Biodiesel from rapeseed variety "Banaćanka" using KOH catalyst

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Abstract

This paper presents a complete characterization of rapeseed oil, of Banaćanka variety, as well as the potential use of oil generated after filtering, in order to obtain biodiesel. The research interest was based on the fact that Banaćanka is the oldest domestic rapeseed variety, a so-called "double-zero" or 00-rapeseed (low in erucic acid, below 5%, and gluco-sinolates below 30 mmol g⁻¹), suitable for use in the region, since it is low-temperature tolerant, posseses high genetic potential for seed yield of about 5.2 t/ha and high oil content of around 45%. Transesterification was carried out in a Parr 4520 batch reactor, with KOH as a catalyst. Cold pressed oil without prior treatment was used as feedstock for transesterification. The paper analyses the effects of temperature, reaction duration, catalyst amount and rate of agitation on the synthesis of biodiesel at constant pressure and molar methanol/oil ratio.

Keywords: transesterification; domestic rapeseed oil, homogeneous alkali catalyst KOH, fatty acid methyl esters (FAME).

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Biodiesel is a non-toxic, biodegradable fuel prepared from vegetable oil or animal fat originated triglycerides, *via* transesterfication using metanol. It represents an environmentally friendly and renewable fuel [1,2]. From an environmental point of view, the use of biodiesel globally contributes to the reduction of the emission of greenhouse gases (CO, CO₂ and SO₂), particles (soot) and aromatics (benzene, toluene, etc.), while the emission of NO_x is slightly higher than the corresponding emission from diesel of fossil origin [3]. The advantages of biodiesel use over classical diesel fuel are based on the increased oxygen content which provides better engine combustion, as well as the absence of certain contaminants that are inevitably contained by the diesel of fossil origin.

Bearing in mind the engineering aspects, biodiesel produced in line with the EN 14214 standard represents a high quality fuel for diesel engines, which is according to certain properties even better than standard diesel based on fossil origin. Certain properties, such as good lubricity reduces the potential engine damage, and thus contributes to its higher efficiency and durability. In terms of use, particularly interesting features are its high cetane number, high flashpoint and acceptable low temperature properties, such as the cold filter plug point (CFFP), making it an even more acceptable alternative fuel [4]. Being environmentally friendly, and based on all its benefiting properties, bio-

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diesel provides better storage utilization and handling in comparison to diesel of fossil origin. These factors partially compensate for the lack of energy content. The main disadvantage, constraining its wider use is still the high cost of the raw material (comparing to classical fuel), as well as relatively high costs of catalytic transesterification refining.

The transesterfication reaction of raw rapeseed oil to biodiesel (fatty acid methyl ester (FAME), Figure 1, may be catalysed by an alkali, acid or enzyme [5,6]. The alkaline catalysis includes homogeneous and/or heterogeneous alkaline catalysts usage [1]. In alkaline catalytic route as homogeneous catalysts NaOH, KOH and their alkoxides are mostly used. Homogeneous alkaline-catalyst reaction is much faster than acid-catalyst transesterification [7]. Although chemical transesterification by an alkaline catalyst provides a higher level of conversion of triglycerides into methilesters and short reaction run, this reaction has a series of disadvantages. The reaction is intensive in terms of energy, even traces of water content strongly hinder the reaction, glycerol as a by-product is difficult to remove, it is necessary to remove alkaline catalysts from products, and an additional treatment of alkaline waste water as well as from free fatty acids is required. Common problems occurring in biodiesel technologies using homogeneous catalysts (NaOH or KOH) is that they require complete series of relatively expensive and complex steps of neutralization, flushing and separation [1,8-10]. In addition, purification procedures are not ecologically acceptable since they require the use of a large quantity of water and the production takes place with the aid of strong alkali or acids [1,2]. Furthermore, there is an issue of an expensive procedure of catalyst separation from the product [11–13].

