THE INFLUENCE OF FATTY ACID COMPOSITION ON THE KINETICS OF THE VEGETABLE OIL METHANOLYSIS REACTION

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The base-catalyzed methanolysis of roadside pennycress, olive, melon, grape-seed, hempseed, sunflower, and plum kernel oils was performed in the presence of KOH (1% to the oil weight) at the temperature of 60 °C and the methanol/oil molar ratio of 6:1. The aim of this work was to reveal the influence of the fatty acid composition of the oils on the kinetics of these methanolysis reactions. The irreversible pseudo-first-order reaction was used for modeling the kinetics of the methanolysis reactions, and the reaction rate constant was correlated with the content of unsaturated fatty acids in the oil. The value of the reaction rate constant increases linearly with increasing the unsaturated fatty acids content in the oil. The applicability and reliability of the model were confirmed by high values of the coefficient of determination and low values of the mean relative percentage deviation between the calculated and experimental triacylglycerols conversion degree.

Keywords: biodiesel; kinetics; methanolysis; oil; unsaturated fatty acids

Introduction

The global warming problems and the growing demand for fuel are leading the scientific community to search for new fuel types. Special attention has been paid to biodiesel, bioethanol, and biogas. Biodiesel is one of the promising fuels that consisting of a mixture of fatty acids alkyl esters. It is most often obtained by transesterification of triacylglycerols (TAG) with low aliphatic alcohols in the presence of a catalyst. Methanol is the most frequently used alcohol, due to its higher reactivity, lower price, and easy availability compared to ethanol.

The use of biodiesel as a widespread fuel is still limited by its price, which is mostly influenced by the TAG source, as much as 75% of the total biodiesel price [1]. Currently, edible vegetable oils, such as rapeseed, palm, soybean, and sunflower oil, are the most used feedstocks for biodiesel production, but they are primarily used in human nutrition. Therefore, many researchers are directed towards the utilization of non-edible and waste oily feedstocks as TAG sources. So far, many inedible oils [2-6], waste oils from food preparation [7-10], as well as animal fats [11-15], have been used successfully in the fatty acids alkyl esters synthesis. Also, the sources of TAG, having different fatty acid compositions, greatly affect the biodiesel properties. From the biodiesel quality point of view, oily feedstocks for biodiesel production should contain as small as possible a content of polyunsaturated fatty acids because the oils rich in polyunsaturated fatty acids have low oxidative

stability and a high iodine value.

The widely used catalysts for biodiesel production are homogeneous base catalysts due to their high catalytic activity and low price. The main drawbacks of these catalysts are the impossibility to catalyze the alcoholysis of low-quality oily feedstocks containing high free fatty acids (FFA) amounts and the fact that they cannot be reused, as well as the need for biodiesel purification that generates huge wastewater. Some disadvantages of homogeneous catalysts could be overcome by using heterogeneous and enzyme catalysts that have been intensively investigated recently. So far, calcium oxide has been widely used in heterogeneously catalyzed alcoholysis due to its availability, low price, and simple handling. The various waste materials have been used as calcium oxide sources, such as eggshells of different poultry species [16,17], mollusk shells [18,19], and agricultural biomass [20-23]. Some researchers have also dealt with increasing the activity of calcium oxide in the production of biodiesel, by adding organic [24] and eutectic solvents [25] as cosolvents.

The kinetic modeling is of crucial importance for the simulation, control, techno-economic analysis, improvement, and development of processes at pilot and industrial scales. Different kinetic models have been used in the previous kinetic studies of the homogeneously catalyzed methanolysis. According to one group of researchers, the kinetics of the overall methanolysis reaction can be described as an irreversible pseudo-

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first-order reaction [26-30]. On the other side, some researchers suggest the irreversible pseudo-second-order kinetic model [2,10]. A more complex reaction mechanism consisting of three consecutive reversible reactions following the second-order reaction kinetics has also been used [31,32].

The present paper deals with the methanolysis of the oils obtained from roadside pennycress, melon, hemp, sunflower, olive, and grape seeds, as well as plum kernels. The major aims are to investigate the influence of oils' fatty acid composition on the reaction rate and to model the kinetics of these methanolysis reactions. The methanolysis reaction kinetics is modeled by the irreversible pseudo-first-order reaction. The obtained reaction rate constants are correlated with the unsaturation degree of the tested oils.

