Alkali-catalyzed production of biodiesel from waste frying oils

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Abstract: The effects of the transesterification parameters on the yield and quality of the methyl esters (MEs) produced from waste frying oil (WFO) were investigated. A two-step alkali transesterification reaction followed by silica gel purification step was applied. The investigated reaction parameters were the methanol/oil molar ratio (6:1 and 9:1), the catalyst/oil weight ratio (1.0 and 1.5 mass %) and the type of catalyst (NaOH and KOH). The physical and chemical properties of the employed feedstock and the obtained biodiesel were determined in order to investigate the effects of both the properties of the WFO and the reaction parameters on the characteristics and yields of the product. It was found that the properties of the feedstock had a determinant effect on the physical and chemical properties of the MEs, as the majority of them did not differ significantly under the studied reaction parameters. However, the reaction parameters influenced the yields of the product. Higher yields were obtained with a 1.0 than with a 1.5 mass % catalyst to oil ratio. The increasing yield with decreasing catalyst/oil ratio was more pronounced with NaOH (9.15–14.35 %) than with KOH (2.84–6.45 %). When KOH was used as the catalyst, the yields were always higher (the mean yield was 94.86 %) in comparison to those obtained with NaOH (the mean was 84.28 %). Furthermore, the efficiency of KOH in conversion of WFO to purified MEs in comparison to NaOH was even more pronounced in the case of the higher methanol/oil ratio, *i.e.*, for the 9:1 methanol/oil ratio, the yield increase with KOH was about 2 times higher than the yield with NaOH, regardless of the applied catalyst/oil ratio.

Keywords: biodiesel; waste frying oil; alkaline two-step transesterification.

INTRODUCTION

Biodiesel is a non-petroleum-based fuel used in diesel engines and heating systems; hence, this fuel could be regarded as a mineral diesel substitute with the advantage of reducing greenhouse emissions because it is a renewable resource.[1] Sharmer *et al.*[2] estimated that CO_2 production could be reduced by 3.2 kg by using 1 kg of pure biodiesel instead of the same amount of fossil fuel. Although

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the amount of biofuels produced in the EU is growing, the quantities remain small compared to the total volume of mineral-based transport fuels. There are few obstacles that have hindered the wider use of biodiesel. The most important of which is that the selling price of biofuels is higher than that of mineral oil fuels. The biodiesel produced from vegetable oil or animal fat is usually more expensive than petroleum-based diesel fuel by 10 to 50 %.[3] Compared to neat vegetable oils, waste frying oils (WFOs) are lower cost feedstocks, making biodiesel production more competitive to that of petroleum-based diesel fuel. In addition, as WFOs are regularly poured down the drain, resulting in problems for wastewater treatment plants and energy loss, or integrated into the food chain as animal fodder, causing human health problems, the use of waste frying oils in biodiesel production offers a solution to the growing global problem of increased oil waste from households and industrial sources.

Biodiesel is a product of transesterification of triglycerides (the main constituents of vegetable oils or animal fats) with a short chain alcohol (primarily, methanol) in the presence of a suitable catalyst; chemically, it represents a mixture of fatty acid alkyl (primarily methyl) esters. Alkali catalysts, such as sodium or potassium hydroxide, and sodium or potassium methoxide, are most commonly employed in the transesterification. These catalysts are also preferred due to the resulting high yields. The methylate salts are more reactive than the corresponding hydroxides, but are expensive, cause the formation of various by-products and require high quality oils and water-free methanol.[1] Contrary to the numerous references concerning base catalyzed one step transesterification reactions, only a limited number were found for two-step base catalyzed transesterification reactions: two studies were based on experiments with refined oils,[4,5] while waste cooking oil was used in another two.[6,7] In a two-stage alkali transesterification process, the majority of mono-, di-, and triglycerides are removed in the first stage and those remaining in the second stage, resulting in a more purified product. Cayh and Kusefoglu[6] concluded that two-step transesterification of used cooking oil had superiority over a one step method, especially in terms of the high yields obtained. They suggested that the removal of glycerol at the end of the first step may be one of the main reasons why the equilibrium is shifted to the products.

The purpose of this study was to characterize biodiesels (methyl esters) produced from WFO by two-step alkali transesterification with varying parameters in order to examine the influence of the feedstock properties and the reaction conditions on the yield and properties of the obtained product. The varied reaction parameters were the ratio of methanol to oil, the type of catalyst and its amount relative to the amount of feedstock.

