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Comparative kinetics of the alkali-catalyzed sunflower oil methanolysis with co-solvent under conventional and microwave heating with controlled cooling

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TSMPC transesterification of sunflower oil with methanol in the presence of co-solvent

Abstract: The kinetics of the alkali-catalyzed transesterification of sunflower oil with methanol in the presence of co-solvent (TSMPC) were investigated. The kinetics curves of the alkali-catalyzed TSMPC, in the temperature range of 26°C–55°C, were measured for conventional heating (CH) and microwave heating with controlled cooling. The results showed that for both heating modes, the kinetics of the alkali-catalyzed TSMPC reaction can be described with the kinetic model of the pseudo first-order reaction with respect to the concentration of the triglycerides. The values of apparent reaction rate constants, activation energies, and pre-exponential factors are also calculated. The existence of a linear correlation (compensation effect) between the values of apparent kinetic parameters determined for CH and microwave heating with controlled cooling conditions is established. The results confirmed that the increase in the transesterification rate in the microwave heating with controlled cooling conditions is not caused by overheating nor by the existence of hotspots. The model of mechanism of the impact of microwave heating on the kinetics of transesterification is hereby proposed.

Keywords: co-solvent; kinetic; microwave heating with controlled cooling; transesterification.

Abbreviations

CH	conventional heating
DG	diglycerides
G	glycerin
MG	monoglycerides
MWHCC	microwave heating with control cooling
SET	selective energy transfer
TG	triglycerides
THF	tetrahydrofuran

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Symbols

M	(–)	molar ratio methanol to oil
C _k	(%)	catalyst concentration
T	(K)	temperature
r	(rpm)	agitation rate
M _l	(–)	molar ratio methanol to THF
C _{ME}	(%)	methyl ester concentration
ΣA	(–)	total peak area
A _{Ei}	(–)	peak area corresponding to the methyl heptadecanoat
A _{ER}	(–)	peak corresponding to the methyl heptadecanoat of the referent sample
C _{Ei}	(mg l ^{–1})	concentration of the methyl heptadecanoat
V _{Ei}	(ml)	volume of the methyl heptadecanoat
m	(g)	weight of the sample
W _{TG}	(g)	residual weight of the triglyceride molecule in time
W _o	(g)	initial weight of the TG
DE	(%)	degree of esters
C _{TG}	(mol l ^{–1})	residual concentration of the TG
M _{TG}	(gmol ^{–1})	molar mass of the methyl ester
V	(ml)	volume of the sample
α _i	(–)	degree of TG conversion on the particular heating mode
i	(–)	heating mode
C _o	(mol l ^{–1})	initial concentration of the TG
t	(min)	time
(dα _i /dt)	(–)	transesterification reaction rate
A _{i,αj}	(min ^{–1})	pre-exponential factor at a fixed degree of conversion
R	(J K ^{–1} mol ^{–1})	gas constant
E _{ai,αj}	(kJ mol ^{–1})	apparent activation energy for the fixed degree of conversion
lnA _i	(min ^{–1})	logarithm of the pre-exponential factor for the fixed degree of conversion
E _{a,CH}	(kJ mol ^{–1})	apparent activation energy obtained under CH
E _{a,MW}	(kJ mol ^{–1})	apparent activation energy obtained in MWHCC
k _{CH}	(l mol ^{–1} min ^{–1})	rate constant of the pseudo first-order reaction under CH
k _{MW}	(l mol ^{–1} min ^{–1})	rate constant of pseudo first-order reaction under MWHCC conditions
lnA _{CH}	(min ^{–1})	pre-exponential factor obtained in CH conditions
lnA _{MW}	(min ^{–1})	pre-exponential factor obtained in MWHCC conditions

$\ln A_{HM}$	(min^{-1})	logarithm of the pre-exponential factor under different heating modes
E_{HM}	(kJ mol^{-1})	apparent activation energy under different heating modes
k_i	($\text{l mol}^{-1} \text{min}^{-1}$)	rate constant
k_B	(J/K)	Boltzmann constant
h	(Js)	Planck constant
T_{MW}^*	(K)	temperature calculated for the reaction system
T_{ic}	(K)	isokinetic temperature
ν	(cm^{-1})	wave number of the resonant vibration
b	($-$)	slope of the compensation equation
n	($-$)	number of the resonant vibration quanta
n^*	($-$)	approximate value of the number of resonant vibration quanta
x	(cm^{-1})	anharmonicity constant of the oscillator
z	($-$)	occupancy degree of the energy levels.