CH_2 -COO- R_1	R ₁ -COO-R`	CH ₂ -OH
$CH-COO-R_2 + 3R'OH$	$\overrightarrow{\mathbf{R}}$ R ₂ -COO-R` +	CH-OH
CH ₂ -COO-R ₃	R ₃ -COO-R`	CH ₂ -OH
Trigliceride Lower alcohol	Esters	Glicerol

Figure 1. Transesterification reaction.

Despite the evident failings in the use of alkaline catalysts for homogenous catalysis, these processes are still the major ones, due to economic reasons, as well as due to availability. In the processes of alkaline transeserification using methanol, the catalyst dosage used is in the range from of 0.4 to 2% w/w to the feedstock, and the oil to methanol molar ratio is within stoichiometric relation from 1:3 to 1:12.

In this paper, a raw rapeseed oil of "Banaćanka" variety was used as the basic feedstock for the synthesis of biodiesel. The most important characteristic of this variety lies in the fact that this rapeseed oil contains very small quantities of erucic acid (below 5%), so the mixture obtained after pressing may be used as livestock feed. This paper is directed to test the behaviour of such feedstock in the conventional biodiesel production. KOH was selected as the catalyst, which, despite higher prices and greater quantity applied, in comparison to NaOH has one significant advantage namely, by neutralization of excess KOH, after reaction with phosphoric acid, K₃PO₄ (potassium phosphate) is obtained that may be used as a quite successfully applicable fertilizer, which from the agricultural point of view represents a significant by-product.

EXPERIMENTAL

Materials

As a feedstock, cold pressed rapeseed oil was used. The oil was used in transesterification reaction without prior treatment.

Methanol of 99.5% purity (Lach-Ner, max. 0.1% moisture, 50433 0403) was used in the transesterification process and KOH (\geq 85%, Sigma-Aldrich) was used as catalyst in the form of pellets with total impurities of \leq 2.0% K₂CO₃.

In order to perform the post-treatment of biodiesel sample, a micronized natural zeolite clinoptilolite of fraction 60–100 μ m was used, as well as a zeolite sample from the Belgrade Geoinstitute (originated from the Brus municipality, locality "Igroš-Vidojevići") with min. 90% purity (Na,K,Ca)_{2–3}Al₃(Al,Si)₂Si₁₃O₃₆·12H₂O in granulation 1–2 mm.

Feedstock and product characterization

Feedstock was subjected to gas chromatography analysis by GC Chromatograph Clarus 500, according to the instructions given by standard of EN 14214. Analysis findings and literature data were used for the calculation of the molecular mass of the product as well as for the calculation of the iodine number. The separation was performed over a 14 m MET-Biodiesel column with a 0.53 mm internal diameter, 0.16 µm film thickness, and integrated package 2 m×0.53 mm (28668-U). The initial temperature during GC analysis was 150 °C. The column was heated at a rate of 30 °C/min up to a temperature of 350 °C, and this temperature was maintained for an additional 15 min. The analysis was performed using the gas chromatograph equipped with FID detector operating at a temperature of 400 $^\circ$ C. The carrier gas was helium at a flow rate of 15 mL/min. A sample of 1 µL was injected into a cold injector.

Results of the detailed analyses of raw rapeseed oil are presented in Table 1. The results have shown that the obtained values of characteristic physical and chemical values are within the range of internationally declared values.

Biodiesel samples were analysed by a PE Autosystem XL gas chromatograph with a flame ionization detector according to the standard SRPS EN 14103. A 60 m polyethylene glycol capillary column with a 0.32 mm internal diameter and 0.3 µm film thickness were used. Analysis of the standard mixture of methyl esters RM-1 was carried out using a reference probe sample of 0.6 µL at split ratio 30:1. The injector and detector temperatures were 240 °C, and the analysis was performed in isothermal conditions at 210 °C. Helium was applied as the carrier gas with a flow rate of 1.8 mL/min. Methyl heptadecanoate (purity > 99%, Fluka) was used as an internal standard. The only modification of the method employed was the reduction of the quantity of the internal standard solution from 5 mL to 2 mL, due to the limited quantity of the internal standard available. In the same ratio, the sample weighed amount was reduced (from 250 to 100 mg) according to the standard procedure. Experimental results showed that this reduction did not affect the accuracy of results.