EXPERIMENTAL

Materials and methods

Waste frying sunflower oils were collected from local restaurants and were used as feedstocks. Prior to transesterification, the WFO samples were dried over calcium chloride ($CaCl_2$) and filtered through a cellulose filter to remove any suspended matter and $CaCl_2$ crystals. Chromatographic grade methanol (99.5 %), phosphoric acid, potassium hydroxide, sodium hydroxide, anhydrous sodium sulfate and calcium chloride were supplied by Lachema (Neratovice, Czech Republic), silica gel from Fluka (Buchs, Switzerland), while the reference standard for the gas chromatographic determination of fatty acid methyl esters was obtained from Supelco (Bellefonte, USA).

Transesterification procedure

Methyl esters (biodiesel) were synthesized in a batch type reactor using alkali catalysts. The ester preparation involved a two-step transesterification followed by purification and drying. The amount of WFO used in the reaction was 200 g, which was placed in a dry two-necked flask equipped with a thermometer and a reflux condenser. Dryness was absolutely necessary as water in the reactor would consume some of the catalyst, thereby slowing the reaction. The methanol and catalyst were added into the flask in the quantities to obtain the desired ratios relative to the oil. Namely, the study was realized using a mole ratio of methanol to WFO of 6:1 and of 9:1, whereas the catalyst (either NaOH or KOH) was added in quantities equivalent to 1 and 1.5 mass % of WFO. In the first step, the mixture was stirred for 30 min at 30 °C and 400 rpm, and then it was poured into a separation funnel. After one hour separation, glycerol was removed from the bottom of the flask, while the top esters layer was transferred into second two-necked flask, heated to 60 °C and mixed with a second methanol/catalyst solution. After stirring the mixture for 30 min at 400 rpm, it was poured into a separation funnel and allowed to separate for 12 h. The glycerol was removed by gravity settling and the methanol was removed from the thus-obtained crude esters layer by rotary evaporation at 65 °C and 20 kPa. The obtained crude methyl esters were weighed and further purified by passing them through a bed of silica gel with a top layer of anhydrous sodium sulfate in order to remove the remaining salts and glycerol, as it was shown previously that high yields could be obtained in this manner from acidic feedstocks, such as WFOs.[7] The obtained dried methyl esters were then bottled and kept for characterization studies.

Characterization of feedstocks and methyl esters

The feedstock WFO was characterized after drying and filtering (*i.e.*, prior to transesterification) in a series of tests. Furthermore, the physical and chemical properties of the methyl esters (ME) obtained by two-step alkali transesterification after purification on silica gel were determined by the methods listed in the JUS EN 14214:2004 standard.[8] This standard is equivalent to EN 14214: 2004 and defines the requirements and test methods for fatty acid methyl esters (FAME) to be used in diesel engines. The procedures employed for characterization are summarized in Table I. Even though it is not required by JUS EN 14214:2004, the saponification value (*Sv*) was also determined using the titration method described in ISO 3657:2002. The iodine value (*Iv*) and *Sv* were also calculated based on the fatty acid (methyl ester) composition determined by gas chromatography and using the equations (given in Table I) proposed by Kalayasiri *et al.*[9] In this way, an attempt was made to see if the calculated values could predict satisfactorily these two properties and be alternatively employed instead of the corresponding experimental procedures for their determination. A method for an estimation of the cetane index (*CI*) based on *Sv* and *Iv* was previously described,[10] as a simpler

and more convenient method than the experimental procedure, for the determination of the cetane number utilizing a cetane engine (EN ISO 5165:1998). In this work, the experimentally obtained values of Sv and Iv were used for calculating CI. However, the proposed equation for CI is not recommended for feedstock characterization as it has been previously documented that the cetane indexes of oils are generally much lower than those of methyl ester derivates, despite the fact that they have similar Sv and Iv values.[10] Thus, the CI of the WFO will not be discussed.

TABLE I. Methods used to characterize the feedstocks and the methyl esters

Property	Method
Density at 15 °C[a], ρ / kg m^{-3}	JUS EN ISO 3675:2005 Crude petroleum and liquid petroleum products – laboratory determination of density – hydrometer method
Kinematic viscosity at 40 °C[a], v / mm^2 s^{-1}	JUS ISO 3104:2003 Petroleum products – transparent and opaque liquids – determination of kinematic viscosity and calculation of dynamic viscosity
Acid value (Av)[a], mg KOH/g oil	EN 14104:2003 Fatty and oil derivates – fatty acid methyl esters – determination of the acid value
Iodine value (Iv)[a], g J$_2$/100 g (experimental)	EN 14111: 2003 Fatty and oil derivates – fatty acid methyl esters – determination of the iodine value
Iodine value (Iv), g J$_2$/100 g (calculated)	Azam et al.:[9] $Iv = \Sigma(254DA_i)/MW_i$[b]
Cold filter plugging point (CFPP)[a]	EN 116: 1981 Determination of the cold filter plugging point of diesel and domestic heating fuels
Saponification value (Sv), mg KOH/g oil (experimental)	ISO 3657: 2002 Animal and vegetable fats and oils – determination of the saponification value
Saponification value (Sv), mg KOH/g oil (calculated)	Azam et al.:[9] $Sv = \Sigma(560A_i)/MW_i$[b]
Cetane index (CI)	Krisnangkura Equation:[10] $CI = 46.3 + 5458/Sv - 0.225Iv$
Fatty acid methyl ester composition, mass %	Capillary gas chromatography (GC) with flame ionization detection
Mean molecular mass of WFOs, kg mol^{-1}	Calculated according to the fatty acid profile obtained by GC

