THE KINETICS OF BASE-CATALYZED METHANOLYSIS OF WASTE COOKING OIL

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The homogeneous base-catalyzed methanolysis of waste cooking oil (WCO) was investigated at a methanol:WCO molar ratio of 6:1, the initial KOH amount of 1% (based on the oil weight) and moderate temperatures (30 °C to 60 °C) with the aim to model the methanolysis reaction kinetics. It was observed that the methanolysis reaction occurred via a pseudo-homogeneous regime where the chemical reaction controls the overall process kinetics and with no mass transfer limitation. It was shown that irreversible pseudo-first and –second order reactions were reliable for describing the methanolysis reaction. However, a better fitting of experimental data was observed by using the irreversible pseudo-second order kinetic model. The reaction rate constant increased with increasing the reaction temperature and at 60 °C the WCO conversion of 97% was achieved in 3 minutes. The final products satisfied the EN 14214 biodiesel standard specifications.

Keywords: biodiesel; kinetics; methanolysis; waste cooking oil.

Introduction

Technological development, global warming and the increase of the environmental pollution have directed scientific research towards alternative and ecologically acceptable energy resources. One of them, biodiesel, which is a mixture of fatty acid alkyl esters (FAAE) derived from different renewable sources rich in triacylglycerols (TAG), has a great significance. The basic feedstocks for industrial biodiesel production are edible vegetable oils but their usage is restricted by their consumption in human nutrition and food industry, as well as by their high cost. In order to overcome these limitations, the researchers and biodiesel manufacturers focus their attention on using low-cost feedstocks such as waste cooking oil (WCO).

WCOs are promising feedstocks for the biodiesel production because of their lower price than that of pure edible vegetable oils, relatively easy availability and possibility for solving their dumping problems and pollution of the water and land resources [1]. An important fact is that the use of WCO as a feedstock reduces the biodiesel production cost by about 60–70% [1]. Although there is a lack of information of the worldwide WCO production, Lam et al. [2] have reported that there is enough WCOs to be considered as a significant feedstock for the biodiesel production. The biodiesel production from WCOs depends on their physico-chemical properties and primarily on their content of free fatty acids (FFAs) and water.

In the biodiesel production from WCOs, both catalyzed and non-catalyzed alcoholysis reactions have been employed. The homogeneously-catalyzed reaction is still most often used for the biodiesel production. Base-catalyzed alcoholysis is used for biodiesel synthesis from WCO with the lower content of FFA. Acid catalysts are suitable for the biodiesel production from WCOs with the high FFA content since they simultaneously catalyze esterification and the alcoholysis reaction [3]. Requiring stronger reaction conditions and longer time for completion, acid-catalyzed methanolysis is less important than the base-catalyzed reaction [4,5]. Two-step processes for the biodiesel production consisting of acid-catalyzed esterification of FFA in WCO and base-catalyzed methanolysis of the treated oil from the first step are promising for the biodiesel production from WCOs with the high FFA content. The use of acid catalysts allows the FFA conversion to alkyl esters, thus reducing the FFA content, and the alcoholysis of the treated oil over a base catalyst can be performed. A short review of one- and two-step processes for FAAE synthesis from WCOs is given in Table 1.

The knowledge of the alcoholysis reaction kinetics is fundamental for the process development and the reactor design, operation, scale-up, analysis and control. The alcoholysis reaction kinetics is necessary for establishing the mathematical model describing the reaction rate

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and the product yield. In the studies of homogeneously catalyzed methanolysis two stages are well-recognized. The initial heterogeneous stage is controlled by the mass transfer rate caused by the incomplete miscibility of the reactants, while the second, pseudo-homogeneous stage is chemically controlled.

The kinetics of the methanolysis reaction of various oily feedstocks is described by different kinetic models. Some of them are based on the stepwise reversible alcoholysis reaction [17,18] and include the side saponification reactions [19]. Recently, the models that assume the irreversible overall reaction have been more frequently used because of their simplicity, no complex computation and good accuracy. The most often used reaction kinetic models are irreversible pseudo-first order [20-26] or –second order [22,23,27-32] and irreversible pseudo-

second order followed by reversible second-order [33-37].

The present paper deals with the KOH-catalyzed methanolysis of the WCO collected from food cooking in a local household. The reaction was examined at a methanol:WCO molar ratio of 6:1, the initial KOH amount of 1% (based on the oil weight) and moderate temperatures (30 °C to 60 °C). The main aim was to model the reaction kinetics using simple irreversible reaction rate laws like pseudo – first and – second order, and to select the more appropriate one with respect of the goodness of fit and accuracy. Furthermore, the obtained ester product was purified and characterized in order to estimate its quality for the use as biodiesel.