The physical and chemical characterization of the raw rapeseed oil and the obtained biodiesel was performed in compliance with EN 14214. Raw rapeseed oil (Banaćanka variety) represented the basic feedstock for the synthesis of biodiesel.

Complete analysis of the content of fatty acids in cold pressed oil "Banaćanka" was performed and the results are given in Table 2, which is also in compliance with analyses given in literature. The obtained raw oil belongs to the group of highly olefin rapeseed oils, with low content of erucic acids. Feedstock analysis was performed by GC, according to the method EN 14214 and

Drenertu	11-24			Standard values acc.	
Property	Unit	Method	Measured value	Min.	Max.
Density	kg/m ³	EN ISO 3675 –		900	930
Cetane number	-	ASTM D613	37.6	-	-
Caloric value	kJ/kg	DIN 51900-3	39709	35000	-
Cinematic viscosity at 40 $^\circ$ C	mm²/s	SRPS ISO 3104	37.0	-	38.0
Cloud point	°C	SRPS ISO 3015	-3.9	-	-
Freezing point	°C	-	-31.7	-	-
Flash point	°C	SRPS B.H8.047	246	220	-
Carbon	mass%	EN ISO 10370	0.12	-	0.4
Sulphur content	mg/kg	ASTM D5453-93	6.7	-	20.0
Ash content	mass%	DIN EN ISO 6245	< 0.01	-	0.01
Water content	mass%	EN ISO 12937	0.01	-	0.075

Table 1. Physical and chemical properties of raw rapeseed oil

based on the performed analysis and literature data molar mass of the product and iodine number were calculated (Table 2).

The calculated iodine number of 107.1792 matches the literature data (94–120). In addition to the content

of fatty acids, the physical properties of refined rapeseed oil were also determined by GC analysis [8]. The results of GC analyses of rapeseed oil were corresponding with the results of analyses of similar rapeseed variety previously published [14].

Table 2. Calculation of molar mass and iodine number based on GC analysis EN 14214, feedstock – refined rapeseed oil of "Banaćanka" variety

Fatty acid	Oil mass%	Acid molar mass	Triglyceride factor (F)	F* mass%	Rapeseed oil, molar shares Number of moles and <i>i</i> -th components in 100 g of mixture <i>g_i/M_i</i>	Multiplication of quantity (2) and acid molar mass $(g_i/M_i)/(g_i/M_i) \times M_i$
Myristic acid (tetradecanoic acid) CH ₃ (CH ₂) ₁₂ COOH or C14:0	0.071	228.4	-	-	0.000310858	0.199791192
Palmitic acid (hexadecanoic acid) CH ₃ (CH ₂) ₁₄ COOH or C16:0	4.553	256.4	-	-	0.01775741	12.81196193
Stearic acid (octadecanoic acid) CH ₃ (CH ₂) ₁₆ COOH or C18:0	1.648	284.4	-	-	0.005794655	4.637406821
Oleic acid CH ₃ (CH ₂) ₇ CH=CH(CH ₂) ₇ COOH or C18:1	66.19	282.4	0.8599	56.88152	0.234238669	186.1406698
Linoleic acid $CH_3(CH_2)_4CH=CHCH_2CH=$ CH(CH ₂) ₇ COOH or C18:2	17.82	280.4	1.7315	30.97998	0.063808845	50.34738037
Linolenic acid CH ₃ CH ₂ CH=CHCH ₂ CH=CH(CH ₂) ₇ COOH or C18:3	6.905 I	278.4	2.6151	18.05726	0.024802443	19.43039691
Arachidic acid (eicosanoic acid) CH ₃ (CH ₂) ₁₈ COOH or C20:0	0.524	312.5	-	-	0.0016768	1.474515276
Eicosenoic $C_{20}H_{38}O_2$ CH ₃ (CH ₂) ₇ CH=CH(CH ₂) ₉ COOH or C20:1	1.373	310.5	0.7853	1.078216	0.0044219	3.863567698
Behenic acid (docosanoic acid) CH ₃ (CH ₂) ₂₀ COOH or C22:0	0.413	340.5	-	-	0.001212922	1.162165666
Erucic acid CH ₃ (CH ₂) ₇ CH=CH(CH ₂) ₁₁ COOH or C22:1	0.252	338.6	0.723	0.182196	0.000744241	0.709118033
Lignoceric acid CH ₃ (CH ₂) ₂₂ COOH or C24:0	0.222	368.6	-	-	0.000602279	0.62469922
	100	-	_	_	0.355371022	281.4016729
		JB = sum(F*mas%) M = M _{glic} + 3(s -Mol mas		$M = M_{glic} + 3(sum(x_iM_i) - Mol mas H_2O)$		
	JB =107.1792015)15	M =882.26	