Experimental

Materials and chemicals

Grapeseed oil (GO), olive oil (OO), and sunflower oil (SO) were purchased in a local supermarket and hempseed was procured at a local market. Roadside pennycress was harvested on the Pasjača Mountain (south of Serbia) while melon seeds and plum kernels were collected from a household (Žitorađa, Serbia). Before use, the seeds and kernels were stored in paper bags in a dark room. Methanol and *n*-hexane (both HPLC grade) were obtained from Promochem LGC (Germany), and 2-propanol, also HPLC grade, from Carlo Erba (Italy). Hydrochloric acid (36.5%) and KOH (85%) were purchased from Centrochem (Serbia) and Merck-Alkaloid (FYR of Macedonia), respectively.

Recovery and characterization of the oils

Roadside pennycress oil (RPO), hempseed oil (HO), and plum kernels oil (PO) were obtained by cold pressing using a hydraulic oil press (Komet, Germany) through 8 mm nozzles. The obtained oils were filtered under vacuum to remove the residual solids. The extraction of melon seed oil (MO) was carried out in a Soxhlet apparatus using *n*-hexane as a solvent at a solvent-to-seed ratio of 10:1 v:w for 3 h. The obtained liquid extract was evaporated at 50 °C under vacuum (Hei-VAP, Heidolph, Germany) to constant weight.

Acid and iodine values of the obtained oils were determined by AOCS official methods [33]. The fatty acid composition of the oils was determined by gas chromatography after their methylation as described elsewhere [34].

Equipment, reaction conditions, and experimental procedure of the oil methanolysis

Methanolysis of the tested oils was carried out in a three-neck flask (250 ml) equipped with a reflux condenser and a magnetic stirrer (600 rpm). The flask was set in a thermostated water bath at the desired reaction temperature. The reactions were performed at methanol/oil molar ratio 6:1, in the presence of KOH as a catalyst

(1% based on the oil weight) at 60 °C and under atmospheric pressure. Initially, the reactor was charged with the desired amounts of methanol and KOH, and the mixture was thermostated at 60 °C. Afterward, the oil (thermostated separately) was added to the reaction flask and the reaction was timed. The reaction mixture samples (0.5 ml) were taken during the reaction and immediately neutralized by an HCl solution (11%vol) to stop the reaction. The oily-ester layer was separated by centrifugation (Sigma, Germany) at 3,500 rpm and dissolved in 2-propanol:*n*-hexane (5/4 v/v) mixture in the ratio of 1:200, filtered through a 0.45 µm Millipore filter, and analyzed by the HPLC method [35]. The TAG conversion degree (x_A) was calculated from the TAG content in the reaction mixture at the beginning and any time of the reaction (TAG_0 and TAG , respectively, in %) using the Eq. (1):

$$x_A = 1 - \frac{TAG}{TAG_0} \dots \dots \dots (1)$$

Modeling the methanolysis reaction kinetics

The methanolysis reaction consists of three reversible, simultaneous reactions through which TAG is stepwise converted to diacylglycerol, monoacylglycerol, and glycerol. In every reaction step, one mol of methyl ester is obtained. The following overall reaction has mostly been used for the kinetic modeling:

where A is TAG, B is methanol, R is FAME, and S is glycerol

In modeling the methanolysis reaction, it is assumed that:

a) the reaction mixture is a pseudo-homogeneous system having a uniform composition due to an intensive agitation (600 rpm), so the overall reaction is controlled by chemical reaction and there are no mass transfer limitations,

b) the methanolysis reaction is considered as irreversible pseudo-first-order with respect to TAG because of the methanol excess,

c) the neutralization and saponification reactions can be neglected due to an insignificant FFA content in the oils and a low initial catalyst amount.