Table 1. A review of one-and two-step processes of homogeneous catalyzed WCO alcoholysis

Feedstock	Type, volume of reactor, cm ³ / Type of agitator, agitation intensity, rpm	Alcohol	Alcohol:oil molar ratio, mol/mol	Catalyst/concentration ^a	Temperature, °C	Optimal reaction conditions Reaction conditions	Yield (Conversion), %/Time, h	Reference
One step processes								
WCO	Two-necked Woulf flask / Magnetic	Methanol	3.6:1-5.4:1	NaOH, 0.2-1%	65	4.8:1; 0.6%	≈90/1	[6]
WCO (olive and sunflower oil)	Spherical reactor, 500 / Mechanical	Methanol	3:1-9:1	NaOH, KOH, CH ₃ ONa, CH ₃ OK, 0.1-1.5%	25-65	6:1; KOH; 1%; 65°C	≈95/2	[7]
WCO	Flat bottom two necks flask, 500 / Magnetic	Methanol	3:1-10:1	KOH, 0.5-2.0%	70	6:1; 1%	98.2/1	[8]
WCO (sunflower oil)	Glass reactor ^b / Magnetic, 1100	Methanol	4:1-6:1	CH ₃ ONa, 0.5-1.5%	55-65	6:1; 1%; 60°C	(99)/0.08	[9]
WCO (sunflower oil)	-	Methanol	3:1-9:1	KOH, NaOH, 0.5 and 1.0%	25 and 65	6:1; 1% KOH; 65°C	96 /1	[10]
WCO (corn, sunflower and canola oils)	-	-	-	-	-	-	94.5 /1	-
WCO	Three-neck flask, 500 / Mechanical	Methanol	5:1-12:1	KOH, 0.5-1.5%	30-70	7:1-8:1; 0.75%, 30-50°C	88-90/1.3-1.5	[11]
WCO	Stainless-steel reactor, 5000 / Mechanical, 100-600	Methanol	50:1-250:1	H ₂ SO ₄ , 1.5-3.5 ^c	70 and 80	400 rpm: 245:1; 1.5 mol%: 80°C	99.4/4	[4]
WCO	Stainless steel continuous reactor	Methanol	50:1	H ₂ SO ₄ , 15%	80 ^d	-	(97)/4	[5]
WCO	-	Methanol	10:1-24:1	H ₂ SO ₄ , 3-6%	95	20:1; 4%	>90/10	[12]
Two-step (acid/base catalyzed) processes								
WCO	Round bottom two necks flask / Magnetic, 400	Methanol	3:1 – 20.3:1	H ₂ SO ₄ , 0.5-1.5%	45-55	6.1:1; 0.68%; 51°C	-/1	[13]
		Methanol	5.2:1 – 13:1	KOH, 0.5-1.5%	50-60	9:1; 1%; 55°C	90.6/1	
WCO		Methanol	30:1	H ₂ SO ₄ , 5%	65	-	-/3	[14]
		Methanol	15:1 – 35:1	KOH, 0.05-0.15%	60-70	25:1; 0.15%; 60°C	93.2/1	
WCO	Conical flask, 150 / Magnetic, 900 ^e	Methanol	0.5:1 – 0.8:1	H ₂ SO ₄ , 1 – 3%	60-66	0.8:1; 3%	(97.6)/0.13	[15]
		Methanol	14.2:1	NaOH, 0.91%	-	26-60°C	98.8/0.08	
WCO	Microtube reactor, i.d. 0.508 mm and length 1.2 m; Batch reactor	Methanol	4.5:1 – 18:1	H ₂ SO ₄ , 0.5 – 2%	55-70	Microtube reactor; 9:1; 1%; 65°C	(77.5)/0.001	[16]
		Methanol	4.5:1 – 12:1	KOH, 1%	65	9:1	91.8/0.001	

Theoretical background

For the purpose of modeling the kinetics of KOH-catalyzed methanolysis of WCO, the following assumptions are introduced:

a) The methanolysis reaction is shown by the following overall stoichiometric equation:

where A is TAG, B is methanol, R is fatty acid methyl esters (FAME) and S is glycerol.