Measurements of feedstock and product densities were measured using a Parr digital density meter DMA 35, obtaining densities of 0.882 g/cm³ for cold pressed rapeseed oil and 0.791 g/cm^3 for methanol.

In order to confirm the accuracy of the results, water content was determined by ASTM D-6304 method, coulometer Metro HM, which is used for determination of water content in petroleum products, lubricants and additives by coulometric method based on Karl Fischer titration.

FAME Yield calculation

The experimental results were obtained by variation of transesterification conditions. In all experiments the yield was calculated by the following correlation:

mixed with a magnetic agitator at a pre-set number of rpm.

Pastelles of commercial KOH catalyst (Sigma-Aldrich, \geq 85% purity) were dissolved in the same quantity of methanol, in the container for decanting and added to the Parr 4520 reactor, after reaching the reaction temperature. The procedure was conducted in such a manner in order to determine the zero reaction time.

In experiments, the same quantity of Banaćanka variety (882.26 g) rapeseed oil was repeteadely used, as well as the same quantity of methanol 192.24 g (Lach-Ner, 99.5%, max. 0.1% of water). These quantities were selected in order to obtain the desired 6:1 methanol to oil molar ratio. The catalyst quantity was

FAME Yield (%) =
$$\frac{\text{Average amount of ME layer (g)} \times \text{Purity of ME layer (%)}}{\text{Amount of edible oil, feedstock (g)}}$$
(1)

After decanting, all product samples were weighed and it was identified that the average amount of ME was 892.2 g. By involving the values of the average ME amount and the amount of edible oil in Eq. (1), yield is obtained as a function of purity of ME layer:

FAME Yield (%) =
$$\frac{892.2 \text{ g} \times \text{Purity of ME layer (\%)}}{882.26 \text{ g}} = 1.0163 \times \text{Purity of ME layer (\%)}$$
 (2)

Apparatus and reaction procedure

Transesterification was performed in a batch reactor Parr 4520, of 2 L volume, at 350 °C as the maximum operating temperature and pressure of 150 bar. The reactor was equipped with a catalyst basket of 150 cm³ volume (\emptyset 70 mm×80 mm and \emptyset 50 mm×80 mm, working volume was in the space between two coverage surfaces with 1 mm openings) and an agitator with a variable number of rotations and impeller in annular area. The reactor was equipped with a transducer, a J type thermocouple and manometer. Temperature and rotation per minute (rpm) control were performed by a Parr 4842 microprocessor controller, with triple regulation and adjustable parameters.

If the experiment was conducted at ambient pressure in an open system, it would be impossible to test the effect of temperatures above the methanol boiling point (64.7 °C), since the effect of decreased methanol in liquid phase could not be eliminated due to evaporation. For this reason it was decided to conduct the experiment at 10 bar, with the assumption that all of the methanol is in liquid phase over the entire observed temperature range.