1 Introduction

Biodiesel is a mixture of fatty acids' methyl esters, and is widely used as an alternative fuel (a substituent to petrol diesel) for internal combustion engines. Biodiesel is commonly produced by the alkali-catalyzed transesterification reaction of triglycerides (TG) with different alcohols (CH_3OH , $\text{C}_2\text{H}_5\text{OH}$) in the presence of a homogeneous or heterogeneous catalyst (NaOH , KOH , and CH_3ONa). Eckey [1] proposed the mechanism of the alkali-catalyzed transesterification reaction. According to that mechanism, transesterification reaction is described as a three reversible second-order reaction, by which the TG are transformed into diglycerides (DG), monoglycerides (MG), and finally into glycerol (G). The tetrahedral intermediate is formed in each of those steps through the direct nucleophilic attack of the alkoxide on the TG molecules.

The effects of different factors on the isothermal kinetics of the alkali-catalyzed transesterification of oil with alcohols in two- and one-phase systems have been investigated in numerous works. For example, Nouredini and Zhu [2] investigated the effects of variation in mixing intensity and temperature on the rate of the base-catalyzed transesterification of soybean oil with methanol. Based on the obtained results, they concluded that the kinetics of the base-catalyzed transesterification can be described with the model of three consecutive second-order reversible reactions. They proposed the reaction mechanisms coming from three regions: the mass transfer-controlled region followed by the reaction controlled region and finally the equilibrium region. The influences of the impeller speed, temperature, and catalyst concentration on the kinetics of the transesterification of sunflower oil with methanol was investigated by

Vicente et al. [3], who confirmed the applicability of the abovementioned kinetic model and reaction model on the sunflower oil transesterification proposed by Nouredini and Zhu. Bambase et al. [4] investigated the effects of agitation speed, temperature, catalyst loading, and the methanol/oil mole ratio on the kinetics of the transesterification of crude sunflower oil. The authors concluded that kinetic model and reaction mechanism proposed by Nouredini and Zhu can be applicable on the crude sunflower oil [4]. Georgogianni et al. [5] studied the conventional and *in situ* transesterification of sunflower seed and found that the alkali-catalyzed transesterification of sunflower seed can be described with the kinetic model of the pseudo first-order reaction. Stamenković et al. [6] investigated the kinetics of the sunflower oil methanolysis at lower temperatures ($T = 10^\circ\text{C} - 30^\circ\text{C}$) and established the sigmoidal shape of the kinetic curves. They attributed the established kinetic curve shapes to the existence of the initial TG mass transfer-controlled region, followed by the irreversible second-order reaction-controlled region. Assuming that the rate of the transesterification of oil is controlled by the solubility of the oil in the catalytically active phase, Gunvachai et al. [7] developed a new solubility model to describe the biodiesel formation kinetics.

The effects of interfacial area on the kinetics of the transesterification of sunflower oil with methanol are presented in the work of Bibalan and Sadrameli [8]. Likoazar and Levec [9] proposed a novel model of base-catalyzed transesterification of different oils and alcohols. Their model is based on the detailed analyses of changes in the concentrations of the reactants, intermediates, and the products as well as on the simultaneous modeling of mass transfer, reaction kinetics, and chemical equilibrium. The authors calculated diffusivities, distribution, and mass transfer coefficients for individual components, along with the kinetic parameters for each particular stage. They found that the values of the pre-exponential factor and the activation energies were correlated with the structures of the reactants, the intermediates and the products, and considering the number of carbons, on the double bonds and alkyl branches. Likoazar and Levec [10] presented a detailed description of the kinetics of the base-catalyzed transesterification of canola oil. They reported that the calculated values of the activation energies and the pre-exponential factor for both forward and backward reactions depended on the component structure, thus confirming the same mechanism for all three transesterification steps, but with a decrease of steric hindrance with a lesser number of bonded fatty acid. Using the previously mentioned model, Likoazar and Levec [11] modeled the transesterification of canola oil to biodiesel in a