It is considered that the overall reaction occurs in one step, although it actually occurs via three consecutive reversible reactions where TAG stepwise converted in glycerol and FAME. This assumption is proved by too small concentrations of mono- and diacylglycerols (MAGs and DAGs, respectively) because of their much faster consumption rates in comparison to that of TAGs.

b) Because of the agitation intensity of the reaction mixture, the reaction mixture is considered as a pseudo-homogeneous system without the mass transfer limitation, so the overall process kinetics is chemically controlled [38-40]. Also, the reaction mixture is perfectly mixed, ensuring its uniform composition.

c) The methanolysis reaction is an irreversible pseudo-first- or -second order reaction with respect to TAG [22,23,32]. Because of the excess of methanol and a low product concentration in the early reaction period, the reverse reactions are negligible.

d) The neutralization reaction of FFAs is ignorable because of their very low content (section 3.1). The saponification reaction is also negligible at the low initial catalyst amount and reaction temperature. Vicente et al. [41] showed that the saponification reactions were insignificant because it accounted for a FAME yield loss of no more than 3 mol% when the sunflower oil methanolysis was carried out at 65 °C, using 1% of KOH and a 6:1 sunflower oil:methanol molar ratio. We expected the FAME yield loss to be even lower for the reactions carried out at lower temperatures.

According to the assumption (c), the TAG conversion rate can be expressed as irreversible pseudo-first order or -second order kinetic law, respectively:

$$(-r_A) = -\frac{dc_A}{dt} = k_1 c_A \quad (2)$$

and

$$(-r_A) = -\frac{dc_A}{dt} = k_2 c_A^2 \quad (3)$$

where k_1 and k_2 are reaction rate constants for the irreversible pseudo-first and -second order reaction, respectively, and c_A is TAG concentration in the oil phase. Since:

$$c_A = c_{A0}(1 - x_A) \quad (4)$$

where X_A is TAG conversion degree, Eqs. (2) and (3) can be transformed into the following expressions, respectively:

$$\frac{dx_A}{dt} = k_1 c_{A0}(1 - x_A) \quad (5)$$

and

$$\frac{dx_A}{dt} = k_2 c_{A0}^2(1 - x_A)^2 \quad (6)$$

where c_{A0} is the initial TAG concentration. Taking into account the initial reaction condition ($t=0$, $x_A=0$), the integration of Eqs. (5) and (6) gives the following equations, respectively:

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

and

$$\frac{x_A}{1 - x_A} = k_2 c_{A0} \cdot t \quad (8)$$

The reaction rate constants k_1 and k_2 can be estimated from the slope of the linear dependence of $-\ln(1 - x_A)$ and

$$\frac{x_A}{1 - x_A} \text{ on } t, \text{ respectively.}$$

The significance of the model was statistically evaluated based on the mean relative percent deviation (MRPD) and the coefficient of determination (R^2) calculated by Eqs. (9) and (10), respectively:

$$MRPD = \frac{100}{n} \sum_{i=1}^n \left| \frac{x_{Apl} - x_{Aai}}{x_{Aai}} \right| \quad (9)$$

$$R^2 = \frac{\sum_{i=1}^n (x_{Apl,i} - x_{Aai,i})^2}{\sum_{i=1}^n (x_{Apl,i} - x_{Am})^2} \quad (10)$$

where X_{Ap} and X_{Aa} are predicted and experimental values of the TAG conversion degree, respectively, X_{Am} is the mean value of the TAG conversion degree (%) and n is the number of experimental runs.

Materials and methods

Materials

The used WCO was collected in a local household from food cooking using the commercial sunflower oil. The oil was used for several times at the cooking temperature of about 150 °C. The oil density and viscosity, determined at 20 °C, were 920 g/L and 108 mPa s, respectively. Having the acid value of 0.36 mg KOH/g, the WCO could be processed by the KOH-catalyzed methanolysis [42]. The iodine and saponification values of the oil were 128 g I₂/100 g and 184 mg KOH/g, respectively. The water content of the WCO, measured by the cou-

lometric Karl Fischer volumetric titration was 380 ppm (0.38%), which was slightly above the limited value of 0.3% [42]. The fatty acid composition of the WCO was determined by GC and GC-MS analysis [43]. The WCO consisted of palmitic (7.25%), stearic (3.47%), arachidic (0.15%), oleic (29.36%), linoleic (59.43%) and linolenic (0.14%) acid. Methanol (99.5%) and KOH (pellets; 85%) were from Zorka-Pharma (Serbia) and Lach-Ner (Czech Republic), respectively. HCl (36%) and anhydrous Na_2SO_4 were purchased from Centrohem (Serbia) and Sigma Aldrich (USA). HPLC grade methanol and *n*-hexane were obtained from Promochem LGC (Germany), while isopropanol was from Carlo Erba (Italy). HPLC standards for methyl esters and glycerides were obtained from Sigma Aldrich (USA).