Based on the assumptions a) and b), the TAG conversion rate can be expressed by Eq. (3) [10]:

$$(-r_A) = -\frac{dc_A}{dt} = k_1 \cdot c_A \dots \dots \dots (3)$$

where k_1 is the rate constant of the irreversible pseudo-first-order reaction, C_A is the TAG concentration and t is time. If the TAG concentration, C_A , is expressed via the TAG conversion degree, x_A , and the initial TAG concentration is C_{A0} , the following equation is obtained:

$$(-r_A) = -\frac{dc_A}{dt} = k_1 \cdot c_{A0} \cdot (1 - x_A) \quad (4)$$

and after integration:

$$-\ln(1 - x_A) = k_1 \cdot t \quad (5)$$

The rate constant for the irreversible pseudo-first-order reaction can be obtained as the slope of the linear dependence $-\ln(1 - x_A) = f(t)$.

Results and discussion

Fatty acid compositions of the oils

In Table 1, acid and iodine values and fatty acid compositions of the used oils, the oil yield in the case of oils recovered either by cold pressing or solvent extraction of seeds, the total amount of saturated and unsaturated fatty acids, and the average number of carbon atoms in the fatty acid chain (CL) are presented.

Generally, there are differences in the qualitative composition of the used oils. Palmitic and stearic acid are the dominant saturated fatty acids (SFA) while the major unsaturated fatty acids (UFA) are oleic, linoleic,

and linolenic acid. The content of behenic acid was significant in RPO and low in HO while it was not detected in the other oils. Linolenic, arachidic, eicosenoic, and behenic acids were not detected in PO. Palmitic acid is the most abundant SFA except in RPO that is rich in behenic acid. The most present UFA in RPO, OO, and PO is oleic acid while linoleic acid is the major fatty acid in MO, GO, HO, and SO. The quantitative composition of the tested oils varied. However, all oils are rich in UFA with content in the range from 73.42 to 92.61% while the content of SFA is significantly lower and amounts from 7.31% to 26.38%. The determined iodine values are in accordance with the fatty acid composition of the oils; HO, GO, SO, and MO, which contain predominantly linoleic acid (>56%) have higher iodine values. Such high iodine values of these oils can limit their use in biodiesel production since the European biodiesel standard EN 14214 restricts iodine value to 120 g I₂/100 g. However, this problem can be solved by using bifunctional catalysts [36] or by adding natural antioxidants [37]. The acid values of the oils are below 2 mg KOH/g, so the FAME synthesis can be performed by direct base-catalyzed methanolysis.

Table 1. Fatty acid composition of the oils

Oil	RPO	OO	MO	GO	HO	SO	PO
Extraction method	Pressing	Commercial (pressing)	Soxhlet	Commercial (pressing)	Pressing	Commercial (pressing, solvent extraction)	Pressing
Oil yield, g/100 g	18.16	-	26.05	-	26.89	-	33.84
Acid value, mg KOH/g oil	1.37	0.64	0.68	0.44	0.78	0.35	1.98
Iodine value, g I ₂ /100 g	99.3	80.0	126.2	133.9	153.2	128.9	98.6
C16:0, %	5.82	12.44	9.23	6.72	6.25	6.85	5.59
C18:0, %	1.84	2.68	5.37	3.93	2.96	3.45	1.72
C18:1, %	36.05	74.77	23.70	22.82	13.99	29.31	70.85
C18:2, %	33.27	8.54	60.50	65.62	56.33	59.60	21.76
C18:3, %	4.10	0.24	0.10	0.18	15.63	0.12	
C20:0, %	1.37	0.90	0.16	0.20	0.93	0.04	
C20:1, %		0.42	0.96	0.21	3.47	0.15	
C22:0, %	17.35				0.47		
SFA, %	26.38	16.02	14.76	10.85	10.61	10.34	7.31
UFA, %	73.42	83.97	85.26	88.83	89.42	89.18	92.61
CL	18.51	17.65	17.75	17.75	17.92	17.71	17.82

Base-catalyzed methanolysis

The change of the reaction mixture composition with time in the case of the PO methanolysis is presented in Figure 1. The same dependencies were observed for all used oils. The FAME content increased rapidly at the beginning of the reaction, indicating that the mass transfer did not limit the methanolysis reaction rate. After the period of the fast FAME formation, the reaction rate decreased, and FAME content increased slowly and finally reached equilibrium. The content of TAG decreased during the reaction following the increase

of FAME content. The contents of MAG and DAG first increased, reached a maximum, and then decreased and remained almost constant. Generally, the MAG and DAG contents in the reaction mixture were very low due to their fast conversion rate.