At the start of experiments, the same amount of pressed oil without pre-treatment was measured and added to the Parr 4520 reactor. The oil was heated up to the reaction temperature, at a heating rate of 2 $^\circ\text{C}$ min⁻¹. During the heating process the reactants were

varied from 4.6-5.4 g (calculated for the total mass of input feedstock, this is equal to 0.381-0.5 mass%). All experiments were performed with 10 bar over-pressure of inert gas (N_2) in order to eliminate the impact of temperature on the content of liquid phase methanol.

This paper presents 4 series of experiments (a–d) conducted by varying different parameters and by a blind experiment, in order to determine the temperature effect and net gain of activity due to the presence of catalyst.

Series a of experiments were conducted with a closed reactor without external pressure impact, with a 6:1 methanol/oil molar ratio, constant catalyst content 5.4 g (0.5 mass%) and by varying the transesterification duration (from 15 to 60 min). This experiment was conducted in order to identify the yield as a function of reaction time. KOH catalyst previously dissolved in methanol was used, and the agitator was maintained at 665 rpm during the entire experiment.

Series b of experiments were conducted at a temperature of 65 °C, with a 6:1 methanol to oil molar ratio. The quantity of catalyst was varied (4.6, 5.0 and 5.4 g; which is 0.428, 0.465 and 0.5 mass%), with the maximum number of agitator rotations of 665 rpm. This experiment was conducted at two reaction times of 45 and 60 min in order to establish the change of yield as a function of the catalyst quantity for different reaction durations.

Series c of experiments were conducted within a temperature range (from 50 to 75 °C), at maximum number of agitator rpm (665 rpm), with a 6:1 methanol to oil molar ratio. The experiment was conducted for two different reaction durations of 30 and 60 min. This experiment was aimed to determine the activity as a function of reaction temperature for different reaction times.

Series d of experiments were conducted at a temperature of 65 $^{\circ}$ C, with a 6:1 methanol to oil molar ratio, in duration of 60 min, with a varying number of agitator rpm (from 100 to 665 rpm). This experiment was aimed to determine the change in activity based on the variation of number of agitator rotations.

Separation procedures

After the transesterification reaction was carried out, the separation process was performed in two phases: first, to remove the remaining methanol, flash evaporation was conducted, for 3 h duration, at the temperature of 100 °C, and subsequently, the remaining triglycerides and glycerine were removed by different separation methods. Products separation was conducted in 3 ways in order to determine the efficiency of different methods and their effects on the purity of the product.

Ordinary procedures of decanting were performed in a decanter. All samples were left in the decanting vessel for 24 h and subsequently, a careful decanting procedure of methanol/glycerine mixture was performed.

The next procedures of separation includes decanting and subsequent soaking in a zeolite layer of micro granulation (60–100 μ m). After the first product of transesterification was decanted, the glycerine layer was separated, and the biodiesel layer was soaked in the layer of zeolite of microgranulation for 24 h, after which decanting was repeated.

The third procedures of separation included decanting and subsequent filtering through zeolite layer of certain granulation (1-2 mm).

RESULT AND DISCUSSION

Effect of reaction duration on the level of transesterification

In the first series of experiments, as the reaction time was extended, the level of transesterification increased over the entire observed range (Figure 2). After 15 min of the reaction run, the level of trancesterification is low (85.2%). It is characteristic that over the entire observed range the increase of level of transesterification is not linear. After 40 min of the reaction, the level of transesterification increased by approximately 3.5%, and after 45 min the increase of transesterification level dropped to approximately 1.8%. This can be explained by slowing down of the reaction rate due to dilution of reagents by the final product, methyl esters and by-product glycerine, by which the contact surface of reagents and catalyst is reduced. This suggests that by decreasing the amount of biodiesel during reaction, much better results could be obtained and the reaction time might be reduced.



Figure 2. Effect of reaction time on the level of transesterification (FAME yield); constant methanol/oil molar ratio, 6:1; catalyst content, 5.4 g (0.5 mass%); 665 rpm.