continuous tubular reactor with a static mixer at different temperatures, volumetric flow rates, phase fractions, and catalyst contents. Assuming that the transesterification reaction occurred in the methanol phase, a number of authors have suggested that the addition of a co-solvent can enhance the miscibility of the phases and increase the reaction rate due to the disappearance of the inter-phase mass transfer in the heterogeneous two-phase reaction system [12].

Various organic substances have been used as co-solvents, which include the following: (a) low molecular weight ethers [methyl tertiary-butyl ether (MTBE), dimethyl ether (DME), diethyl ether (DEE), tetrahydrofuran (THF)], and (b) acetone, hexane, heptane, CO_2 , and ionic liquid [13–15]. Boocock et al. [13] investigated a single-phase reaction system for the methanolysis of soybean oil with THF as a co-solvent at ambient temperature (molar ratio methanol:oil $M=6$ and THF: methanol volumetric ratio of 1.25). In such a system, the addition of THF provides for a single-phase system, in which methanolysis is almost as fast as butanolysis. Mao et al. [16] studied a pseudo single-phase methanolysis of soybean oil with THF under basic conditions, with the $M=6$ at $T=23^\circ\text{C}$. Fast reaction rates were observed in single-phase at the beginning of the reaction, whereas slower reaction rates occurred when the two-phase system was formed by the sudden shift in the reaction. Ataya et al. [17] studied the kinetics of canola oil transesterification in both two- and single-phase systems with the addition of THF as a co-solvent. They described the kinetics of transesterification in a single-phase system with the kinetic model of the first-order chemical reaction. Bankovic-Ilic et al. [18] investigated the homogeneous base-catalyzed methanolysis of sunflower oil in the presence and absence of THF as a solvent in a continuous concurrent upflow reciprocating the plate reactor. The authors established the sigmoidal shapes of the kinetics curves either in the absence and presence of THF in lower concentrations ($\geq 10\%$ of the oil mass). On the contrary, in the presence of THF in higher concentrations (30% of the oil mass) the kinetics curves were described with the model of the irreversible second-order chemical reaction. Roosta and Sabzpooshan [19] presented the mathematical model for predicting the effects of the co-solvent on the kinetics and the yield of biodiesel. Encinar et al. [14] investigated the influences of the catalyst concentration (KOH), the methanol:oil molar ratio, the methanol:co-solvent molar ratio, the co-solvent type [DEE, dibutyl ether (diBE), tert-butyl methyl ether (tBME), diisopropyl ether (diIPE) and THF], the agitation rate, and the reaction temperature on the yield, quality, and kinetics of the biodiesel from rapeseed oil. Based on

the obtained results, the authors determined the kinetic and thermodynamic parameters and concluded that the kinetics of the base-catalyzed transesterification can be described with the kinetic model of the pseudo first-order reaction.

The process of microwave heating significantly accelerates the chemical reactions and physicochemical processes, gives higher yields, and improves the properties of the products [20]. The established effects of microwave heating on the kinetics of chemical reactions are usually attributed to the effects of overheating [21], the existence of hotspots [22], selected heating [23], or to the specific microwave effects [24]. An extensive critical review of the application of microwave energy in biodiesel production by using different oils, alcohols, catalysts, and reaction systems has been presented in the work of Gude et al. [25].