Figure 1 The change of the reaction mixture composition with the progress of the PO methanolysis (• - FAME, ▲ - MAG, ■ - DAG, ○ - TAG)

Figure 2 shows the variations of FAME content with time in the methanolysis of RPO, OO, MO, GO, HO, SO, and PO. As can be seen, the FAME synthesis is lowest in the case of the RPO methanolysis and fastest in the PO methanolysis, which can be attributed to the increase of the TAG conversion rate with the increase of the UFA content in the oil. The influence of oil composition on FAME synthesis was observed by other researchers who reported that the methanolysis reaction is faster in the case of oils with a higher unsaturation degree and longer fatty acid hydrocarbon chains [38-40,15].

Figure 2 The variation of FAME content during the methanolysis of various oils

Modeling the methanolysis reaction kinetics

To model the kinetics of the overall methanolysis reaction of all used oils, the irreversible pseudo-first-order reaction rate law was accepted. According to Eq. (5),

Figure 3 shows the dependence $-\ln(1 - x_A) = f(t)$. The rate constants of the irreversible pseudo-first-order reactions are calculated from the slope of the linear correlation and their values are presented in Table 2. It can be concluded that the rate constant increases with increasing the UFA content in the oils from RPO to PO. Additionally, Table 2 shows the irreversible pseudo first-order reaction rate constants for methanolysis reactions of several other oily and fatty feedstocks like heated lard (HL), lard (L), and waste lard (WL) [15], waste cooking oil (WCO) [10], *Onopordum acanthium* L. seed oil (OAO) [2], and *Sinapis alba* L. seed oil (SAO) [4] conducted under the same reaction conditions (temperature of 60 °C, methanol/oil molar ratio of 6:1 and 1% of KOH). The increase of the reaction rate constant with increasing the UFA content in the lard was observed by Stojković et al. [15].

Figure 3 Plots of $-\ln(1 - x_A)$ versus time during the methanolysis of various oils (temperature 60 °C, methanol/oil molar ratio 6:1, and 1% of KOH)

Figure 4 shows the rate constant of the irreversible pseudo-first-order reaction as a function of UFA content in the oily and fatty feedstocks used in the methanolysis reactions. Generally, the rate constant can be linearly fitted with the UFA content, with the exception of OAO and SAO. This deviation could be explained by differences in the agitation intensity applied in different methanolysis reactions. The agitation intensity in the SAO methanolysis was 400 rpm [4], which was lower compared to that applied in the methanolysis of the other feedstocks (600 rpm). The influence of agitation speed on the reaction rate was already observed, and the reaction was faster if the agitation was more vigorous [41,42]. Therefore, the reaction of OAO was slower compared to other oily feedstocks. Furthermore, OAO had a higher acidity (2.89 mg KOH/g) than the recommended value for the base catalyzed methanolysis; so that the FAME synthesis from OAO was performed in two steps, i.e., by acid catalyzed esterification followed by the base-catalyzed

methanolysis [2]. The presence of FAME in the initial reaction mixture positively influenced the reaction rate since FAME acted as a mutual solvent for the immiscible reactants and increased the interfacial area and consequently the reaction rate [3,43]. The higher OAO methanolysis rate was a result of the FAME content in the oil formed in the esterification of the original oil. The

reaction rate constants, with exception of OAO and SAO, were linearly correlated with the TAG unsaturation degree ($R^2 = 0.992$):

$$k_1 = 0.01834 \cdot UFA(\%) \quad (6)$$

where k_1 is calculated by Eq. (6).