Effect of catalyst amount/mass (g) to the level of transesterification

The second series of experiments performed comprised test of the effect of catalyst amount to the level of transesterification. Two series of reactor tests were conducted (Figure 3):

Series I: maximum number of rpm (655 rpm), reactor temperature of 65 $^{\circ}$ C and the reaction lasted 60 min.

Series II: maximum number of rpm (655 rpm), reactor temperature of 65 $^{\circ}$ C and the reaction lasted 45 min.



Figure 3. Effect of catalyst amount/mass to the level of transesterification (FAME yield); constant methanol/oil molar ratio, 6:1; temperature 45 and 65 °C; 665 rpm.

This experiment was conducted at two different durations in order to try to eliminate the effect of reaction time and to identify exclusively the trend of transesterification increase with the catalyst amount. As the amount of the catalyst increased, the level of transesterification also increased. The highest level of

esterification was obtained at maximum amount of catalyst used (5.4 g, which is 0.5 mass%) and at the longest reaction time. Considering the effect of catalyst amount and the reaction time on the level of transesterification, it becomes evident that the amount of catalvst has smaller effect on the level of transesterification than the treatment time (11.2% is the increase achieved based on the treatment time, while only 5.7% increase was obtained based on the increase of catalyst amount). Furthermore, it can be concluded that sufficient amounts of catalyst for transesterification were used in the experiments, and that the increase of catalyst amount above the minimum value (taken from literature), does not contribute to the proportional increase of trancesterification level. Both curves show the same trend, with the break-point at 5 g of catalyst. A possible explanation would be that by increasing the catalyst amount the effect of transesterification reaction reversibility is proportionally decreased. The experiment was not followed up to the value when the increase of catalyst amount does not affect the level of transesterification, so it can be assumed that by further increase of the catalyst amount the level of transesterification would be further increased.

Effect of reaction temperature upon the level of transesterification

The third series of experiments was conducted to determine the impact of the reaction temperature on the level of transesterification. In order to separate the effect of the reaction time and temperature, the experiment was conducted in two parts at different reaction times (Figure 4).



Figure 4. Effect of reaction temperature on the level of transesterification (FAME yield); constant methanol/oil molar ratio, 6:1; time, 30 and 60 min; 665 rpm.

As it can be seen in Figure 4, in both temperature modes there is a curve point at 65 °C. When the reaction lasted only 30 min, the reaction product yield within the temperature range of 55–65 °C increased by

6.8%, and within the range of 65–75 °C this increase was only 3.5%. When the reaction was carried out for 60 min, the reaction yield within the temperature range of 55-65 °C shows an increase of 3.6% and within the range of 65-75 °C there is a reduction of 0.7%. The maximum obtained after 30 min was reached at 75 °C and was 91.6% methylesters. For the reaction duration of 60 min, the maximum was obtained at 65 °C and was equal to 96.4%. This can be explained by the reversibility of the transesterification reaction, which was favoured by temperature and by the increase of the concentration of esters and glycerine along with the duration of the reaction run. In case of shorter reaction durations, reversibility is manifested by a decrease of yield dynamic growth, while for longer reaction durations by yield decrease. The general conclusion of this experiment is that at constant velocity of the agitator and at constant catalyst amount, the optimal reaction duration is 60 min at a temperature of 65 °C.