Equipment, reaction conditions and procedure

The experiments were performed in a three-neck glass flask (250 mL) equipped with a condenser and a magnetic stirrer. The agitation intensity was kept constant at 600 rpm in all experiments by using a voltage regulator. The reactor was immersed in a glass chamber filled with water circulating from a thermostated bath in order to maintain the reaction temperature at desired levels. The methanolysis reaction of the WCO was carried out at temperatures 30, 45 or 60 °C, the 6:1 methanol:WCO molar ratio and the KOH amount of 1% (based on the oil weight) under atmospheric pressure.

Methanol (10.14 g) and KOH (0.4596 g) were agitated in the reactor at the desired temperature until the all catalyst amount was dissolved in methanol. The WCO (45.96 g) was thermostated separately and added to the reactor. As soon as the magnetic stirrer was turned on, the reaction was timed. During the reaction, the samples (1 mL) were removed from the reaction mixture, immediately quenched by adding a required amount of the aqueous HCl solution (11% vol.) to neutralize the KOH and then centrifuged (3500 rpm for 15 min). The upper layer was withdrawn, dissolved in the isopropanol/*n*-hexane (5:4 v/v) mixture in a ratio 1:200 and filtered through a 0.45 µm Millipore filter. The obtained filtrate was utilized for the HPLC analysis that gave contents of FAMES, TAGs, DAGs and MAGs in the ester/oil phase [33]. The conversion degree of TAGs during the reaction was calculated from the initial and actual (TAG_0 and TAG , respectively) content of TAGs (%) in the FAME/oil fraction as follows:

$$x_A = 1 - \text{TAG}/\text{TAG}_0 \dots\dots\dots (11)$$

FAME purification and characterization

After the reaction completion, the reaction mixture was poured into a separating funnel and left to separate in two (esters and alcohols) layers. The remained catalyst in the upper ester layer was carefully neutralized by adding the HCl solution (1 mol/L), which was gravitationally separate. Then, distilled water and the ester phase were mixed in the volume ratio of 1:5 in the separating funnel. After shaking, the two-phase mixture was left to

separate to the ester layer and the water phase. At the end, the washed ester phase was dried using anhydrous Na_2SO_4 that was removed by filtration. The final ester product was characterized according to the biodiesel standard methods.

Results and discussion

Analysis of methanolysis reactions

The change of the reaction mixture composition with time at 30 °C is shown in Figure 1. Generally, two reaction periods could be observed: the initial period during which the reaction was very fast, indicating no liquid-liquid mass transfer limitation, followed by the second period, longer than the first one, where the composition evolved slowly towards the reaction completion. Simultaneously, with the increase of the FAME content during the reaction, the TAG content decreased. The shapes of curves are typical for homogeneous base-catalyzed methanolysis of vegetable oils in the absence of mass transfer limitation in the initial reaction period. Depending on the reaction temperature, the FAME content of above 98 % was achieved at all three reaction temperatures, but for different reaction times. In the present study, the high FAME formation was obtained in a much shorter reaction time compared to the conversion degrees for WCO in the previous studies (Table 1). The MAG and DAG concentrations slowly increased in the initial reaction period, then decreased and stayed nearly constant at negligible levels up to the end of the reaction. These very low concentrations verified the assumption (a). At higher reaction temperatures (45 °C and 60 °C), the same type of variations of TAG, MAG, DAG and FAME concentrations were observed, provided that the FAME formation was much faster than that at 30 °C. The positive influence of the reaction temperature on the reaction rate was observed in the previous investigations of WCO methanolysis [7,9,10].

Figure 1. Variations of the reaction mixture composition with the progress of the methanolysis reaction at 30 °C (FAME - ●; MAG - ▲; DAG - ■; TAG - ○)

Modeling the kinetics of the WCO methanolysis reaction

The kinetic of the WCO methanolysis reaction was described by the irreversible pseudo-first and –second order reaction rate law with respect to TAG. In Figure 2, the dependences of $-\ln(1-x_A)$ and $x_A/(1-x_A)$ on time are shown. The observed linear dependences confirm Eqs. (7) and (8). The reaction rate constants k_1 and k_2 were calculated from the slope of the corresponding linear curves, and their values are given in Table 2 along with the coefficient of determination (R^2). As expected, the reaction rate constants increased with increasing the reaction temperature.