[a]Properties and respective test methods required for characterization of methyl esters to be used as fuel in diesel engine by SRPS EN 14214 standard; [b]A_i is in %, D is the number of double bonds and MW_i is the molecular mass of each component

The methyl ester composition was obtained using a gas chromatograph equipped with a DB-WAX 52 column (Supelco) and a flame ionization detector.

All the properties were determined in two replicates and the final results are given as average values.

RESULTS AND DISCUSSION

Feedstock properties

The physical and chemical properties of the waste frying oil, WFO, used as the feedstock for the two-step alkali transesterification are given in Table II. The WFO had an acid value higher than 2.0 mg KOH/g (Table II), which has often been recommended as the limit acid value for an efficient transesterification.[11] Namely, the base catalyzed reaction was reported to be very sensitive to the content of free fatty acids, which should not exceed the recommended limit to avoid deactivation of the catalyst, and the formation of soaps and emulsion.[11,12–14] An elevated content of free fatty acids, expressed as the acid value, is not surprising for waste frying oils, as it is known that during the frying process under high temperatures in the presence of air and moisture, a variety of degradation reactions can occur, leading eventually to changes in the properties of the oil, including an increase in the viscosity and in the content of free fatty acids.[15]

TABLE II. The characteristics of waste frying oil used as the feedstock

Characterization test	Waste frying oil from restaurant (WFOR)	
Density, ρ, at 15 °C, g/cm^3	0.933	
Kinematic viscosity, ν, at 40 °C, mm^2/s	44.85	
Acid value, mg KOH/g oil	2.58	
Saponification value, Sv, mg KOH/g oil	Experimental	Calculated
	197	198
Iodine value, g J$_2$/100 g oil	Experimental	Calculated
	119	124
Fatty acid composition, mass %		
C12:0	–	
C14:0	0.25	
C16:0	9.44	
C16:1	1.02	
C18:0	5.71	
C18:1	28.19	
C18:2	53.50	
C18:3	0.34	
C20:0	0.44	
Total unsaturated	83.05	
Total saturated	15.84	

Considering the fatty acid composition of the WFO used in this study, it consisted mainly of methyl esters of linoleic (C18:2) > oleic (C18:1) > palmitic (C16:0) > stearic (C18:0) acids. The contents of the other evidenced acids were about 1 mass % or less. Such a composition reflects the sunflower origin of the WFO. The iodine value of the feedstock, which is a measure of the degree of unsaturation, was approximately 120 mg I$_2$/100 g. The calculated iodine values were about 4 % higher than the experimentally determined ones. The iodine value of

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the WFO was lower than the values (120 and 140 mg I_2/100 g) reported for frying sunflower oils used in Portugal.[1] However, the used oils have a variety of qualities as a consequence of the different frying conditions and the periods of use. Comparing sunflower oils with other vegetable oils, it is well known that, typically, the former have higher iodine values because of their higher levels of unsaturated fatty acids, primarily linoleic acid (two double bonds), than other vegetable oils.[5] Considering the saponification value, good agreement between the experimental and calculated values was obtained.

Influence of the transesterification parameters on methyl ester yields

The product yield considering either crude or purified esters is defined as the mass percentage of the final product relative to the initial mass of WFO introduced into the transesterification. The yields of methyl esters (MEs) obtained by two-step alkali transesterification of the WFO under varying reaction conditions are given in Table III. The obtained yields coincide with the previous findings of Predojević[7] that a two-step alkali transesterification with a silica gel purification treatment could be recommended for obtaining high biodiesel yields from waste frying oils, despite the elevated acid values. Namely, it is known that the more acidic the feedstock is, the lower yield that could be obtained by base transesterification because of the more pronounced deactivation of the catalyst and soap formation by the free fatty acids in the feedstock.[1] It was previously reported[7] that a two-step transesterification procedure, also applied in this study, could be satisfactorily employed for biodiesel production from waste frying oils with acid values up to $\approx$ 2.5 mg KOH/g, without a significant decrease in the MEs yields.

