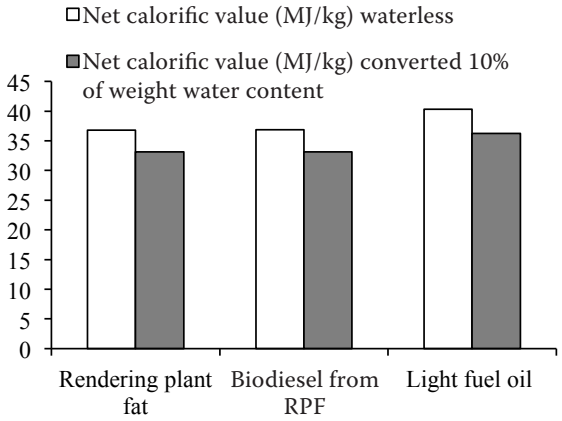

Fig. 6. The net calorific value of fuel samples in waterless state and the net calorific value converted in 10% of weight water content

Table values A are set by a regression equation on the basis of graphic representation of carbon dioxide in dependence on oxygen in combustion products.

Table values B are from stoichiometric dependences and represent volume concentration of carbon dioxide in big combustion products during perfect combustion when $n = 1$.

Oxygen concentration in combustion products can be set in many ways. One of the possibilities is the method based on the magnetic-mechanical or thermo-magnetic principle (from all gases oxygen has the highest positive magnetic susceptibility and unlike the majority of gases oxygen is a paramagnetic substance). Another possibility how to set the oxygen concentration are sensors working on the electrochemical principle (absorption and radiation of electrons). A manifold representative of potentiometer with solid electrolyte is a so called lambda-sensor. The lambda-sensor of oxygen is predominantly used for measuring residual oxygen in exhaust fumes etc. (Malaťák, Vaculík 2008).

The dependence set in this way determines how many per cent of carbon dioxide the combustion products contain during combustion of the given sample. For practical use it is necessary to know the real value of oxygen (O_2) content in combustion products in the measured place.

The graphic dependences expressed in this way or determined by a linear dependence serve for a quick adjustment of the amount of combustion air into combustion space. In practice, it brings an optimization of combustion processes primarily an optimal adjustment of the amount of combustion air and hereby an increase of net calorific value and reduction of heat losses and emissions from combustion appliances.

The values of the chemical analysis were compared with the values of other fuels including reference ones in original state such as original rendering plant fat, rape oil, fatty acid methyl esters of rape oil, fuel oil, light fuel oil and others. The content of water and ash, which is the ballast of fuel because it lowers the net calorific value, does not show eminent differences between biodiesel from rendering plant fat and the original fuel oil or other reference fuels. The values are low, which has a positive effect on heating of the fuel. The analysed net calorific value of biodiesel from rendering plant fat has comparable values as other reference fuels. The

Table 4. Values A and B (Eq. 2)

Sample	A	B
Rendering plant fat (original)	–0.7876	15.519
Biodiesel from RPF (original)	–0.7791	15.343
Light fuel oil (original)	–0.782	15.455
Brown coal	–0.9368	18.574

analysed gross calorific value is analogous. Slightly lower carbon content is caused by a slightly lower value of gross calorific value and net calorific value, it is in a good correlation with them but it fulfils the parameters for combustion appliances. In light of assessing the emission, the amount of sulphur, chlorine and nitrogen are the most serious. The sulphur content is slightly higher, chlorine concentration is on a very low level. More problematic could be a higher content of nitrogen even if it was reduced up to more than a half (60%) against the original sample by modifying the rendering plant fat. Higher oxygen content in fuel can be problematic as well because it binds oxygen to water, oxides or hydroxides. Other values of the element analysis fulfil the optimal parameters for the use of the fuel samples in combustion appliances. The resulting values of the stoichiometric analysis of biofuel show similar values as light fuel oil and prove very good thermal-emission parameters of the analysed samples.

On the basis of the results the fuels from rendering plant fats can be counted as fuels comparable to classic liquid fuels such as light fuel oil or to fuels on a basis of plant mass.

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