In the present study, with the aim of establishing the effects of microwave heating on the kinetics of alkali-catalyzed transesterification of sunflower oil with methanol in the presence of co-solvent (TSMPC), we performed comparative analyses of the kinetics data (kinetic and conversion curves, kinetics model, and values of kinetic parameters), which were obtained under isothermal conventional heating (CH) and microwave heating with control cooling (MWHCC).

2 Materials and methods

The refined sunflower oil was obtained from Dijamant-AD (Zrenjanin, Serbia). The physicochemical properties of the used oil were determined according to the AOCS official methods [26]. The results are presented in Table 1. Supplementary Figure 1 shows the homogeneous single-phase reaction system (methanol, oil, and THF).

Methanol of 99.8% purity was purchased from Merck (Darmstadt, Germany). The catalyst (sodium methoxide, 30% solution in methanol) was purchased from Sigma-Aldrich (Germany). The co-solvent (THF, 99% purity) was purchased from J.T. Baker (Holland). Zeolite 3A (Phonosorb) was purchased from Grace (Germany).

Table 1: The physicochemical properties of sunflower oil.

Physicochemical property	Value
Fatty acid content	
Palmitic acid (%)	6.6
Stearic (%)	5.1
Oleic (%)	19.6
Linoleic (%)	68.7
Free fatty acid (%)	0.02
Saponification value (mgKOH g^{-1})	193.7
Iodine value ($\text{mgI}_2 \text{g}^{-1}$)	130.4
Water (mg g^{-1})	0.05

Dichloromethane and acetic acid, both p.a., were purchased from Merck (Germany). The transesterifications under the conditions of CH were carried out in 250 ml three-necked batch reactor with a flat bottom. The reactor was equipped with a reflux condenser, mechanical stirrer (IKA RW20, Germany), and a stopper to remove the samples. This reactor was immersed in a constant-temperature water bath capable of maintaining the reaction temperature within $\pm 0.1^\circ\text{C}$. The transesterifications under the conditions of MWHCC were performed in a commercially mono-mode microwave instrument (Discover, CEM Corporation, Matthews, NC, USA), which was modified with a device for maintaining constant temperature in the reaction system [27]. The instrument consisted of a continuously focused microwave power delivery system with a power output of 0–300 W and a frequency of 2.45 GHz.

The temperature during the transesterification reaction was monitored using a calibrated fiber-optic thermometer, which was inserted into the reaction mixture. The magnetron power during reaction was monitored with a sensor incorporated into the modified commercial device provided by the manufacturer of the microwave instrument. The microwave device automatically maintained the required temperature in the reaction system with rapid variation (very fast) in the input power and/or inflow change of the nitrogen vapors. When the sensor of the instrument detected a decrease in temperature of the reacting mixture in relation to the required temperature, the input power of the microwave field was automatically increased and nitrogen flow was decreased. On the contrary, when the temperature in the reacting system increased, the input power of the microwave field automatically decreased and nitrogen flow increased in order to achieve the desired temperature of reacting system.

Figure 1 shows the changes in temperature of the reaction mixture and of the used magnetron power during the transesterification under MWHCC conditions. As can be seen, the temperature of the reaction mixture after 30 s of the reaction is constant within the limits of the measurement error. For the study of transesterification reaction, we can claim with a high degree of reliability that the temperature is maintained constant (within the error limits of 1%).

Figure 1: The variation in the temperature and power (P) in the reaction system during the transesterification under the MWHCC condition ($T=55^\circ\text{C}$ and $P=50\text{ W}$).

The kinetics of the alkali-catalyzed TSMPC under the different heating modes were investigated in the same reaction conditions: $M=6$, molar ratio methanol:THF $M_1=1.6$, and catalyst concentration $C_K=1\%$ in relation to the content of TG; $r=600$ (rpm). For the CH conditions, the following temperatures were applied: 31°C , 37°C , 42°C , 47°C , and 55°C . As for the MWHCC conditions, the following temperatures were applied: 26°C , 33°C , 37°C , 42°C , and 55°C .

