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Transesterification of linoleic and oleic sunflower oils to biodiesel using CaO as a solid base catalyst

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Abstract: The purpose of this work was to characterize biodiesel (*i.e.*, methyl esters, MEs) produced from linoleic and oleic sunflower oils (LSO and OSO, respectively) by alkali transesterification with methanol using CaO as a heterogeneous catalyst under different reaction conditions. The parameters investigated were the methanol/oil mole ratio (4.5:1, 6:1, 7.5:1, 9:1 and 12:1) and the mass ratio of CaO to oil (2 and 3 %). The physical and chemical properties of the feedstocks and the MEs, such as density at 15 °C, kinematic viscosity at 40 °C, acid value, iodine value, saponification value, cetane index and fatty acid (methyl ester) composition, were determined in order to investigate the effects of the properties of the LSO and OSO and reaction parameters on the product characteristics, yields and purity. The properties of the feedstocks had a decisive effect on the physical and chemical properties of the MEs. The studied reaction conditions did not significantly affect the properties of the MEs. The produced MEs generally met the criteria required for commercial biodiesel; in fact, the only exception was the iodine value of the ME produced from LSO. The product yields only slightly changed with the applied conditions; the highest yield (99.22 %) was obtained for the ME-LSO produced at 6 mol % methanol to oil ratio, while the lowest one (93.20 %) was for ME-OSO produced under the lowest methanol/oil mole ratio (4.5:1). The applied amounts of catalyst had a similar influence on the oil conversion to biodiesel. The yields of the ME-LSOs were, in general, somewhat higher than those obtained for the ME-OSOs under the same conditions, which was attributed to the influence of the respective acid value and viscosity of the feedstock.

Keywords: biodiesel; calcium oxide; heterogeneous catalysis; transesterification; linoleic and oleic sunflower oils.

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INTRODUCTION

Biodiesel is a non-petroleum-based fuel defined as fatty acid methyl or ethyl esters produced by transesterification of triglycerides, the main constituents of vegetable oils or animal fats, with a short chain alcohol (methanol or ethanol) in the presence of a suitable catalyst. This fuel may be regarded as a mineral diesel substitute with the advantage of reducing greenhouse emissions because it is a renewable resource. However, the high cost of biodiesel is the major obstacle for its commercialization. An important contribution to the final cost arises from the catalytic transesterification. The primary commercial process used today for biodiesel production is alkali catalyzed transesterification, performed in batch or continuous stirred tank reactors at temperatures ranging from 60 to 200 °C using homogeneous catalysts, most frequently NaOH or KOH dissolved in methanol.¹ However, the use of homogeneous base catalysts requires neutralization and a difficult separation from the final reaction mixture, which lead to a series of environmental problems related to the use of high amounts of solvents and energy. Furthermore, the operational problems in the conventional production process are associated with the catalyst (*e.g.*, NaOH and KOH) because they are hazardous, caustic and corrosive.¹ Replacement of the homogeneous catalysts by heterogeneous solid catalysts has various advantages, such as, lower consumption of the catalysts, easier separation from the reaction mixture and the possibility of recycling the catalyst, lower production costs and less environmental endangerment since there is no need for purification of waste effluents. Therefore, the possibility of replacing the homogeneous with heterogeneous solid catalysts in biodiesel production is of increasing interest. In recent years, a considerable research effort is being devoted to the heterogeneous catalyzed methanolysis of vegetable oils. As a result, a great variety of catalysts, such as alkali earth metals oxides and hydroxides,²⁻⁴ alkali metals hydroxides or salts supported on γ -alumina,⁵⁻⁷ zeolites,⁸ hydrotalcites,⁹ *etc.*, have hitherto been used under different reaction conditions and with variable degrees of success.

Among the alkali earth oxides, CaO is one of the solids that has displayed higher transesterification activities.^{10,11} The application of CaO as a solid base catalyst for soybean oil transesterification was investigated by Liu *et al.*³ and a reaction mechanism was proposed. The catalyst lifetime was longer than that of calcined $K_2CO_3/\gamma-Al_2O_3$ and $KF/\gamma-Al_2O_3$ catalysts. CaO maintained its activity even after being repeatedly used for 20 cycles and the biodiesel yield at 1.5 h was not substantially affected in the repeated experiments. Granados *et al.*² studied the activity of activated CaO as a heterogeneous catalyst in the conversion of sunflower oil to biodiesel. They demonstrated that CaO could be reutilized for eight runs without significant deactivation, stressing the possibility of its use as compared with the conventional homogeneous catalyst, KOH dissolved in methanol. Even though the transesterification activity of CaO is not as large as that

of KOH or NaOH homogeneous catalysts, this could be compensated for by employing a larger concentration of CaO, as long as the CaO can be reutilized for a greater number of runs.² Veljković *et al.*⁴ examined the methanolysis of sunflower oil in the presence of CaO in order to determine the optimal temperature for CaO calcination.

The purpose of this work was to study the transesterification of two types of sunflower oils, differing in their unsaturated fatty acids profiles (*i.e.*, primarily in their contents of linoleic and oleic acids), to biodiesel using methanol and CaO, as a solid base catalyst. The aim was to investigate the effects of the properties of the feedstocks and the transesterification reaction conditions, such as the methanol/oil molar ratio and the catalyst/oil mass ratio, on the properties, yields and purity of the obtained methyl esters. This is the first study that explores simultaneously the heterogeneous conversion of these two types of sunflower oils to biodiesel.