TABLE III. Comparison of methyl esters (MEs) yields (%) obtained with varying reaction parameters during the employed two-step alkali transesterification

Catalyst	Catalyst amount mass %	Methanol/oil mole ration			
		6:1	6:1	9:1	9:1
		Crude MEs	Purified MEs	Crude MEs	Purified MEs
NaOH	1.0	92.95	86.81	96.04	79.53
	1.5	82.85	79.53	86.98	69.55
KOH	1.0	97.33	96.17	98.15	95.84
	1.5	92.94	90.34	95.44	92.66

In order to compare the yields obtained under different reaction conditions, the relative yields are shown in Figs. 1 and 2. It can be seen that the yields were always higher with the lower quantity of catalyst, *i.e.*, higher yields were obtained with 1.0 mass % than with 1.5 mass % catalyst to oil (Table III; Fig. 1). The yield increase with decreasing catalyst/oil ration was more pronounced for NaOH (9.15–14.35 %) than for KOH (2.84–6.45 %, Fig. 1). In other words, the mass ratios of KOH studied here had a similar influence on the methyl ester conversion, whereas the higher ratio of NaOH (*i.e.*, 1.5 mass % of oil) suppressed

the conversion in comparison to the lower ratio (*i.e.*, 1.0 mass %). Furthermore, the bar diagram shown in Fig. 2 shows that yields were always higher when KOH was used as the catalyst (the mean yield was 94.86 %) in comparison to the yields obtained with NaOH (the mean yield was 84.28 %), which coincides with the findings of other authors.[1,16,17] Sharma *et al.*[11] reported a better yield with NaOH as the catalyst than with KOH when a magnetic stirrer was used, while when a mechanical stirrer was employed, the yield was same with an equal amount of NaOH and KOH (0.50 mass %). These authors also observed that during the separation of the final products from glycerol, KOH was more convenient. Potassium soaps, being softer than sodium soaps, did not block the bottom of separation funnel, unlike the later, and were easily removed. Hence, KOH as the catalyst is preferred over NaOH on the industrial level of application.[11]
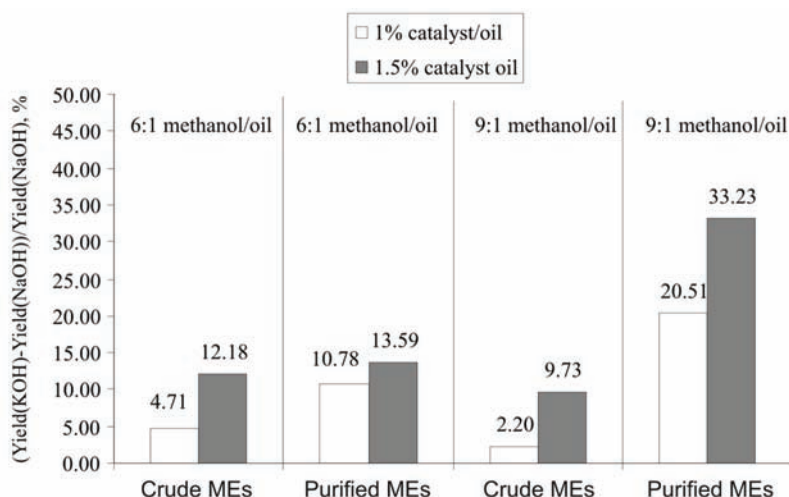

Fig. 1. Comparison of methyl esters yields obtained with different transesterification parameters: the percentage increase of the yield with 1.0 mass % of catalyst to oil relative to the yield with 1.5 mass %.

It can be also seen that the efficiency of KOH the in conversion of the WFO to purified MEs in comparison to NaOH was even more pronounced in the case of the higher methanol/oil ratio, *i.e.*, for the 9:1 methanol/oil ratio, the yield increase with KOH was about 2 times higher than the yield with NaOH, regardless of the catalyst/oil ratio applied (Fig. 2). The methanol/WFO ratio is one of the most important variables because of its influence on the separation of the methyl esters from the glycerol layer and, consequently, on the yield of biodiesel. Stoichiometrically, three moles of alcohol are required for each mole of triglyceride but, in general, a higher molar ratio is often employed for maximum ester production, depending on the type of feedstock, amount of catalyst, temperature,