The transesterification under CH conditions was performed as follows: the reactor was initially charged with 50 ml of sunflower oil, placed in the constant-temperature bath with its associated equipment, and then heated to a predetermined temperature. Next, 1.5 ml of sodium methoxide dissolved in 13 ml methanol was heated up to the required temperature and added to a reactor, followed by the addition of a co-solvent (16 ml of THF). The reactor was supplied with a mechanic stirrer. During the experiment, 0.1 ml samples were taken out from the reaction mixture at predetermined reaction time intervals. The samples were poured immediately into 1 ml of water containing the corresponding amount of acetic acid to stop the reaction. The mixture was extracted twice with 5 ml of dichloromethane each, after which the organic layers were separated, dried with 3A zeolite, and evaporated.

The ester content of the samples was determined by gas-capillary chromatography methods according to EN 14103 [28]. The sample preparation was reformed according to the work of Schober et al. [29].

The methyl ester concentration, C_{ME} , is calculated according to EN14103, using Eq. 1 and expressed as percentage (wt.%)

$$C_{ME} = \frac{(\Sigma A) - (A_{EI} - A_{ER})}{(A_{EI} - A_{ER})} \cdot \frac{C_{EI} \cdot V_{EI}}{m} \cdot 100, \quad (1)$$

where ΣA is the total peak area from the methyl ester C_{14} to that in $C_{24:1}$, A_{EI} is the peak area corresponding to the methyl heptadecanoate, A_{ER} is the peak corresponding to the methyl heptadecanoate of the referent sample, C_{EI} is the concentration of the methyl heptadecanoate solution being used, V_{EI} is the volume of the methyl heptadecanoate solution being used, and m is the weight of the sample.

The TG content is calculated by the expression

$$W_{TG} = W_0 \left(1 - \frac{DE}{100} \right), \quad (2)$$

where W_{TG} is the residual weight of the TG after time t , W_0 is the initial weight of the TG, and DE is the degree of ME in the moment of time.

The residual concentration of TG in the reaction mixture, C_{TG} , is calculated by the expression

$$C_{TG} = \frac{W_{TG} / M_{TG}}{V}, \quad (3)$$

where M_{TG} is molar mass of the TG, and V is the volume of the sample.

The degree of TG conversion on the particular heating mode, α_i , is calculated using Eq. 4

$$\alpha_i = \frac{C_{TG}}{C_0}, \quad (4)$$

where C_0 is the initial concentration of the TG in the reaction mixture, and i is heating mode.

2.1 Differential isoconversion method

The transesterification reaction rate ($d\alpha_i/dt$) on the fixed degree of transesterification (α_i), in accordance with the Friedman differential isoconversion method [30], can be determined by using Eq. 5

$$(d\alpha_i/dt)\alpha_j = A_{i,\alpha_j} \exp\left(-\frac{E_{ai,\alpha_j}}{RT}\right) f(\alpha_j), \quad (5)$$

where E_{ai,α_j} is the apparent activation energy for the fixed degree of conversion; $\ln A_{i,\alpha_j}$ is the pre-exponential factor for fixed degree of conversion; and R is the gas constant. From the slope and intercept of the dependence of $\ln(d\alpha_i/dt)\alpha_j$ versus $1/T$ (Eq. 5), the values of the kinetic parameters, E_{ai,α_j} and $\ln A_{i,\alpha_j}$ are obtained.

3 Results and discussion

The chromatograms obtained from the samples taken from the reaction mixture during the investigation of the reactions of the alkali-catalyzed TSMPC under the CH (on $T = 42^\circ\text{C}$ at $t = 5$ min) and MWHCC (on $T = 42^\circ\text{C}$ at $t = 3$ min) conditions are presented in Figure 2A and B. The chromatograms shown in Figure 2A and B show the characteristic peaks corresponding to the fatty acid methyl esters, whose intensity increases with increase of the degree of TG transesterification.

Table 2 presents the important chemical and physical properties of methyl esters as a final product (methyl

Figure 2: The chromatograms obtained from the reaction mixture (A) for CH, $T = 42^\circ\text{C}$, $t = 5$ min (B) for MWHCC, $T = 42^\circ\text{C}$, $t = 3$ min.