EXPERIMENTAL

Materials and methods

To prepare biodiesel by alkali catalyzed transesterification, linoleic and oleic sunflower oils (LSO and OSO, respectively) were used. Since there is insufficient information on the working parameters for the heterogeneous CaO transesterification of such oils, especially of OSO, it was decided to work with refined oils, despite the fact that they cost much more than the biodiesel to be produced from them; similarly, many researchers have used refined edible oils in the first stages of their studies in order to investigate the influence of the basic properties of the oily feedstocks and of the working conditions on the properties and yields of the obtained biodiesel, thereby avoiding the introduction of impurities into the process.^{3,12-15} Methanol chromatographic grade (99.9 %), and CaO (ReagentPlus 99.9 % trace metals basis) in a form of powder were supplied by Aldrich, while the reference standard for the gas chromatographic determination of the fatty acid methyl esters was obtained from Supelco (Bellefonte, USA). Concerning the CaO powder, the supplier notes that *ca.* 10 % of the mass is lost by calcinations at 1000 °C, indicating that CaO was partially carbonated and hydrated. Such CaO was stored under vacuum in a desiccator with silica gel and KOH pellets to remove H₂O and CO₂ from the residual desiccator atmosphere, as previously described by *Granados et al.*²

Transesterification procedure

Methyl esters were synthesized in a batch type reactor using CaO powder as the catalyst. All experiments were performed in a three-neck round-bottom flask equipped with a thermometer, reflux condenser and magnetic stirrer, which was immersed in a water bath. In all batches, 150 g of oil was used in the reaction. The transesterification reaction was performed using different methanol/oil mole ratios (4.5:1, 6:1, 7.5:1, 9:1 and 12:1) and various amounts of catalyst relative to the mass of oil (2 and 3 %). The mixture was vigorously stirred at 400 rpm and at 65 °C (*i.e.*, around the boiling point of the mixture) under methanol reflux for the required reaction time of 1.5 h, in accordance to a previous study of Liu *et al.*³ According to the results of Liu *et al.*,³ the chosen temperature of 65 °C is an optimum reaction temperature for the transesterification of oil to biodiesel using solid CaO; it was found that at lower temperatures, reaction rate was slow and the biodiesel yield was low, while a more rapid reaction

rate could be obtained at higher temperatures, but at temperatures higher than 65 °C, the methanol vaporized and formed a large number of bubbles that could inhibit the reaction on the interfaces in the three-phase system methanol–oil–catalyst.³ After completion of the reaction, the mixture was poured into a separation funnel and left for separate for 12 h. The upper layer of esters was then filtered through filter paper and the residual methanol from the filtrate was removed *via* rotary evaporation (at 60 °C and 20 kPa) prior to analysis. A similar transesterification procedure was used previously but with different solid base catalysts, *i.e.*, CaO,³ NaX zeolite with a KOH coating⁸ and KNO₃ loaded alumina.^{5,6}

Characterization of feedstocks and methyl esters

Most of the physical and chemical properties of the used feedstocks (LSO and OSO) and the obtained methyl esters (designated as ME-LSO and ME-OSO, respectively) were determined by the methods listed in the SRPS EN 14214:2005 standard,¹⁶ which defines the requirements and test methods for fatty acid methyl esters (FAME) for use in diesel engines.

Measurements of the density at 15 °C by hydrometer method and of the kinematic viscosity at 40 °C were realized according to SRPS EN ISO 3675:2005¹⁷ and SRPS ISO 3104:2003,¹⁸ respectively. The acid value (AV) was determined by titration in accordance to EN 14104:2003;¹⁹ the iodine value (IV) was obtained by the Hannus method (EN 14111:2003).²⁰ Even though it is not required by SRPS EN 14214:2005,¹⁶ the saponification value (SV) was also determined using the titration method described in EN ISO 3657:2003.²¹ This property was previously used for biodiesel characterization.^{22–25} The method for the estimation of the cetane index (CI) based on the saponification (SV) and iodine (IV) values was previously described²⁶ as simpler and more convenient than the experimental procedure for the determination of the cetane number utilizing a cetane engine (SRPS ISO 4264:2002).²⁷ For CI calculation, the Krisnangkura Equation as follows was used:²⁶

$$CI = 46.3 + 5458/SV - 0.225IV \quad (1)$$

This equation is not recommended for feedstock characterization as it was previously documented that the cetane indices of oils are generally much lower than those of methyl ester derivatives despite the fact that they have similar SVs and IVs.²⁶ Thus, a discussion on the CI of the feedstocks will not be made.

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

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

Principal component analysis (PCA)

PCA is a multivariate analytical tool used to reduce a set of original variables and to extract a small number of latent factors (principal components, PCs) for analyzing relationships among the observed variables (*i.e.*, physical and chemical properties of biodiesels in this study) and for classification of samples (*i.e.*, biodiesels produced under different working conditions). The newly extracted variables, *i.e.*, PCs, are linear combinations of the original ones and are sorted in descending order according to the amount of variance that they account for in the original set of variables. The loadings express how well the principal components correlate with the old variables. PCA shows which kinds of variables are similar to each other, *i.e.*, carry comparable information, and which ones are unique. Relationships among the samples could be seen on the score plots, whereas the loading plots show the extent to which each variable contributes to the sample separation (grouping). Alternatively, variable loadings and sample scores can be combined into a unique graphical presentation called a biplot. Since

the magnitude of the loadings and scores are not the same, it is advisable to divide each loading and score value with respect to the maximum value obtained for a particular PC; in this way, the biplot presents the relative positions of the element loadings and the sample scores within the range from -1 to $+1$. Thus, the interpretation of the correlations among variables and their impact on the classification of the samples could be more evident. It is also possible to search for the possible presence of outliers using PC biplots. Outliers are in fact measurements that are far removed from the others in the plot because they have exceptionally high and/or low concentrations of the variables.²⁸⁻³⁰

In this study, the input data set consisting of columns with physical and chemical properties determined in this investigation and of rows with biodiesels produced under different conditions were firstly mean-centered (column means subtracted from each matrix element). Then each matrix element was divided by the standard deviation of the respective column and the established matrix was submitted to PCA. The number of PCs extracted from the variables was determined by the Kaiser Rule.³¹ This criterion retains only PCs with eigenvalues that exceed one. The algorithm of PCA can be found in standard textbooks.³²

RESULTS AND DISCUSSION

Effects of the properties of the feedstocks on the biodiesel properties

The physical and chemical properties of the LSO and OSO used as the feedstocks for transesterifications are given in Table I.