Table 2. Rate constants for the irreversible pseudo-first-order reaction (values of rate constants are mean values of two experiments)

Oil	SFA, %	UFA, %	k_1 , min ⁻¹	R^2	MRPD, %*	Data	Ref
RPO	25.01	73.42	1.179	0.988	±2.7	9	This work
OO	16.02	84.87	1.393	0.997	±0.8	11	
MO	14.78	85.21	1.455	0.988	±2.2	11	
GO	10.86	89.14	1.544	0.996	±2.7	12	
HO	10.61	89.39	1.607	0.999	±2.2	12	
SO	10.35	89.65	1.619	0.988	±7.0	12	
PO	7.32	92.68	1.935	0.983	±3.8	12	
HL	54.97	45.03	0.949	0.967	±1.5	10	[15]
L	45.61	54.39	1.060	0.965	±1.6	11	[15]
WL	38.28	61.68	1.163	0.997	±3.7	11	[15]
WCO	10.87	88.79	1.805	0.970	±2.1	10	[10]
OAO	8.43	91.17	2.337	0.980	±3.9	12	[2]
SAO	2.61	97.36	1.196	0.984	±4.7	8	[4]

* values were calculated by Eq. (7) using the values from Eq. (6)

Figure 4 The dependence of k_1 on the UFA content in the feedstocks: RPO, OO, MO, GO, HO, SO, PO (this work), HL, L, WL [15], WCO [10], OAO [2], and SAO [4]

The validity of the irreversible pseudo-first-order kinetic model was checked by comparing the calculated and experimental values of TAG conversion degree with the progress of the methanolysis reaction. The TAG conversion degree is calculated by the following equation:

$$x_A = 1 - \exp(-k_1 \cdot t) \quad (7)$$

Figure 5 The comparison of the irreversible pseudo-first kinetic models (line) and the experimental data (symbols) during methanolysis of RPO, OO, MO, GO, HO, SO and PO

As can be concluded from Figure 5, there is a good agreement between the model and the experiment, which is confirmed by the low value of the mean relative deviation percentage (MRPD) (±3.1% for 79 data). The reliability of the used kinetic model was also evaluated based on the values of the coefficient of determination (R^2) for the linear dependences shown in Figure 3 and

the *MRPD* between the calculated and experimental values of TAG conversion degree for each oil type (Table 2). In addition, the model was verified for OAO and SAO that were not included in the analysis of dependence of the reaction rate constant on UFA content. The low *MRPD* value between experimental and calculated value of the conversion degree of OAO and SAO ($\pm 3.9\%$ and $\pm 4.7\%$, respectively) validated the developed model.

Conclusion

The kinetic study of the RPO, OO, MO, GO, HO, SO, and PO methanolysis catalyzed by KOH showed that the reaction was controlled by chemical reaction while the reaction rate was influenced by the unsaturation degree of the oils. The conversion of TAGs into FAMES followed the irreversible pseudo-first-order reaction kinetics. The reaction rate constant was linearly related to the UFA content in the oil. It was highest in the case of the PO methanolysis and lowest for RPO methanolysis. The used model is reliable for describing the methanolysis reaction rate as confirmed by a very good agreement between the model and the experiment data.

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Izvod

UTICAJ SASTAVA MASNIH KISELINA NA BRZINU REAKCIJE METANOLIZE BILJNIH ULJA

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Bazno katalizovana metanoliza ulja iz semena smrdljive čestike, semena dinje, konoplje, jezgra šljive, kao i maslinovog, suncokretovog i ulja iz semenki grožđa je vršena u prisustvu KOH (1%, računato na masu ulja), temperaturi od 60 °C i molskom odnosu metanol:ulje 6:1. Cilj ovog rada je modelovanje kinetike reakcije transesterifikacije i ispitivanje uticaja masno-kiselinskog sastava ulja na konstantu brzine reakcije konverzije triacilglicerola u metil estre masnih kiselina. Za modelovanje reakcije metanolize biljnih ulja korišćen je model nepovratne reakcije pseudo-prvog reda, a konstanta brzine reakcije je korelisana sa udelom nezasićenih masnih kiselina u ulju. Vrednosti konstante brzine reakcije povećavaju se linearno sa povećanjem udela nezasićenih masnih kiselina u ulju. Visoke vrednosti koeficijenta determinacije i niske vrednosti srednjeg relativnog procentnog odstupanja primenjenog kinetičkog modela pokazuju da je model primnjljiv i pouzdan za modelovanje reakcije metanolize biljnih ulja.

Ključne reči: biodizel; kinetika; metanoliza; nezasićene masne kiseline: ulje