Effect of agitator rpm to the level of transesterification

The fourth series of experiments was conducted in order to determine the optimal rate of agitation rotation and the impact of agitation rate to the transesterification reaction. The amount of catalyst was 5.4 g (0.5 mass%), reaction time was 60 min, and the temperature was 65 °C. After changing the number of rotations, two trends became evident: 100-300 rpm and 300-665 rpm (Figure 5). Within the first range, there is a clear increase of transesterification level of 34.8%, and within the second range there was an increase of only 4.3%. This could be explained by the fact that a certain number of rotations actually improve the contact of the reactant and catalyst by turbulence, while being heavier and concentrated in the lower part of the reactor only partially contributes to the decrease of the contact between the reactant and catalyst. By further increase of the number of agitator rotations the mixture of reactants, the catalyst and product become approximately equally mixed throughout the entire reactor, which leads to the fact that the positive effect of better contact between reactants by mixing is partially annulled by the increase of the concentration of products in the mixture of reactants. Moreover, it can be concluded that higher level of transesterification might be obtained by decreasing the number of agitator rotations during the reaction. At the lowest product concentration the highest number of agitator rotations is required; then, as the product concentration increases during the course of the reaction, the concentration of the product in the bottom part of the reactor is enabled and the contact area of the remaining reactants in the mixture is undisturbed. The second way to eliminate the effect of "dissolution" by the product of reaction mixture is to conduct the transesterification

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procedure in two phases with a separation between 2 reactions.



Figure 5. Effect of agitator rpm on the level of transesterification (FAME yield); constant methanol/oil molar ratio, 6:1; temperature, 65 °C; time 60 min; catalyst content, 5.4 g (0.5 mass%.

Separation

The first stage of separation was conducted by product evaporation. This operation produced good results and good repeatability. After the evaporation process, and previously decanted biodiesel, it was identified that the purity of biodiesel obtained was increased by approximately 1% in all samples, which confirms that this method of separation of methanol from the product is sufficiently effective and that it is not necessary to apply vacuum evaporation, as stated in the literature [15].

In both methods applying the natural zeolite clinoptilolite (micronized from 60–100 μ m and granulation of 1–2 mm), regularity in the increase of biodiesel purity was not identified, so it can be concluded that its application for such purpose is not adequate, since the adsorption is unselective. The impact of separation procedures upon the level of transesterification is presented in Figure 6.



Figure 6. Impact of separation procedures on the level of transesterification.

Characterization of the biodiesel

After the completion of the transesterification procedure and separation of the product from the byproduct and impurities, a complete analysis of the finished product was conducted and the results are presented in Table 3.

Regarding the properties of the finished product, one can notice that the largest discrepancy was in the case of kinematic viscosity, flash point and water content. Namely, kinematic viscosity can not be influenced since it is a consequence of the type of the feed; however, the flash point, which is a result of the content of unseparated methanol and the water content, can be affected. The authors underline that methanol evaporation under atmospheric pressure and at 120 °C is not sufficient.

After passing the product through the layer of zeolite, analyses of water and flash point were repeated. It was determined that the flash point was increased from 25 to 132 °C, and water content decreased from 1400 to 275 mg/kg. The obtained values of flash point and water content are consistent with the standard EN 14214.

CONCLUSION

It has been concluded, based on the results of transesterification of raw rapeseed oil of domestic rapeseed "Banaćanka", that methyl esters of fatty acid are obtained with regular yield and an adequate purity under the reaction conditions applied. Production of biodiesel from this rapeseed oil variety is highly recommendable, since the obtained residual mixture can be used as livestock feed due to the low content of erucic acid.

The duration of transesterification in the presence of homogenous alkali catalyst KOH up to a certain level positively affects the level of transesterification, and after that moment the reaction is slowed down. The same conclusion can be made for the study of the impact of the reaction temperature. This may be explained by reversibility of the transesterification reaction, which suggests the advantages of two-phase transesterification procedure, with the separation of the product as an inter-phase. The impact of the amount of the catalyst is evident and the reaction increases over the entire range of catalyst dosage. Since the minimal amount of catalyst was used in this paper (according to the listed literature data), further research could be conducted with the increase of the catalyst amount. The rate of agitation drastically increased the level of transesterification up to the middle of the range observed, after which it declined when the number of agitator rotations was increased. It can be concluded that it is recommendable to set up the