TABLE I. Physical and chemical properties of linoleic (LSO) and oleic (OSO) refined sunflower oils used as feedstocks for methyl esters preparation by heterogeneous transesterification

Property	LSO	OSO
Density at 15 °C, g cm ⁻³	0.927	0.920
Kinematic viscosity at 40 °C, mm ² s ⁻¹	25.75	30.32
Acid value, mg KOH g ⁻¹ oil	0.05	0.41
Iodine value, g I ₂ per 100 g	134.16	107.03
Saponification value, mg KOH g ⁻¹ oil	194	191
Fatty acid composition, mass %		
C16:0 Palmitic	6.18	5.20
C18:0 Stearic	3.98	3.36
C18:1 Oleic	21.13	58.91
C18:2 Linoleic	66.79	32.24
C18:3 Linolenic	<0.20	0.20
C20:0 Arachidic	0.20	<0.20
C22:0 Behenic	0.67	<0.20
C24:0 Tetracosanoic	0.24	<0.20
Total unsaturated	87.92	91.35
Total saturated	11.27	8.56

It could be seen that the main differences between the used feedstocks were in acid and iodine values, and the contents of oleic and linoleic acids. The OSO had an almost 3 times higher content of oleic acid, while its acid values was 8 times higher than that of LSO. However, this higher acid value was still far

below the recommendation given for the acid value of feedstocks of less than 2 mg KOH g⁻¹ (*i.e.*, 1 %) ²⁴ for the case of alkaline transesterification. The LSO had a 2 times higher content of linoleic acid and 1.25 times higher iodine value than the OSO. The remaining characteristics analyzed in oils did not differ by more than 1.2 times, and some of the observed differences coincided with the observation of Purdy,³³ who found that high oleic sunflower oils had higher viscosities and lower densities, and lower iodine and saponification values than the “normal” (linoleic) oils, as direct consequences of the higher oleic acid content.

The physical and chemical properties of methyl esters obtained from LSO and OSO (ME-LSO and ME-OSO, respectively) on application of different conditions during the transesterification are given in Tables II and III, respectively.

TABLE II. Characterization of the methyl esters obtained from linoleic sunflower oils (ME-LSO) by transesterification under different experimental conditions (Av. – average values of the parameters)

Parameter	Methanol:oil mole ratio										Av.	RSD %	
	4.5:1		6:1		7.5:1		9:1		12:1				
	Catalyst:oil, mass %												
	2	3	2	3	2	3	2	3	2	3			
Density at 15 °C, kg m ⁻³	889	889	886	887	886	886	887	886	887	886	887	0.13	
Kinematic viscosity at 40 °C, m ² s ⁻¹	4.29	4.25	4.15	3.96	3.98	4.07	3.93	3.76	4.43	4.01	4.08	4.86	
Acid value, mg KOH g ⁻¹ oil	0.05	0.09	0.05	<0.04	0.06	<0.04	0.06	0.06	0.05	0.04	0.06	25.88	
Iodine value, g I ₂ per 100 g	130	129	131	133	131	131	131	131	131	130	131	0.79	
Saponification value, mg KOH g ⁻¹ oil	178	182	187	188	186	185	184	189	178	188	184	2.17	
Cetane index (CI)	47.8	47.2	46.1	45.6	46.3	46.7	46.4	45.8	47.5	46.2	46.6	1.57	
Fatty acid methyl ester composition, mass %													
Palmitic	C16:0	6.78	6.47	6.42	6.30	6.69	6.68	7.06	6.73	6.43	6.39	6.59	3.53
Stearic	C18:0	3.75	3.43	3.55	3.35	3.28	3.48	3.70	3.39	3.71	3.34	3.50	4.89
Oleic	C18:1	22.1	22.8	21.8	23.4	23.8	22.6	22.2	22.5	21.7	22.5	22.6	3.00
Linoleic	C18:2	67.3	67.1	68.1	65.7	65.9	67.2	67.1	67.3	67.2	66.6	66.9	1.04

To gain a better insight into the latent structure (hidden regularities) of the obtained data and to investigate similarities and dissimilarities of the produced biodiesel samples, PCA was applied on the determined physical and chemical properties and the biplot is shown in Fig. 1. Two PCs were retained explaining 86.3 % of the total variance in the data. A clear separation of MEs synthesized from LSO and OSO was obtained on the PC1 vs. PC2 biplot (Fig. 1), with all the ME-LSOs located on the right side of the plot and all the ME-OSOs on the left. The variables governing the sample separation were those with the highest load-

ings on PC1, *i.e.*, iodine value, density and the contents of C16:0-, C18:0-, and C18:2-methyl esters, which had positive loadings, and the cetane index and the content of methyl ester of the C18:1 acid that had negative PC1 loadings. Due to higher contents of the C16:0-, C18:0-, and C18:2- methyl esters, and also of higher iodine values, the ME-LSOs were clearly separated from the ME-OSOs, characterized by a higher cetane index and content of C18:1-methyl ester than the former. The outliers were the biodiesels obtained from both types of feedstocks using the lowest methanol/oil mole ratio (4.5:1) and the ME-LSO obtained with a 12:1 mole ratio of methanol to oil and 2 mass % of catalyst to oil, and ME-OSO synthesized with a 6:1 mole ratio of methanol to oil and 2 mass % of catalyst to oil.