Figure 2. The irreversible pseudo-first (a) and irreversible pseudo-second order (b) reaction models of methanolysis at various reaction temperatures (● - 30 °C, ▲ - 45 °C and ■ - 60 °C)

The high values of R^2 confirmed the acceptability of both proposed kinetic models for describing the kinetic of the KOH-catalyzed WCO methanolysis. Slightly higher R^2 values were observed for the irreversible pseudo-second order reaction, thus indicating that it was more adequate for modeling the kinetics of WCO methanolysis. The accuracy of the applied kinetic models were

also compared based on the $MRPD$ (%) between corresponding predicted and actual values of TAG conversion degree. The value of $MRPD$ for irreversible pseudo-first and –second order kinetic models were $\pm 2.53\%$ and of $\pm 1.45\%$ (for 32 data), respectively. Based on the R^2 and $MRPD$ values, the irreversible pseudo-second order was accepted as more adequate for describing the kinetics of the base-catalyzed WCO methanolysis.

Table 2. Rate constants for the irreversible pseudo-first and –second order reaction

T (°C)	Irreversible pseudo-first order		Irreversible pseudo-second order	
	k_1, min^{-1}	R^2	$k_2, \text{dm}^3/(\text{mol}\cdot\text{min})$	R^2
30	0.384	0.979	1.381	0.991
45	0.949	0.949	4.625	0.989
60	1.805	0.970	11.16	0.990

The irreversible pseudo-second order kinetic model was the most appropriate for modeling the methanolysis reaction of *O. acanthium* L. oil [32] and sunflower oil after the initial mass transfer limitation [36]. The kinetics of base-catalyzed palm and sunflower oil ethanolysis [31,35] was also described by pseudo-second order reaction. Georgogianni et al. [22,23] found out that both irreversible pseudo-first and –second order reactions were reliable for modeling the base-catalyzed conventional (under mechanical stirring and ultrasonication) and *in situ* methanolysis of cottonseed and sunflower oil. However, due to higher R^2 value obtained for the first order reaction, they stated that the reaction was rather pseudo-first than second order.

For determining the activation energies for the KOH-catalyzed methanolysis of WCO, the Arrhenius equation was applied:

$$k = A \cdot \exp(-E_a/RT) \dots \dots \dots (12)$$

where A is the pre-exponential factor, E_a is the activation energy, and R is the gas constant. The values of the activation energy, calculated from the slope of the linear dependence of $\ln k$ vs $1/T$ (Figure 3), were 43.4 kJ/mol and 58.5 kJ/mol for irreversible pseudo-first and –second order reactions. Generally, these values are within the range of the activation energy for methanolysis of different oily feedstock [21,29,32,36,44].

Simulation of methanolysis process

The values of the TAG conversion degree for the irreversible pseudo-first and –second order reactions were calculated by Eqs. (13) and (14), respectively:

$$x_A = 1 - e^{-k_1 t} \dots \dots \dots (13)$$

$$x_A = \frac{k_2 C_{A0} t}{1 + k_2 C_{A0} t} \dots \dots \dots (14)$$

Figure 3. Arrhenius plot of reaction rate constants of TAG methanolysis versus reciprocal of temperature for irreversible pseudo-first (a) and irreversible pseudo-second order (b) reaction models

The comparison of the kinetic model and the experimental data is shown in Figure 4, where the variations of the TAG conversion degree with time are shown. The *MRPD* between the actual and predicted values of the TAG conversion degree at the temperatures of 30 °C, 45 °C and 60 °C were $\pm 3.3\%$, $\pm 2.4\%$ and $\pm 1.8\%$, respectively for the irreversible pseudo-first order kinetic model and $\pm 3.2\%$, $\pm 0.36\%$ and $\pm 0.48\%$, respectively for the irreversible pseudo-second order kinetic model. Lower values of *MRPD* observed for the latter model confirmed its slightly better accuracy in fitting the experimental data than the former model.