etc.[11] The presence of a sufficient amount of methanol during the transesterification reaction is essential to break the glycerin-fatty acid linkages.[11] However, a large excess of alcohol should be avoided as it aggravates the separation of glycerol by increasing its solubility in alcohol, causing the reaction equilibrium to be shifted in the direction that favors the product decomposition reaction, with a consequential decrease in the yield of methyl esters. Leung and Guo[18] suggested that the hydroxyl group of methanol can act as an emulsifier and cause emulsification, making the separation of the ester layer from the aqueous layer difficult. Hence, it could be concluded that the KOH-catalyzed two-step transesterification was less sensitive to the excess of alcohol than the reaction with NaOH, further indication that KOH is more appropriate for practical employment.
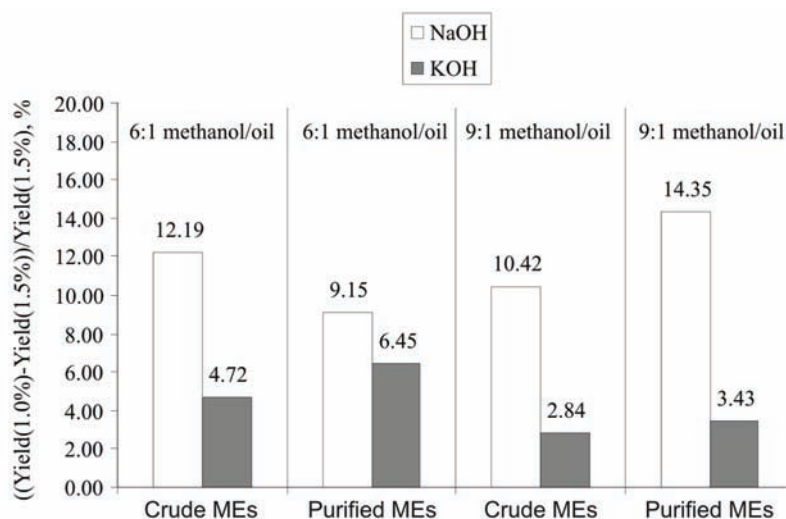

Fig. 2. Comparison of methyl esters yields obtained with different transesterification parameters: the percentage increase of the yield with KOH relative to the yield with NaOH.

Properties of the methyl ester

The physical and chemical properties of the methyl esters obtained by two--step alkali transesterification of the WFO after applying different experimental conditions are shown in Table IV. The properties are compared with the quality of biodiesel required for use in diesel engine in accordance to the JUS EN 14214 standard.[8] In general, very little differences could be observed in the properties of the methyl esters obtained by application of different reaction parameters.

The overall relative standard deviation ($RSD_{overall}$) as a measure of the dispersion of the results was used to detect if there were major differences in the studied properties. $RSD_{overall}$ was calculated by dividing the standard deviation of all values obtained for a particular property, regardless of the reaction con-

ditions applied, with their mean value and then multiplied with 100 to obtain percentage. Considering that the $RSD_{overall}$ for density, saponification value (experimental), iodine value (experimental), cetane index and the content of total unsaturated acids were estimated to be 0.37, 0.66, 0.67, 0.82 and 0.68 %, respectively, it could be concluded that the reaction parameters examined in this study did not significantly influence these properties of the produced methyl esters. The $RSD_{overall}$ for the kinematic viscosities and the total saturated fatty acid content were slightly elevated (2.18 and 3.09 %, respectively), while it was significantly higher (14.67 %) for the acid value, suggesting that the later was influenced by the reaction parameters investigated here.

TABLE IV. The characteristics of the methyl esters obtained with different reaction parameters during the employed two-step alkali transesterification of waste frying oils

Property	MeOH/oil mole ratio							
	6:1		9:1		6:1		9:1	
	Catalyst amount, mass %							
	NaOH				KOH			
	1	1.5	1	1.5	1	1.5	1	1.5
ρ, 15 °C, g/cm³	0.891	0.889	0.890	0.889	0.893	0.891	0.892	0.898
v, 40 °C, mm²/s	4.75	4.56	4.63	4.59	4.77	4.70	4.81	4.75
Av, mg KOH/g	0.38	0.39	0.39	0.27	0.39	0.36	0.43	0.41
Iv, gJ₂/100g (Experimental)	119	119	118	118	119	120	119	118
Iv, gJ₂/100g (Calculated)	119	118	117	117	119	119	119	118
PP, °C	±0	±0	±0	±0	+1	±0	±0	+1
$CFPP$, °C	–1	±0	–3	–4	–2	–2	–4	–5
Sv, mg KOH/g (Experimental)	193	193	193	191	191	192	192	190
Sv, mg KOH/g (Calculated)	192	192	192	191	192	191	191	190
CI	47.7	47.9	48.1	48.4	48.1	47.8	47.9	48.8
Fatty acid composition, mass %								
C12:0	0.10	0.05	–	–	0.29	–	–	–
C14:0	0.33	0.29	0.37	0.62	0.35	0.29	0.29	0.66
C16:0	9.61	9.95	10.60	10.17	9.61	9.59	9.55	9.53
C16:1	1.16	1.09	1.14	1.05	1.10	1.17	1.16	1.03
C18:0	6.29	6.30	6.23	6.44	5.87	5.77	5.87	5.79
C18:1	28.26	28.74	28.44	28.34	28.32	28.33	28.22	28.32
C18:2	53.94	53.13	53.22	52.86	53.66	54.23	54.18	53.75
C18:3	0.19	0.31	–	0.41	0.29	0.20	0.32	0.37
C20:0	0.12	0.14	–	0.11	0.50	0.42	0.42	0.55
Total unsaturated	83.55	83.27	82.8	82.66	83.37	83.93	83.87	83.47
Total saturated	16.45	16.73	17.2	17.34	16.63	16.07	16.13	16.53

