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INFLUENCE OF ESTERIFICATION OF WASTE FATS PROCESS PARAMETERS ON AGRICULTURAL BIOFUEL PRODUCTION FACILITIES

The paper presents the influence of esterification process parameters in waste fats on their level of reaction. Raw materials contained: frying rapeseed oil, animal lard, methyl alcohol and potassium hydroxide as a catalyst, necessary for reaction in non-pressure conditions. Esterification was carried out at 35–40 °C and 60–65 °C in two separate esterificators differing from one another with mixing systems. It has been established that in terms of contents of non-reactants allowed the obtained product meets the European EN 14214 standard, determining the quality of biodiesel.

1. INTRODUCTION

In search of alternative fuels, Szlachta [1] pointed at methyl esters of higher fatty acids, their properties being close to those of motor oil. In the nineties, a research was conducted in Poland on capabilities to produce biofuels by farmer producers out of raw rapeseed oil [2], based on the technology of low-temperature transesterification [3]. From the moment of publishing the information on a prototype low-efficiency installation for fuel production [4], there has been an increasing interest among farmers. In 2007, a rapid increase in rape prices [5] along with a decrease in oil prices caused the farmers to seek other inexpensive sources to produce methyl esters.

Walisiewicz-Niedbalska and Podkówka [6] proposed to utilize frying oils and animal fats for biofuels production for own use. Research conducted by Sulewski et al. [7], Wang et al. [8], Leong et al. [9], Predojević [10], Phan [11] have shown that methyl esters from frying oils from various sources have similar properties. Animal fats are solid at room temperature due to high content of saturated fatty acids [12]. As shown in the studies performed by Tashtoush et al. [13], Wyatt'a et al. [14], Golimowski and Nowak [15] biofuels made from animal fats as well as frying oils have sim-

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ilar properties as diesel fuel, except for their freezing point, which takes positive values. Biodiesel, based on frying oil, is manufactured on industrial scale in Austria, where it contributes to 1.5% of fuel's national supply [16]. In Denmark, the Daka company produces biodiesel from animal fats [17].

The analyses of waste fats-based biofuel properties performed so far, in most cases did not determine the presence of free glycerol and unreacted particles. According to Strenziok and Wickboldt [18], an excessive presence of these particles can cause serious damage to the engine. A research conducted by Golimowski et al. [19] on the production of biofuels based on low-temperature esterification technology from refined rapeseed oil as well as from fresh animal lard, has shown increased participation of di- and triglyceride in the ester phase. This proves low reaction level of triglycerides.

The study aimed at evaluating the influence of the reaction environment and the kind of raw materials on the occurrence of glycerol groups in methyl esters of higher fatty acids. Present knowledge provides no information on the quality of waste fat-based biofuels, manufactured in homesteads for own use.

2. MATERIALS AND METHODS

Raw materials used in the research were waste rapeseed oil (FO) and animal lard (AL), which went rancid on behalf of bad storage. Substrates necessary for esterification were methyl alcohol with molar part of 6 to 1 and a 2% addition of potassium hydroxide. 8 kg of raw materials were used for one trial.

Table 1

Physical and chemical properties of materials used

Parameters	FO	AL
Acid value, mg KOH·g ⁻¹	2.6	7.3
Thickness at 20 °, kg·m ⁻³ ·C	912	915
Kinematic viscosity at 40 °C, mm ² ·s ⁻¹	53.99	42.63
Combustion temperature, °C	242	244
Calorific value, MJ·kg ⁻¹	38.9	39.1

Physicochemical properties of the materials were described and compared to those of food fats. The results obtained are given in Tables 1 and 2. In the next stage of the study, frying oil and animal fats underwent the esterification process, which was carried out in two separate esterificators: hydraulically mixed (EH) and mechanically mixed (EM) at 35–40 °C and 60–65 °C after mixing the substrates for 30 minutes. Post-reactive product was placed in sedimentation columns for 24 h, where it distributed into two phases: ester phase and glycerol phase. After two weeks, the concentra-

tion of unreacted particles and free glycerol in the ester phase was determined using the gas chromatography (Clarus 600, PerkinElmer). The measurement was performed in accordance to the Polish standard PN-EN 14105, regarding free and total glycerol and mono-, di-, triglycerides.