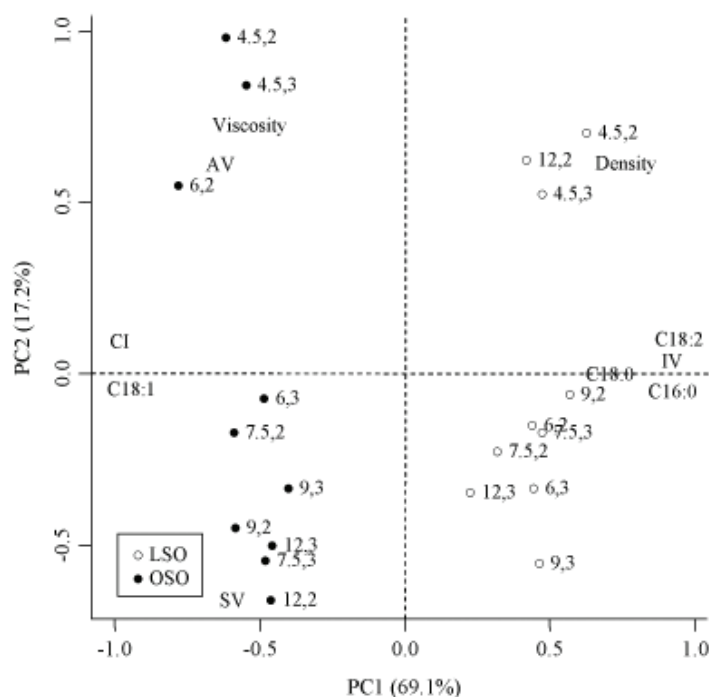


Fig. 1. The PCA biplot PC1 vs. PC2 obtained for the input data set consisting of the physical and chemical properties of the biodiesel produced under the investigated experimental conditions (the first digit indicates the molar ratio of methanol to oil, while the second is mass percentage of catalyst to oil). Percentages given in parentheses are the shares of the total variance explained by each PC.

Density at 15 °C

Fuel density is a property important mainly in airless combustion systems because it influences the efficiency of the fuel atomization.³⁴ The small difference seen between density values of the feedstocks (LSO and OSO, Table I) was also observed between the respective methyl esters (ME-LSO and ME-OSO,

Tables II and III); namely, regardless of the applied working parameters, the ME-LSOs produced from LSO, which was slightly denser than OSO, always had slightly higher densities than the ME-OSOs. This was expected since it is a well-known fact that biodiesel density is influenced primarily by the choice of vegetable oil and, to some extent, by the applied purification steps, since it depends primarily on the content of methyl esters and slightly on the quantity of residual methanol (up to 0.2 % m/m according to SRPS EN 14214^{16,24}). The mean values of density for ME-LSOs and ME-OSOs were 0.887 and 0.884 g cm⁻³ (Tables II and III) with deviations lower than 0.20 %, calculated as the relative standard deviation, *RSD* (ratio of the standard deviation and the average value of all values obtained for a particular property of the MEs from one feedstock, regardless of the working conditions, multiplied by 100). This implied that working parameters applied in this study had no influence on the densities of the MEs, coinciding with the fact that this biodiesel characteristic depends primarily on the origin of the feedstock.³⁵ The percentages of the decrease in density between the feedstocks and the corresponding methyl esters (calculated as the ratios of the density differences between a particular SO and ME and the initial density values for the SO multiplied by 100) were about 4 %. This reduction rate was very similar to the one obtained in a previous study of Predojević,²⁴ who obtained a 5 % reduction of the densities of the feedstocks when a homogenous two-step alkali transesterification procedure was applied on waste frying sunflower oils. Obviously, regardless of the feedstock and the system applied (homogenous or heterogeneous), the density of feedstocks could be reduced by ≈4–5 % on alkali transesterification. All MEs met the density value specified by SRPS EN 14214,¹⁶ *i.e.*, were within the range 0.860–0.900 g cm⁻³ at 15 °C.

TABLE III. Characterization of methyl esters obtained from oleic sunflower oil (ME-OSO) by transesterification under different experimental conditions (Av. – average values of the parameters)

Parameter	Methanol:oil mole ratio										Av.	<i>RSD</i> %
	4.5:1		6:1		7.5:1		9:1		12:1			
	2	3	2	3	2	3	2	3	2	3		
Density at 15 °C, kg m ⁻³	887	887	884	884	883	883	883	884	883	882	884	0.19
Kinematic viscosity at 40 °C, m ² s ⁻¹	4.78	4.86	4.75	4.30	4.14	4.40	4.35	4.23	4.03	4.18	4.40	6.66
Acid value, mg KOH g ⁻¹ oil	0.38	0.23	0.36	0.11	0.20	<0.04	0.08	0.05	0.10	0.05	0.16	80.8
Iodine value, g I ₂ per 100 g	104	102	105	102	101	102	103	103	105	103	103	1.29
Saponification value, mg KOH g ⁻¹ oil	187	186	188	186	187	192	191	188	191	187	188	1.18
Cetane index (<i>CI</i>)	52.0	52.8	51.7	52.7	52.9	51.7	51.7	52.2	51.1	52.1	52.1	1.11

TABLE III. Continued

Parameter		Methanol:oil mole ratio										Av.	RSD %
		4.5:1		6:1		7.5:1		9:1		12:1			
		Catalyst:oil, mass %											
		2	3	2	3	2	3	2	3	2	3		
Fatty acid methyl ester composition, mass %													
Palmitic	C16:0	5.08	4.92	4.84	5.73	4.90	4.85	5.16	5.40	4.90	5.06	5.08	5.61
Stearic	C18:0	3.06	3.25	2.79	2.96	3.04	3.49	2.96	3.29	3.30	3.27	3.14	6.74
Oleic	C18:1	59.6	58.9	58.5	59.6	58.1	57.4	60.1	58.9	59.6	57.92	58.8	1.51
Linoleic	C18:2	32.2	32.6	32.6	31.7	33.6	33.2	31.8	32.7	32.1	33.6	32.6	2.10