Table 2: The physicochemical properties of methyl esters as final products (for CH: $T=55^{\circ}\text{C}$ after 20 min of the reaction, for MWHCC: $T=55^{\circ}\text{C}$ after 10 min).

Property	FAME _{CH}	FAME _{MW}	EN 14214	Method
Ester content % (m m^{-1})	99.6	99.85	Min. 96.5	EN 14103
Monoglycerides % (m m^{-1})	0.18	0.10	Max 0.7	EN 14105
Diglycerides % (m m^{-1})	nd	nd	0.2	EN14105
Triglycerides % (m m^{-1})	nd	nd	0.2	EN 14105
Methanol content % (m m^{-1})	0.05	0.05	0.2	EN 14110
Free glycerine % (m m^{-1})	0.003	nd	0.02	EN 14106
Total glycerine % (m m^{-1})	0.080	nd	0.25	EN 14105
Water content (mg kg^{-1})	120	100	500	EN ISO 12937
Acid value mg KOH/g	0.03	0.02	0.5	EN 14104
Iodine value ($\text{mgI}_2 \text{ gr}^{-1}$)	128	128	Max. 120	EN 14111
Density (15°C) (kg m^3)	885	884	860–900	EN ISO 12185
Viscosity 40°C ($\text{mm}^2 \text{ s}^{-1}$)	3.7	3.7	3.5–5.0	EN 1405

nd: Not determined.

ester content, MG, DG, TG, methanol content, free glycerine, total glycerine, water content, acid value, iodine values, density, and viscosity) obtained from the samples upon completion of the transesterification reactions (for CH in $T=55^{\circ}\text{C}$ after 20 min, for MWHCC in $T=55^{\circ}\text{C}$ after 10 min).

Next, the established properties of the methyl esters obtained as a final products were compared with the required properties of the methyl ester prescribed by the EN 14214 standard. Considering the results presented in Table 2, it can be seen that the properties of the methyl esters, synthesized both in the CH and MWHCC conditions in the presence of a co-solvent, entirely relate to the properties of the methyl ester recommended by the EN 14214 standard, with an exception of the iodine value, which is higher than the recommended value for both the heating modes. The value of the iodine number is related to the content of the unsaturated fatty acids in the sunflower oil. In comparison with the above properties of the methyl esters, obtained under the CH and MWHCC conditions, the MWHCC conditions provide the higher content of ester phase, lower MG content, and lower water content.

The kinetics curves of the alkali-catalyzed TSMPC (dependence of C_{TG} on reaction time) on different temperatures in the MWHCC and CH conditions are shown in Figure 3A and B. As can be seen, the kinetics curves have identical shapes for both heating modes on all the investigated temperatures. The two characteristic shapes (linear and concave) can also be clearly distinguished for the decrease in C_{TG} with time. At the beginning of the reaction, the C_{TG} decreases linearly with time; then, the C_{TG} decreases slowly with time and becomes concave until the TG completely disappears in the reaction mixture. For

both heating modes, with the increase of temperature, the slope of the linear change of C_{TG} with time increases and the time required to achieve the complete conversion of TG into ME is shortened. Comparing the MWHCC and CH conditions, the slope of the linear decrease of C_{TG} with time is higher, and the time for the complete conversion of TG into ME is shorter in the MWHCC conditions. This implies an increase in the reaction rate of the alkali-catalyzed TSMPC under MWHCC compared to that under the CH condition. This finding also implies an increase in the reaction rate with an increase in temperature for both heating modes.

Based on the shape of the experimentally obtained kinetics curves of the alkali-catalyzed TSMPC, the fitting with the model of the pseudo first-order is done. For the pseudo first-order reaction, the dependences of $\ln(C_0/C_{\text{TG}})$ on time for both the CH and MWHCC conditions should be a straight line. The dependences of $\ln(C_0/C_{\text{TG}})$ on time under the CH and MWHCC conditions are shown in Figure 4A and B, respectively.