Figure 4. The comparison of the irreversible pseudo-first (a) and irreversible pseudo-second order (b) kinetic models (line) and the experimental data (symbols) during methanolysis at reaction temperatures: $\circ$ - 30 °C, Δ - 45 °C and $\square$ - 60 °C

Biodiesel properties

The characteristics of the final FAME product obtained by the WCO methanolysis are given in Table 3. For comparison, the characteristics of the esters obtained in the previously reported studies of the homogeneous base-catalyzed alcoholysis of WCO, as well as the specification of the biodiesel standard quality, are also presented in Table 3. The physico-chemical characteristics of the biodiesel from WCO generally satisfied the EN 14214 standard specifications. The exception was the iodine value, which was higher than the maximum value allowed by the European biodiesel standard EN14214. On the other side, the USA ASTM D6751 standard does not specify its value. Based on the new consideration, the limitation of the iodine value does not seem to be necessary [45].

Table 3. Properties of biodiesel produced from homogeneous base-catalyzed alcoholysis of WCO

Catalyst/Alcohol	KOH / Methanol	KOH / Methanol	KOH / Methanol	NaOCH ₃ / Ethanol	NaOH / Ethanol	EN14214
Property, unit						
FAME content, %	98.8	98.2	90	97.7		96.5
Density at 15 °C, kg/m ³	875 ^a	844	880	888.3 ^b	870	860/900
Viscosity at 40 °C, mm ² /s	2.49	4.7	4.89	2.35	5.03	3.50/5.00
Flash point, °C		159	120	185	164	101 min
Sulfur content, mg/kg					2	10 max
Water content, mg/kg	415		trace	300	0.0	500 max
Acid value, mg KOH/g	0.37		0.43	0.48	0.29	0.5 max
Iodine value, g I ₂ /100 g	131					120 max
Monoglyceride content, %	0.70			2.34	0.29	0.8 max
Diglyceride content, %	0.17			0.0	0.19	0.2 max
Triglyceride content, %	0.10			0.0	0.06	0.2 max
Free glycerol, %					0.022	0.02 max
Total glycerol, %					0.57	0.25 max
Group I metals (Na+K), mg/kg	0.2				66	5.0 max
Group II metals (Ca+Mg), mg/kg					1	5.0 max
Phosphorus content, mg/kg					2	4.0 max
Cloud point, °C		-2	3	-3	-1	Not specified
Pour point, °C		-5	0	-19	-16	Not specified
Reference	This work	[8]	[11]	[9]	[46]	

Conclusion

The KOH-catalyzed methanolysis of WCO was studied at moderate reaction temperatures. The methanolysis reaction was shown to be only chemically controlled. Based on the lower *MRPD* values between the experimental and calculated values of the TAG conversion degree and higher *R*² values, the irreversible pseudo-second order reaction rate was chosen for modeling the reaction kinetics. A higher conversion degree (97%) within a shorter reaction time (3 min) was obtained at the highest reaction temperature of 60 °C. The activation energy of the WCO methanolysis reaction was in the range of the values reported for methanolysis of different oily feedstock. The final products satisfied the EN 14214 biodiesel standard specifications.

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Izvod

KINETIKA BAZNO KATALIZOVANE METANOLIZE OTPADNOG KORIŠĆENOG ULJA

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Otpadno korišćeno ulje je ispitivano kao sirovina za dobijanje biodizela postupkom homogene bazno-katalizovane metanolize pri umerenim reakcionim uslovima: molski odnos metanol:ulje 6:1, količina KOH kao katalizatora 1% (računato na masu ulja) i na temperaturama od 30 °C do 60 °C, sa ciljem modelovanja kinetike reakcije. Zapaženo je da ne postoje maseno-prenosna ograničenja brzine procesa u njegovom početnom periodu i da se reakcija metanolize odigrava u pseudo-homogenom režimu, u kome hemijska reakcija određuje ukupnu brzinu procesa. Kinetika reakcije metanolize otpadnog korišćenog ulja je modelovana primenom nepovratne reakcije pseudo-prvog i pseudo-drugog reda. Iako su oba modela bila pouzdana za opisivanje kinetike reakcije, bolje slaganje eksperimentalnih i izračunatih vrednosti stepena konverzije ulja je dobijeno u slučaju primene modela nepovratne reakcije pseudo-drugog reda. Konstante brzine reakcije se povećavaju sa povišenjem temperature. Konverzija ulja od 97% je ostvarena za 3 minuta trajanja reakcije na temperaturi 60 °C. Karakteristike dobijenog biodizela su u okviru vrednosti propisanih standardom kvaliteta bodizela EN14214.

Ključne riječi: biodizel; kinetika; metanoliza; otpadno korišćeno ulje