Kinematic viscosity at 40 °C

Even more than density, the kinematic viscosity at 40 °C is an important property regarding fuel atomization and distribution. The viscosities of the ME-LSOs were slightly lower than those of the ME-OSOs (Tables II and III, respectively), as was the case for the viscosities of their respective feedstocks (Table I). The average viscosity of the ME-LSOs was 4.08 mm² s⁻¹, while that of the ME-OSOs was 4.40 mm² s⁻¹. The respective *RSD* values were 4.86 and 6.66 %, respectively, which coincide with the *RSD* values calculated for the contents of fatty acid (primarily stearic) methyl esters in the produced MEs. Thus, the observed dispersion of the viscosities among the MEs could be ascribed to the changes of viscosities influenced by slight changes in the FAME composition of the MEs. The produced methyl esters met the required values that must be between 3.5–5.0 mm² s⁻¹.¹⁶

The viscosities of the MEs were about 6–7 times lower than those of their respective oils. The average decrease in the viscosities going from the feedstocks to the corresponding MEs due to the applied transesterification method was about 85 % (calculated by dividing the difference between the viscosities of the SO and the respective ME with the viscosity of the SO, and finally multiplying by 100 to obtain the percentage value). A similar reduction rate for the viscosity (≈ 89 %) was obtained in a previous study of Predojević,²⁴ in which a homogenous two-step alkali transesterification procedure for biodiesel production from the waste frying sunflower oils was applied.

Acid value

The acid value measures the content of free fatty acids in sample, which have influence on fuel aging. It is measured in terms of the quantity of KOH required to neutralize sample. As it has been previously mentioned, base catalyzed transesterification is very sensitive to the content of free fatty acids in the feedstocks, which should not exceed 2 mg KOH g⁻¹ recommended as a limit to avoid deactivation of the catalyst, and the formation of soaps and emulsions.²⁴ In this

study, the acid values of the feedstocks were well below this limit, since refined oils were used (due to reasons explained previously), which did not have a decisive influence on the efficiency of the applied process. The acid values of the MEs were less than $0.5 \text{ mg KOH g}^{-1}$, specified as the maximum allowed value according to SRPS EN 14214.¹⁶ The average acid value of the ME-LSOs was 0.06 mg KOH g with an *RSD* of $\approx 26 \%$ (Table II), while of ME-OSOs it was $0.16 \text{ mg KOH g}^{-1}$ with an *RSD* of $\approx 81 \%$ (Table III). The *RSD* value for the ME-LSOs could not be ascribed to the influence of the different working parameters on the acid values, since all the values were rather small ($<0.04\text{--}0.09 \text{ mg KOH g}^{-1}$), *i.e.*, near the method detection limit and also similar to the value determined for the LSO ($0.05 \text{ mg KOH g}^{-1}$); thus, the calculated *RSD* ($\approx 26 \%$) more probably reflects the experimental error in the acid values determination at levels near the detection limit. However, the acid values of the ME-OSOs covered a wider range ($<0.04\text{--}0.38 \text{ mg KOH g}^{-1}$) than was the case with the values for the ME-LSOs, indicating, most probably, an influence of the different working conditions on this property. In Table III, it could be seen that higher acid values were obtained for the ME-OSOs produced using the lower methanol/oil mole ratios (4.5:1 and 6:1) and the lower catalyst/oil mass ratio (2 %). Apparently, no (or only a very slight) neutralization of the free fatty acid in the SO by CaO occurred in these cases. With a methanol/oil ratio of 7.5:1, a 50 %-reduction of the initial acid value of the feedstock was achieved with 2 % catalyst/oil mass ratio, while acid value was reduced below the method detection limit when the catalyst/oil mass ratio was 3 %. With the two highest levels of the methanol/oil molar ratios applied in this study (9:1 and 12:1), the acid values of the produced methyl esters were very low and comparable with the ones obtained under the same conditions from LSO.

Iodine value

The iodine value (*IV*) is a measure of the average amount of unsaturation of fats and oils and is expressed in terms of the number of centigrams of iodine absorbed per gram of sample (or g I_2 per 100 g oil, *i.e.* % of iodine absorbed by the oil).³⁶ The MEs obtained in this study had *IV*s in a very narrow range, *i.e.*, 129–133 g I_2 per 100 g for ME-LSO and 101–105 g I_2 per 100 g for ME-OSO. The higher iodine values of the ME-LSOs could be related to their higher content of linoleic acid with two double bonds (C18:2), since *IV* is proportional to the number of double bonds and the amount of a fatty compound.³⁶ Comparing the iodine values of the SOs and the respective MEs, it could be seen that this property was not influenced by the transesterification procedure, since the MEs had almost the same iodine values as their feedstocks. Obviously, this property depends strongly on the feedstock origin and this finding could be supported by the low

RSD values calculated for the *IVs* of the MEs, irrespective of the applied working parameters (Tables II and III).