The linear dependence of $\ln(C_0/C_{\text{TG}})$ on time confirms that the kinetics of the alkali-catalyzed TSMPC can be described with the model of the pseudo first-order chemical reaction, which means that the rate of alkali-catalyzed TSMPC is proportional to the concentration of the C_{TG} remaining in the reaction mixture. Based on the known values of the slope of the dependence of $\ln(C_0/C_{\text{TG}})$ on time, the value of the apparent rate constants of the alkali-catalyzed TSMPC k_{CH} and k_{MW} under CH and MWHCC conditions, respectively, can be determined. The calculated values of the apparent rate constants are shown in Table 3 (columns 2 and 5). As can be seen, the values of k_{MW} are higher than the corresponding values obtained under the CH condition. This confirms the

Figure 3: The kinetics curves of the transesterification under (A) the CH condition and (B) the MWHCC condition in different temperatures.

Figure 4: The dependence of $\ln(C_0/C_{TG})$ on t (A) under the CH condition and (B) under the MWHCC condition in different temperatures.

Table 3: Calculated values of the rate constants and apparent kinetic parameters of the alkali-catalyzed TSMPC under the CH and MWHCC conditions.

T (K)	k_{CH} (min ⁻¹)	Kinetic parameters	T (K)	k_{MW} (min ⁻¹)	Kinetic parameters
304	0.21	$E_{aCH} = 12.1 \pm 0.1$ (kJ mol ⁻¹)	299	0.28	$E_{aMW} = 28 \pm 1$ (kJ mol ⁻¹)
310	0.23	$\ln A_{CH} = 3.2 \pm 0.1$ (min ⁻¹)	306	0.36	$\ln A_{MW} = 12.3 \pm 0.5$ (min ⁻¹)
315	0.25	$S^2 = 0.9998$	310	0.42	$S^2 = 0.9996$
320	0.27		315	0.50	
328	0.30		328	0.76	

S^2 , Coefficient of correlation.

above assumption, which states that the rate of the alkali-catalyzed TSMPC under the MWHCC condition is higher than that in the CH condition. In addition, the value of the rate of the alkali-catalyzed TSMPC is higher than the rate constant of the alkali-catalyzed transesterification of the sunflower oil with methanol without the presence of co-solvent [2]. Given the values of the rate constant of the alkali-catalyzed TSMPC increase with temperature in accordance with the Arrhenius equation for both heating modes. By using the Arrhenius equation, the values of the apparent kinetic parameters of the alkali-catalyzed TSMPC under the CH and MWHCC conditions were calculated. The values are presented in Table 3 (columns 3 and 6). The calculated values of the E_{aMW} and $\ln A_{MW}$ are significantly higher than the corresponding values E_{aCH} and $\ln A_{CH}$. Bearing in mind that the isothermal values of k_{MW} for all investigated temperatures are higher than the isothermal values of k_{CH} , we can conclude that the increase in the rate of alkali-catalyzed TSMPC in the MWHCC condition compared with the CH condition, is the consequence of an increase of the value of $\ln A_{MW}$. The calculated values of E_{aMW} and E_{aCH} suggest that alkali-catalyzed TSMPC is a mass transfer-controlled reaction.

The values of E_a for different steps of the transesterification reaction under CH, obtained from different authors most frequently cited in literature, are summarized in

Table 4. The presented values for E_a of the transesterification reaction in the CH condition in the two- and single-phase reaction, obtained from different authors, differ significantly. Moreover, all of them are higher than the values of the apparent E_{aCH} of the alkali-catalyzed TSMPC reaction obtained in the present research. This confirms the abovementioned assumptions that the alkali-catalyzed TSMPC is not a kinetically controlled reaction, but that this alkali-catalyzed TSMPC is kinetically controlled with the mass-transfer of the reactants, as previously mentioned.