No	Property, unit	Measured value —	Values acc. to St	tandard (EN 14214)	Mathad
NO.			Min.	Max.	Method
1.	Density at 15 °C, kg/m ³	878.4	860	900	SRPS ISO 12185
2.	Distillation, start , °C	296	-	-	SRPS EN ISO 3405
	10 vol.%, °C	340	-	-	
	20 vol.%, °C	343	-	-	
	30 vol.%, °C	345	-	-	
	40 vol.%, °C	346	-	-	
	50 vol.%, °C	347	-	-	
	60 vol.%, °C	349	-	-	
	70 vol.%, °C	350.5	-	-	
	80 vol.%, °C	352	-	-	
	90 vol.%, °C	359, cracking	-	-	
	Residue, vol.%	9.5	-	-	
	Loss, vol.%	0.5	-	-	
3.	Cinematic viscosity at 40 $^{\circ}\text{C}$, $\text{mm}^2\text{/s}$	6.359	3.5	4	SRPS ISO 3104
4.	Flash point, °C	25	120	-	SRPS B.H8.047
5.	Cloud point, °C	-2	-	-	SRPS ISO 3015
6.	Filterability point, °C	-8	-	-	EN 116
7.	lodine number	107.3 g/100 g	-	120	SRPS ISO 3961
8.	Sulphur content, mg/kg	0,6	-	10	ISO 20846
9.	Water content, mg/kg	1400	-	500	SRPS ISO 12937
10.	Cetane index	54.0	51	-	SRPS ISO 4264
11.	Corros. Cu band, 3 h/50 °C	1a	-	1	SRPS ISO 2160
12.	Lubricity at 60 °C, μm	323	-	-	SRPS ISO 12156-1
13.	Transparency	Clear, transp.	-	-	Visually
14.	Colour	L 0.5	-	-	SRPS ISO 2049
15.	Coke content, mass%	1.85	-	0.03	SRPS ISO 10370
16.	Caloric value, kJ/kg	40449	-	-	DIN 51900-3

Table 3. Results of the analysis of the finished product

reaction with the maximal number of rotations at start time, and after that it is necessary to reduce the number of rotations, for the purpose of better separation of the product and reactant.

Neutralization of alkali waste solution was successfully conducted with phosphoric acid. The by-product obtained can be successfully applied as mineral fertilizer in agriculture.

Based on the results mentioned above, it can be concluded that the application of zeolite clinoptilolite, for the purpose of additional treatment of biodiesel and separation of water and methanol is highly desirable and efficient.

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IZVOD

DOBIJANJE BIODIZELA OD ULJANE REPICE SORTE "BANAĆANKA" KORIŠĆENJEM KOH KATALIZATORA

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(Stručni rad)

U ovom radu je ispitivana mogućnost korišćenja ulja dobijenog ceđenjem uljane repice sorte "Banaćanka" za proizvodnju biodizela. Korišćeno ulje, kao i zaostala uljana sačma su potpuno okarakterisani. Sorta "Banaćanka", najstarija domaća sorta uljane repice, je interesantna zbog niskog sadržaja eruka kiseline i glikozinolata, zbog čega je svrstna u sorte "00". Transesterifikacija neobrađenog, sirovog repičinog ulja je vršena u šaržnom reaktoru u prisustvu KOH kao katalizatora. Ispitivan je uticaj temperature, vremena tretmana, količine katalizatora, brzine mešanja i molarnog odnosa metanol/ulje na sintezu biodizela. Optimizovana je metoda prečišćavanja sintetisanog biodizela. Sadržaj metil-estra u prečišćenom proizvodu je određen GC u skladu sa metodom SRPS EN 14103. U analizi rezultata naglašen je pojedinačni uticaj ispitivanih parametara kao i njihov odnos, pri čemu je konstatovan poseban značaj brzine mešanja, zbog prirode sirovina koje su nemešljive. Finalni proizvod, biodizel, je prečišćen zeolitom i utvrđen je njegov uticaj na sadržaj vlage i tačku paljenja. Ključne reči: Transesterifikacija • Banaćanka • Uljana repica • Homogeni bazni katalizator KOH • Metil-estri masnih kiselina (FAME) • Procesni parametri