The *IV* is currently the most usual parameter for assessing the oxidative stability of biodiesel, since it is well known that the auto-oxidation of unsaturated fatty compounds proceeds at rates depending on the number and position of the double bonds.³⁷ The rationale is that the higher the unsaturation of biodiesel, the higher the tendency of the unsaturated compounds to polymerize and form engine deposits. Many automotive biodiesel standards specify an upper *IV* limit for fuel; for example, Europe's EN 14214¹⁶ standard allows a maximum of 120 g I₂ per 100 g of biodiesel for use as diesel fuel, Germany's DIN 51606³⁸ set maximum *IV* at 115 g I₂ per 100 g, while according to the South African Standard SANS 1935³⁹ for biodiesel, *IV* of biodiesel should be less than 140 g I₂ per 100 g. The USA ASTM D6751⁴⁰ does not specify the *IV* as a requirement for biodiesel. It should be emphasized that the European and German specifications result in a *de facto* ban on soy-based biodiesel, which often have *IV* higher than 120 g I₂ per 100 g (*e.g.*, 120–143 g I₂ per 100 g).³⁶ Furthermore, virgin sunflower oils are also known for typically higher iodine values (*e.g.*, 110–143 g I₂ per 100 g) because of their higher levels of unsaturated fatty acids, primarily linoleic acid (two double bonds) than other vegetable oils (*e.g.* the *IVs* of corn, palm and rapeseed oils are in ranges 103–128 g I₂ per 100 g, 50–55 g I₂ per 100 g, and 94–120 g I₂ per 100 g, respectively).³⁶ Accordingly, the ME-LSOs with *IVs* higher than the limit of 120 g I₂ per 100 g (Table II) were not in compliance with the biodiesel standard SRPS EN 14214,¹⁶ while the ME-OSOs met this requirement. However, there are some studies implying that higher *IVs* of ME-LSOs (ranged from 129–133 g I₂ per 100 g, Table II) do not necessarily indicate an unsuitable oxidative stability of the biodiesel. Namely, Knothe³⁶ explained that the difference between the *IV* of rapeseed methyl esters (115) and soy methyl ester (131) was low, not causing engine deposition. Moreover, Prankl *et al.*⁴¹ found no significant differences in engine use of rapeseed methyl ester, sunflower methyl ester and camelina methyl ester, which had *IVs* of 107, 132, and 150, respectively. There is some evidence that, for example, storage conditions may have a greater influence on oxidation than the *IV*.⁴²

Saponification value

The saponification value (*SV*) represents the milligrams of KOH required to saponify one gram of fat or oil. The *SV* of fatty acid methyl esters increases with decreasing molecular mass; for instance, the *SV* of methyl palmitate is 207.45, while those of methyl oleate, linoleate and linolenate are 189.23, 190.53 and 191.84 mg KOH g⁻¹.³⁶ For biodiesel, the overall *SV* depends on the amount of each ester and its molecular mass (*i.e.*, individual *SV*).

The results in Tables II and III indicate that the produced esters had saponification values similar to those of the corresponding oils; namely, the mean value for the ME-LSOs was 184 mg KOH g⁻¹ oil (5 % lower than the initial SV of the feedstock LSO, Table I), while for the ME-OSO, the average value was 188 mg KOH g⁻¹ oil (1.6 % lower than the initial SV of the feedstock OSO, Table I). This was not surprising knowing that a triglyceride has 3 fatty acid chains; hence, each triglyceride will give 3 methyl esters during transesterification; thus, stoichiometrically, it may be expected that the same number of fatty acid carbon chains in the neat feedstock oil and the biodiesel will react with the same amount of KOH giving soaps, *i.e.*, their SVs will be the same. It should be noted that in this study, the SV was determined only for the purpose of calculating the cetane index according to Krisnangkura.²⁶ The SV is not a restricted property of biodiesel according to the EU and the Serbian standards, for this reason, it was not regularly determined in the relevant literature studies. For the MEs produced in the study of Šiler-Marinković and Tomašević²³ from sunflower seeds by *in situ* transesterification and for those produced from waste frying sunflower oils in the study of Predojević,²⁵ the respective SVs were 179–186 mg KOH g⁻¹ oil and 204–212 mg KOH g⁻¹ oil. Thus, the MEs obtained in the present study had saponification values in the range of those found in the literature.

The low levels of the RSDs obtained for the SVs of the MEs (Tables II and III) indicated that the working conditions of the transesterification reaction did not influence this property. Thus, the results clearly indicated that the SV of the biodiesel originated from the feedstock quality.

Cetane index

As an alternative to the cetane number, the cetane index is also an indicator of ignition quality of a fuel and it is related to the time that passes between injection of the fuel into the cylinder and onset of ignition.⁴³ Krisnangkura²⁶ proposed Eq. (1) for the estimation of cetane index (*CI*) based on the SV and IV, recommending it not be used for oils, only for methyl esters. Namely, it was previously documented that despite the fact that triglycerides (*i.e.*, feedstock oils) and the respective MEs have similar SVs and IVs, as was also obtained in this study, the cetane indices of oils are generally much lower than those of the corresponding methyl ester derivatives.⁴⁴ Thus, the *CI* values of the SOs were not calculated. In this work, the ME-LSOs had lower *CI* values (the mean was 46.6) than the ME-OSOs (the mean was 52.1). Šiler-Marinković and Tomašević²³ also used the *CI* for the characterization of methyl esters produced from crude (linoleic) sunflower oils, and the estimated values ranged from 49.7 to 50.9. The differences between the *CI* values of the respective MEs expressed as the RSD values were rather low (below 1.6 %, see Tables II and III) regardless of the applied working param-

ters, implying that *CI* was also a property influenced primarily by the feedstock origin.

Fatty acid composition

The compositions of fatty acid methyl esters of the produced biodiesels are presented in Tables II and III; only the major components are given, not those present in amounts equal to or less than 1 mass %. It could be seen that the biodiesels had almost the same composition as the feedstocks (Table I). The ME-LSO consisted mainly of linoleic (C 18:2) > oleic (C 18:1) > palmitic (C 16:0) > stearic (C 18:0) acids, while oleic acid (C 18:1) was dominant in the ME-OSOs over linoleic (C 18:2) > palmitic (C 16:0) > stearic (C 18:0) acids. Regardless of the applied working parameters, similar fatty acid profiles were observed in the biodiesels with *RSDs* of up to about 7 %. Thus, it could be concluded that applied transesterification conditions did not change the methyl ester composition of the feedstocks.