Table 2

The contribution of fatty acids [%]

Fatty acids	Systematic name of the acid	Carbon number	Measurement results		Rapeseed oil [20]	Lard [21]
			FO	AL		
Saturated	tetradecanoic	14:0	–	2.28	0.06	0.58
	pentadecanoic	15:0	–	0.25	–	–
	hexadecanoic	16:0	5.45	26.79	4.5	22.77
	heptadecanoic	17:0	–	0.75	–	–
	oktadecanoic	18:0	2.19	17.76	1.8	13.10
	eicosanoid	20:0	0.65	0.21	0.6	–
	docosanoic	22:0	0.33	–	0.3	–
Total			8.62	48.04	7.26	36.45
Monounsaturated	tetradecenoic	14:1	–	0.24	–	–
	hexadecenoic	16:1	0.27	2.49	0.2	2.32
	heptadecenoic	17:1	–	0.49	–	–
	oktadecenoic	18:1	64.91	37.63	61.4	50.39
	eicosanoid	20:1	1.61	0.74	1.6	2
	decosanoic	22:1	0.68	–	0.3	–
Total			67.47	41.59	63.5	54.71
Polyunsaturated	octadecadienoic	18:2	16.46	4.96	19.4	5.30
	oktadecatrienoic	18:3n3	5.15	0.49	9.3	1.15
Total			21.61	5.45	28.7	6.45
Other			2.30	2.46	0.4	–
Total			100	97.07	99.86	97.69

3. RESULTS AND DISCUSSION

Based on the analysis of physicochemical properties (Table 1) it has been established that the fats used in the research were partially biodegraded. This is shown by a high acid value: $2.6 \text{ mg KOH}\cdot\text{g}^{-1}$ in frying oil and $7.3 \text{ mg KOH}\cdot\text{g}^{-1}$ in animal fats. FO's high viscosity of $53.99 \text{ mm}^2\cdot\text{s}^{-1}$ at $40 \text{ }^\circ\text{C}$ results from high mechanical pollution, also confirmed organoleptically. The analysis of raw materials showed an increased content of saturated acids in relation to fresh fats (Table 2). The increased content of saturated acids results from progressive degradation of the fats.

Results of the research confirming the presence of unreacted particles and free glycerol are given in Tables 2 and 3. Tests 1–4 were performed under the following conditions:

Test 1 – EH reaction at 35–40 °C,
 Test 2 – EM reaction at 35–40 °C,
 Test 3 – EH reaction at 60–65 °C,
 Test 4 – EM reaction at 60–65 °C.

Table 3

Contents of mono-, di-, triglycerides and free glycerol in MEAL [%]^a

Test No.	Triglycerides		Diglycerides		Monoglycerides		Free glycerol		Total	
	M	A	M	A	M	A	M	A	M	A
1	0.02	0.02	0.06	0.06	0.24	0.24	0.26	0.23	0.58	0.55
	0.02		0.06		0.23		0.23		0.54	
	0.02		0.06		0.24		0.21		0.53	
2	0.02	0.02	0.09	0.10	0.31	0.34	0.12	0.11	0.54	0.57
	0.01		0.11		0.39		0.14		0.65	
	0.03		0.11		0.31		0.08		0.53	
3	0.02	0.02	0.06	0.05	0.21	0.22	0.18	0.20	0.47	0.48
	0.02		0.05		0.21		0.19		0.47	
	0.01		0.05		0.23		0.22		0.51	
4	0.03	0.04	0.09	0.14	0.31	0.45	0.02	0.13	0.45	0.76
	0.03		0.12		0.33		0.12		0.60	
	0.06		0.20		0.71		0.25		1.22	
Standard EN14214		0.20		0.20		0.80		0.02		

^aM – measurement, A – average.

The presence of tri-, di- and monoglycerides in the methyl esters in question complied with the European standard EN 14214, regarding biodiesel quality. In all examined samples, the concentration of di- and triglycerides was below 0.2% and the concentration of monoglycerides was below 0.80%. The content of free glycerol was increased, several times higher than the limit value of 0.02%. This shows that the removal of post-reaction products is incomplete. Therefore, it is necessary to implement additional refining processes, such as rinsing with hot water, phosphoric acid or silica gel. A comparison of the refining methods mentioned above show that their effectiveness is similar, although Predojević [10] observed that the use of silica gel provides the smallest losses in biodiesel. It cannot be established based on Tables 3 and 4 alone, whether the environment of the reaction had any impact on pollution levels in methyl esters. A statistical analysis has been performed, taking a 95% confidence level, in order to describe the importance of the environment impact on the participation of unreacted particles and free glycerol. Independent variables with one degree of freedom are the following: temperature of the reactions and the equipment used for esterification reaction processes. Dependent variables are: contents of tri-, di-, monoglycerides and of free glycerol.