Density at 15 °C. This property is important mainly in airless combustion systems because it influences the efficiency of atomization of the fuel.[1] The results obtained (Table IV) showed that all the methyl ester produced in this study had a density in the range 0.86–0.90 g/cm^3, specified according to the standard JUS EN 14214.[8] The mean value (±standard deviation) of the densities calculated for the MEs obtained with NaOH was 0.890±0.001 g/cm^3, while the MEs produced with KOH had slightly higher densities with a mean value 0.893±0.003 g/cm^3.

Kinematic viscosity at 40 °C. Even more than the density, the kinematic viscosity at 40 °C is an important property regarding fuel atomization and distribution. The higher is the viscosity, the greater is the tendency of the fuel to form engine deposits. The viscosities of the MEs (Table IV) were much lower than that of the feedstock oil (about 10 times) and they met the required values that must be between 3.5–5.0 mm^2/s.[8] As in the case of the densities, the values of kinematic viscosities were slightly higher for the MEs obtained with KOH (4.76±0.05 mm^2/s) than those obtained with NaOH (4.63±0.08 mm^2/s). It is known that viscosity increases with chain length and with increasing degree of saturation (*i.e.*, with decreasing degree of unsaturation).[19] However, this could not be observed in this study, as the differences in the iodine value, as a measure of the unsaturation, were negligible (the $RSD_{overall}$ was 0.67 %). Additionally, it was observed that when the methanol/WFO or the catalyst/WFO ratios were increased, the viscosity of the methyl esters decreased (see Table IV).

Acid value. The acid value is defined as the milligrams of potassium hydroxide required to neutralize the free acids in 1 g of sample. The acid values of the MEs varied from low 0.266 to 0.429 mg KOH/g and they were less than the 0.5 mg KOH/g specified as the maximum value according to JUS EN 14214.[8] As was previously mentioned, the greatest dispersion of the results was obtained for this property of the MEs produced under varying conditions (the $RSD_{overall}$ was 14.67 %). Again, the mean acid value of the MEs obtained with NaOH (0.354± ± 0.060 mg KOH/g) was lower than the mean of that obtained by transesterification with KOH (0.400±0.029 mg KOH/g). However, the greatest differences in the acid values were only observed for the higher methanol/oil ratio (9:1), whereas in the case of the lower ratio (6:1), acid values were almost the same regardless of the catalyst type or the catalyst/oil ratio.

Iodine value. The iodine value is an important measure for the determination of the unsaturation in fatty acids, which is only dependent on the vegetable oil. This property greatly influences fuel oxidation and the deposits formed in the injector of diesel engines.[1] With increasing iodine value of unsaturated fatty acids, the effect of polymerization is stronger. According to JUS EN 14214,[8] MEs used as diesel fuel must have an iodine value of less than 120 g I_2 per 100 g of sample. The MEs obtained in this study had an iodine value in the very narrow range of 118–120 g I_2/100 g. The mean iodine value of the MEs produced using NaOH

was 118±1 g I$_2$/100 g and of those using KOH was 119±1 g I$_2$/100 g. The calculated iodine values were in a very good agreement with those experimentally obtained.

Saponification value. The saponification value represents the milligrams of potassium hydroxide required to saponify one gram of fat or oil. The saponification value is not a property of biodiesel restricted according to EU or Serbian standards, which is the reason why it was not regularly determined in the relevant literature studies.