Effects of the properties of the feedstocks and the working parameters on biodiesel yield and purity

The changes in the biodiesel yield as a function of the methanol/oil molar ratios and the catalysis/oil mass ratios are graphically illustrated in Fig. 2. The product yield is defined as mass percentage of final product relative to the initial mass of oil introduced into the transesterification.⁴⁵ The results presented in Fig. 2

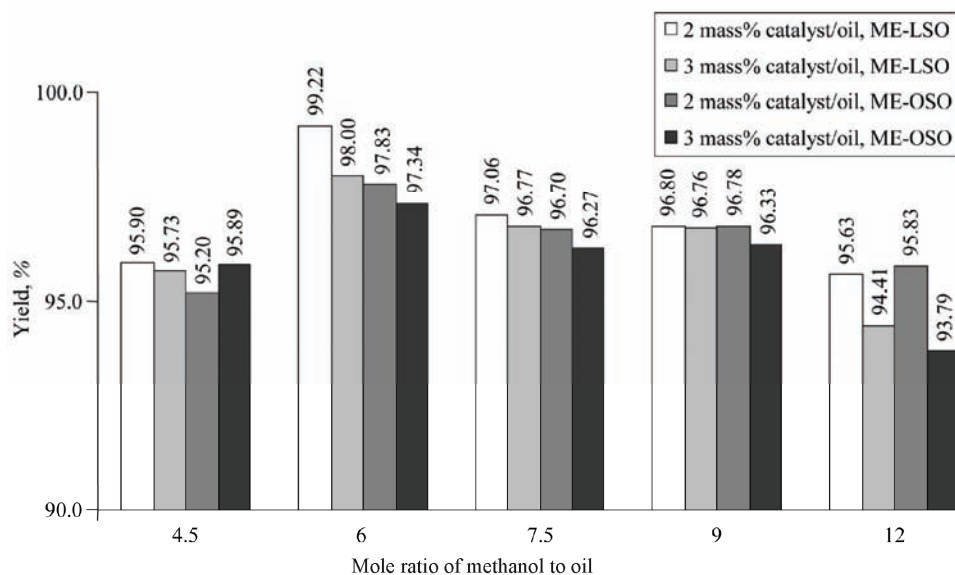


Fig. 2. Effects of the methanol to oil mole ratio and of the catalyst to oil mass ratio on the biodiesel yield.

show that the yields were rather similar with slightly higher values obtained at a methanol/oil ratio of 6 mol % and when the lower amount of catalyst relative to oil was used. To be more specific, the highest yield of $\approx 99\%$ (Fig. 2) was obtained by transesterification of LSO at a CaO/oil mass ratio of 2 % and a methanol/oil ratio of 6:1.

The molar ratio of methanol to oil is one of the important parameters that affect the conversion to methyl esters. Stoichiometrically, 3 moles of methanol are required for each mole of triglyceride; but, in practice, the presence of a sufficient amount of methanol during the transesterification reaction is essential to break the glycerin–fatty acid linkages and to improve the biodiesel yields by shifting the equilibrium to the right-hand side of the reaction.^{46,47} The employment of excess methanol is also one of the better options for improving the rate of the heterogeneous transesterification reaction, which is diffusion-controlled dependent on mass transfer in a three phase (oil–methanol–catalyst) system.⁴⁶ When the mass transfer is limited in the system, it could be much slower than the reaction rate. On the other hand, excess methanol should be avoided, since it also decreases the catalyst content,³ leading to lower yields, as can be seen for the methanol/oil ratio of 12:1 used in this study (Fig. 2). The product yield was not increased with increasing the methanol/oil mole ratio beyond 6:1; however, it should be taken into account that at a slightly higher methanol amount, as was previously discussed, a more intensive acid value reduction was seen for the ME-OSOs.

The effect of the different amounts of CaO on the biodiesel yield was negligible; a kinetic study at shorter reaction time (<1.5 h) would probably have shown more obviously that the 3 % catalyst results in a faster reaction. The most obvious differences in the yields were observed at the methanol/oil ratio of 12:1, when $\approx 1.5\%$ lower yields were obtained for a mass ratio of CaO to oil (either LSO or OSO) of 3 % (Figure 2). Nevertheless, this could also be ascribed to dilution of the catalyst due to the excess of methanol, as mentioned previously. However, the differences between the yields obtained for different mass ratios could be regarded as negligible and this might also be the consequence of a similar and limited dissolution of CaO in methanol (0.035 mass %) previously studied by Granados *et al.*² Namely, they reasoned that if the reaction is caused by active homogeneous species related to the dissolution of CaO in methanol, similar yields should be obtained on using different loadings of catalyst, since the presence of homogenous species is in principle controlled by the solubility product of the solid in the reaction media and therefore a constant value of dissolved CaO should be obtained irrespective of the CaO amount used in catalytic reaction.

The yields of the ME-LSOs were in general somewhat higher than those obtained for the ME-OSOs under the same conditions. Since the main differences between the feedstocks, LSO and OSO, were in their acid values and viscosity (Table I), it might be presumed that these parameters also influenced the bio-

diesel yields. This is in agreement with previous observations of Felizardo *et al.*³⁴ and Predojević,²⁵ who found that the lowest biodiesel yields after alkali transesterification were obtained with more acidic feedstocks, because of the more pronounced deactivation of the catalyst and the soap formation by the free fatty acids from the feedstock. Moreover, Leung and Guo⁴⁵ concluded that a higher viscosity of the oil could also have a negative impact on the product yield, slowing down dissolution of the oils in the methanol and reducing the contact between oil and methanol molecules, consequently leading to a lower conversion of triglycerides. Thus, slightly higher yields of the ME-LSOs over the ME-OSOs could be ascribed to the lower acid value and the viscosity of the LSO compared to the OSO.

The purity of biodiesel product denoted by its ester content is defined as the mass percentage of methyl esters in the final product. In fact, it closely represents the percentage of triglycerides converted to methyl esters.⁴⁵ The purity of the ME-LSO produced with the highest yield under a methanol/oil mole ratio of 6:1 and a catalyst/oil mass ratio of 2 % is shown in Fig. 3. According to SRPS EN 14214,¹⁶ the minimum acceptable purity for biodiesel is 96.5 % in methyl esters. With respect to the obtained results (Fig. 3), the produced biodiesel satisfied this requirement.