Table 4

Contents of mono-, di- and triglycerides and free glycerol in MEFO [%]^a

Test No.	Triglyceride		Diglyceride		Monoglyceride		Free glycerol		Total	
	M	A	M	A	M	A	M	A	M	A
1	0.11	0.12	0.11	0.08	0.16	0.16	0.09	0.05	0.47	0.41
	0.17		0.12		0.16		0.04		0.49	
	0.09		0.01		0.15		0.03		0.28	
2	0.28	0.12	0.18	0.11	0.16	0.14	0.11	0.08	0.73	0.45
	0.08		0.09		0.12		0.06		0.35	
	0.01		0.05		0.13		0.08		0.27	
3	0.00	0.00	0.11	0.12	0.24	0.22	0.08	0.08	0.35	0.39
	0.00		0.11		0.23		0.08		0.42	
	0.00		0.13		0.19		0.07		0.39	
4	0.03	0.02	0.11	0.10	0.21	0.21	0.09	0.06	0.44	0.38
	0.02		0.10		0.22		0.07		0.41	
	0.00		0.08		0.19		0.02		0.29	
Standard EN14214		0.20		0.20		0.80		0.02		

^aM – measurement, A – average.

Table 5

Multifactorial analysis of variance for the participation of glycerides and free glycerol in methyl esters of higher fatty acids from frying oil (MEFO) and animal lard (MEAL)

Independent variables	MEFO		MEAL	
	$F_{calc.}$	Risk of making a mistake (p)	$F_{calc.}$	Risk of making a mistake (p)
	Triglycerides			
A. Mixing system	1.672	0.232	0.019	0.894
B. Temperature	3.425	0.101	7.268	0.027
A:B	2.551	0.149	0.037	0.851
	Diglycerides			
A. Mixing system	0.627	0.451	0.016	0.903
B. Temperature	14.157	0.006	0.251	0.630
A:B	1.412	0.269	0.769	0.406
	Monoglycerides			
A. Mixing system	0.492	0.503	2.381	0.161
B. Temperature	6.277	0.037	38.095	0.000
A:B	1.004	0.346	0.095	0.766
	Free glycerol			
A. Mixing system	0.078	0.787	0.999	0.347
B. Temperature	6.832	0.031	1.000	0.347
A:B	0.558	0.477	1.003	0.346

Based on the analysis of multifactorial variance, it has been established that only temperature influenced the content of glycerol particles. Neither the esterificator type nor factorial interactions between the two variables had any impact. Also, a correlation was observed between the dependent variables. The correlation for dependent variables has been calculated, including variable temperature, which had a major impact on the results. These results are shown in Table 6.

Table 6

Correlation matrix of dependent variables and temperature

	MEAL	Temperature	Triglycerides	Diglycerides	Monoglycerides	Free glycerol
MEFO						
Temperature			-0.69	0.17	0.89	0.30
Triglycerides		0.47		0.45	-0.46	-0.24
Diglycerides		0.76	0.85		0.28	0.08
Monoglycerides		0.63	0.88	0.96		0.48
Free glycerol		-0.66	0.07	-0.11	0.07	

As a result of the statistical factorial analysis, it has been established that the participation of triglycerides in MEAL falls with the increasing temperature, whereas the participation of monoglycerides increases. In the case of MEFO, there is a positive correlation between temperature and the participation of glyceride particles as well as a strong positive intergroup correlation. This means that the higher the temperature, the higher the contents of glyceride particles. A negative correlation of free glycerol suggests that with the increasing temperature, the contents of free glycerol particles decreases.

4. CONCLUSION

Presence of unreacted fat particles in biodiesel obtained based on low-temperature esterification technology from waste fats is compliant with the European standard EN 14214 regarding biodiesel quality.

Increased content of free glycerol in all samples points at the necessity of implementing initial filtration of biodiesel in order to separate free glycerol particles.

As a result of a statistical analysis, a major impact of temperature on the content of the particles in question has been observed. A temperature increase results in decreased reaction efficiency by increase of the content of glyceride particles in methyl esters from frying oil and decrease of the content of free glycerol. In the case of methyl esters from animal lard, a partly inversed correlation exists. Increasing temperature of the reaction causes the concentrations of monoglycerides to increase and of triglycerides to decrease.

SYMBOLS

AL	– animal lard
FO	– frying oil
ME	– methyl esters of higher fatty acids
MEFO	– methyl esters of higher fatty acids from frying oil
MEAL	– methyl esters of higher fatty acids from animal lard
EH	– hydraulically-mixing esterificator
EM	– mechanically-mixing esterificator

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