The difference in the saponification values of the MEs produced in this study was negligible, with a mean value for the MEs obtained using NaOH of 192±1 mg NaOH/g, and for those using KOH of 191±1 mg KOH/g. There was no significant difference in the calculated and experimental saponification values. The values were only slightly lower than that of the WFO (197 mg KOH/g). It is generally expected that an oil and the corresponding MEs have the same saponification value, as it is known that a triglyceride has 3 associated fatty acid chains and that each triglyceride will give three methyl esters; hence, stoichiometrically, it is to be expected that the same amount of fatty acid carbon chain in the neat feedstock oil and the biodiesel will react with the same amount of KOH giving soaps. However, is this assumption applicable to waste frying oils knowing that their properties differ significantly from the neat oils as a consequence of polymerization and degradation of the triglycerides that occur during frying.[15]

Cold flow properties. Compared with fossil diesel fuel, one of the major problems with the employment of biodiesel is its poor low temperature properties, such as cloud point (*CP*), pour point (*PP*) and cold filter plugging point (*CFPP*). The *CP* is the temperature at which a liquid is cloudy due to formation of crystals of size up to 1 mm, which make the suspension cloudy or hazy.[20] The *PP* is the lowest temperature at which a material will still flow due to crystal agglomeration. The *PP* is useful for characterizing the suitability of a fuel for large storage and pipeline distribution.[20,21] The *CFPP* is defined as the lowest temperature at which 20 ml of oil safely passes through a filter within 60 s. The cold flow properties of methyl esters such as the *PP* and *CFPP* depend on the structure of the fatty acids. In general, biodiesel made from feedstocks containing higher concentration of high melting point saturated long-chain fatty acids have relatively poor cold flow properties.[19,22] It was previously found that the difference between the CP and PP of methyl esters is relatively small[20] so that the filterability test, *i.e*., *CFPP*, could better a better indication of engine performance during low temperature operation.

The experimentally determined values of the CFPP and PP for the methyl esters samples were in the range from –5–0 °C and around 0 °C, respectively (Table IV), implying that the obtained biodiesels could be suitable for use in summer time. The low temperature properties of a biodiesel depend on the quality and

composition of the raw material, but they can be improved by blending with diesel fuel D2 or with polymer additives.[19]

Cetane index. This property could be regarded as an indicator of the cetane number, which is a property that reflects the ignition quality of biodiesel. The cetane number is related to the time that passes between injection of the fuel into the cylinder and the onset of ignition. It is known that the exhaust emission of nitrogen oxides (NO_x) is lower with increasing time. The reduction of NO_x exhaust emissions is an important problem facing biodiesel as it is known that it is slightly increased when using biodiesel in comparison to fossil diesel.[23] The structure of fatty esters can also influence emissions, with the NO_x emissions being lower with increasing saturation. Saturated compounds have higher cetane numbers (*i.e.*, cetane index) than unsaturated compounds. For instance, Freedman and Bagby[24] reported cetane numbers for methyl palmitate (C16:0) and methyl stearate (C18:0) as 74.3 and 75.6, while Klopfenstein[25] reported 74.5 and 86.9, respectively. Unsaturated methyl oleate (C18:1) and methyl linoleate (C18:2) have much lower cetane numbers, *i.e.*, 47.2 and 28.5 , respectively.[26] Contrary to the determination of the cetane number that requires tedious experimental procedure, the cetane index can be obtained by simple calculation.

The mean cetane index, *CI*, obtained for the MEs produced with NaOH was 48.03±0.29 and 48.15±0.44 for the MEs obtained using KOH. Šiler-Marinković and Tomasević[16] also used the Krisnangkura equation to calculate the *CI* for the characterization of MEs produced from crude sunflower oils and the estimated values were very similar to the values obtained in this study, ranging from 49.7 to 50.9.

Fatty acid composition. As can be observed from Table IV, the fatty acid methyl ester profiles of the produced biodiesels reflected the fatty acid composition of feedstock. A typical gas chromatogram of the obtained methyl esters is shown in Fig. 3. The biodiesels consisted mainly of methyl esters of palmitic (C16:0), stearic (C18:0), oleic (C18:1), and linoleic (C18:2) acids, which also occurred in large amounts in the feedstock. Mittelbach[27] proposed to limit the content of unsaturated fatty acids in biodiesel, especially unsaturated fatty acids such as linolenic acid (C18:3). The maximum content of linolenic acid in the MEs obtained in this study was less than 0.4 mass %.