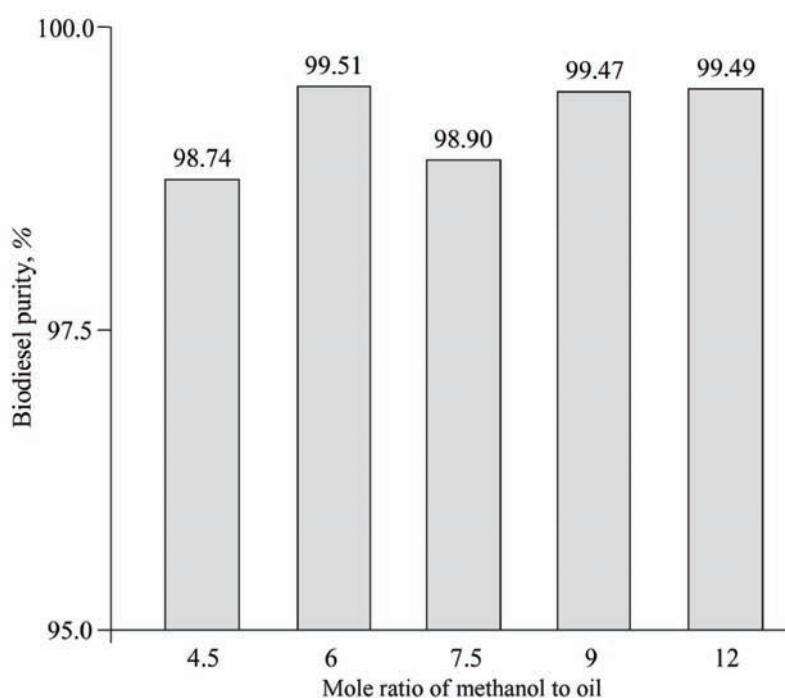


Fig. 3. Purity of methyl esters obtained by heterogeneous alkali transesterification of linoleic sunflower oil with a catalyst/oil ratio of 2 mass % and different methanol/oil ratios.

CONCLUSIONS

The feedstock origin has a detrimental impact on the physical and chemical properties of the produced biodiesel. Of all the biodiesel properties analyzed, the acid value seems to be the only one influenced by the reaction conditions varied in this study. The heterogeneous transesterification of sunflower oils with different amounts of unsaturated fatty acids could be efficiently accomplished using a 6:1 mole ratio of methanol to oil, with either a 2 or a 3 % CaO/oil mass ratio, and holding the reaction mixture at 65 °C for 1.5 h. The results also indicated that a higher methanol/oil ratio could be favorable in the case of a feedstock with a higher acid value, since under such conditions, reduction of the acid value in the biodiesel would be more pronounced. The biodiesel produced generally met the criteria required of a diesel substitute; in fact, the only exception was in the case of the iodine value of the biodiesel produced from the feedstock with iodine value higher than the value required by the SRPS EN 14214 standard,¹⁶ which defines the requirements for fatty acid methyl esters to be used in a diesel engine, since this property remained almost unchanged during the transesterification reaction. However, there is evidence that a biodiesel with an iodine value of ≈ 130 g I₂ per 100 g oil would be oxidatively stable. The yields of the biodiesels were above 93 %, while their purities were above the minimum acceptable purity value of 96.5 %, according to SRPS EN 14214¹⁶

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ИЗВОД

ТРАНСЕСТЕРИФИКАЦИЈА СУНЦОКРЕТОВОГ УЉА ЛИНОЛНОГ И ОЛЕИНСКОГ ТИПА У БИОДИЗЕЛ КОРИШЋЕЊЕМ СаО КАО БАЗНОГ КАТАЛИЗАТОРА

ЗЛАТИЦА Ј. ПРЕДОЈЕВИЋ, БИЉАНА Д. ШКРБИЋ И НАТАША ЂУРИШИЋ-МЛАДЕНОВИЋ

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Сврха овог рада је карактеризација биодизела (тј. метил естера, МЕ) произведеног из сунцокретовог уља линолног и олеинског типа (ЛСУ и ОСУ, респективно) алкалном трансестерификацијом са метанолом и СаО хетерогеним базним катализатором, под различитим реакционим условима. У току реакције варијације су следећи параметри: молски однос метанол/уље (4,5:1; 6:1; 7,5:1; 9:1 и 12:1) и масени однос СаО према уљу (2 и 3 %). Испитивана су следећа физичко-хемијска својства сировине и МЕ, као што су: густина на 15 °C, кинематска вискозност на 40 °C, киселински број, јодни број, сапонификациони број, цетански индекс, састав масних киселина (метил-естера), у циљу испитивања утицаја ЛСУ и ОСУ и параметара реакције на принос, чистоћу и карактеристике произведеног биодизела. Својства сировина имала су изразити утицај на физичка и хемијска својства МЕ, међутим, вредности већине карактеристика МЕ, нису се значајно разликовале варирањем услова реакције. Генерално, карактеристике добијеног МЕ задовољавају стандардом прописане критеријуме комерцијалног биодизела, а једини изузетак је вредност једног броја МЕ произведеног од сунцокретовог уља ЛСУ типа. При испитиваним реакционим условима постиже се незнатна промена приноса; највећи принос (99,22 %) добијен је за МЕ-ЛСУ произведеног при мол-

ском односу метанол/уље 6:1, а најнижи (93,20 %) је за МЕ–ОСУ при најнижој вредности молског односа метанол/уље (4,5:1). Масени односи катализатор/уље су имали сличан утицај на конверзију уља у биодизел. Приноси МЕ–ЛСУ су нешто већи у односу на приносе МЕ–ОСУ под истим реакционим условима, што се може објаснити утицајем киселинског броја и вискозности одговарајуће сировине.

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