CONCLUSIONS

The production of biodiesel by alkali two-step transesterification of waste frying oil (WFO) with an acid value higher than 2 mg KOH/g is feasible without any previous treatment under the conditions applied in this study. On varying the type of the catalyst (NaOH or KOH), the methanol/oil mole ratio (6:1 or 9:1) and the catalyst/oil mass ratio (1 mass % and 1.5 mass %) it was found that the investigated characteristics of the methyl esters (MEs) were not influenced significantly by the transesterification parameters. The exception was the acid va-
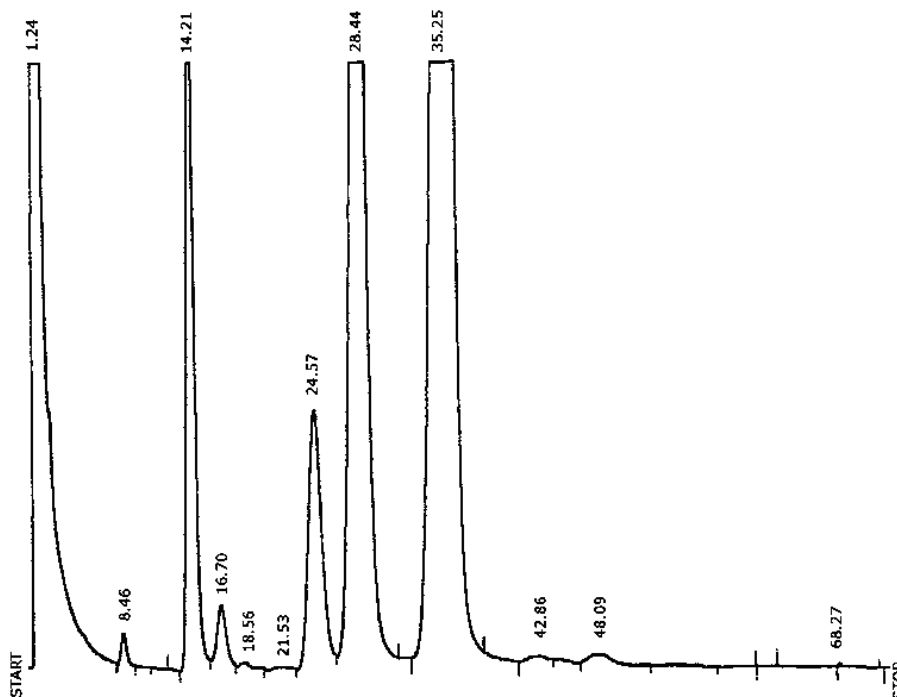
Fig. 3. Typical gas chromatogram of the investigated methyl esters obtained by transesterification of waste frying oil.

lues obtained with the higher methanol/oil ratio, but further investigations are required in order to elucidate the found deviations. Good agreement was observed between the experimental and calculated iodine and saponification values of MEs, suggesting that the results of gas chromatographic analysis of the composition of the fatty acid methyl esters could be satisfactory used for the predicttion of these properties as an alternative to the experimental procedures. The reaction conditions influenced the yields of the produced biodiesel in a following way: KOH induced a more efficient conversion of WFO to MEs than NaOH; higher yields were obtained with the lower catalyst/oil ratio (1.0 mass%) than with the higher (1.5 mass %). In the case of KOH, the methanol/oil mole ratio had no marked influence on the yield of MEs.

И З В О Д

ДОБИЈАЊЕ БИОДИЗЕЛА ИЗ ОТПАДНОГ УЉА БАЗНО-КАТАЛИЗОВАНОМ ТРАНСЕСТЕРИФИКАЦИЈОМ

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Испитиван је утицај параметара трансестерификације на принос и квалитет метил естра, МЕ, добијеног из коришћеног, отпадног уља. Алкална трансестерификација је вођена у два степена, а за пречишћавање сировог метил естра коришћен је силика гел. Варирани су реакциони параметри: однос алкохол/уље (6:1 и 9:1), масени однос катализатор/уље (1 и 1,5 mass %) и тип катализатора (NaOH и КОН). Одређене су физичко-хемијске карактеристике коришћене сировине и добијеног биодизела, да би се испитао утицај и сировине и параметара реакције на карактеристике и принос продукта. Уочено је да карактеристике сировине имају одлучујући утицај на физичко-хемијске карактеристике метил естара. Већина од одређених карактеристика се значајно не разликују за испитиване параметре реакције. Међутим, реакциони параметри имају утицај на принос производа. Већи принос се добија при односу катализатор/уље 1,0 у односу на 1,5 mass %. Принос се повећава смањењем односа катализатор/уље и то изразитије за NaOH (9,15–14,35 %) у односу на КОН (2,84–6,45 %). Принос је увек већи при коришћењу КОН катализатора (средња вредност приноса је 94,86 %) у поређењу са приносом добијеним са NaOH (средња вредност приноса је 84,28 %). Штавише, ефикасност КОН у степену конверзије сировине у пречишћен МЕ је изразитија при већем односу метанол/уље, односно при односу метанол/уље 9:1, остварен принос са КОН је већи у односу на принос са NaOH, без обзира на однос катлизатор/уље. Релативно повећање приноса са КОН је два пута веће у односу на NaOH.

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