The calculated values of the kinetic parameters of the alkali-catalyzed TSMPC under the CH condition in this work are lower than those of the kinetic parameters shown in the work of Encinar et al. [14] for rapeseed oil, which is most probably the consequence of using different oils and experimental conditions (higher value of $M = 9$, higher $C_k = 0.7$ wt.%, and lower amount of co-solvent $C = 1.0$ wt.%). The values of the kinetic parameters of the alkali-catalyzed TSMPC under the MWHCC condition are higher than the corresponding values under the CH condition. Mazubert et al. investigated the transesterification of waste cooking oil under the microwave and CH conditions, and reported the activation energies of 37.1 (kJ mol⁻¹) for the microwave condition and 31.6 (kJ mol⁻¹) for the CH condition [34].

Table 4: The values of E_a for the particular reaction steps of the transesterification.

Reaction	E _a (kJ mol ⁻¹)						
	Reference						
	Vicente et al. [3]	Bambase et al. [4]	Klofutar et al. [31]	Darnoko and Cheryan [32]	Eze et al. [33]	Likoazar and Levec [9]	Roosta and Sabzpooshan [19]
TG→DG	31.66	58.69	95.9	61.4	58.7	47–61	33.8
TG←DG	30.01	44.89	92.8		44.9	44–31	39.9
DG→MG	41.56	67.09	27.3	59.4	67.1	58.5	34.6
DG←MG	41.11	58.14	241.3		58.1	32.4–44.4	29.5
MG→G	5.96	29.97	48.1		30.0	55–57	27.85
MG←G		45.94	63.5	26.8	74.0	46–40	32.6

Figure 5: The dependence of the $E_{ai,oj}$ on α_i under the CH (●) and MWHCC (■).

Considering that (a) different authors in the literature described the kinetics of the alkali-catalyzed transesterification by various reaction schemes, and (b) the function that describes the dependence of transesterification rate on the degree of transesterification, $f(\alpha_i) = 1 - \alpha_i$, does not change with temperature, then the degree of kinetic complexity and reaction scheme of the alkali-catalyzed TSMPC reaction can be preliminary determined by using the Freedman method [30]. The shape of the dependence of $E_{ai,oj}$ on α_i has been examined [35]. The dependences of $E_{ai,oj}$ on α_i under the CH and MWHCC conditions are presented in Figure 5. Based on the results presented in Figure 5, one can conclude that the $E_{ai,oj}$ for TSMPC for both heating modes are independent of α_i . The calculated values of $E_{aCH} = 12$ (kJ mol⁻¹), and $E_{aMW} = 28$ (kJ mol⁻¹) are entirely in agreement with the values of E_a , which are calculated by using the kinetic model of the pseudo first-order chemical reaction.

By comparing the values of the determined apparent kinetic parameters of the alkali-catalyzed TSMPC for both heating modes, one can conclude that the values of the kinetic parameters of the alkali-catalyzed TSMPC exist between the linear correlation relationship–compensation effects, which can be described in Eq. 6

$$\ln A_{HM} = -3.72 + 0.572 E_{aHM}, \quad (6)$$

where $\ln A_{HM}$ is the pre-exponential factor under different heating modes, and E_{aHM} is the apparent activation energy under different heating modes.

The acceleration of the chemical reactions in the MWHCC condition is commonly explained as a

Table 5: The calculated values of T_{MW}^* and ΔT .

T (K)	T_{MW}^* (K)	$\Delta T(K) = T_{MW}^* - T$
299	317.7	18.7
306	337.8	31.8
310	348.5	38.5
315	363.4	48.4
328	414.9	86.9

consequence of overheating or the existence of hotspots in the reaction systems [21, 22]. In relation to this, knowing the reaction rate constant of the alkali-catalyzed TSMPC in the CH and MWCC conditions, along with the values of kinetic parameters under CH, offers the possibility of accurately calculating the temperatures in the reaction system (T_{MW}^*). T_{MW}^* corresponds to the calculated value of k_{MW} as shown in Eq. 7

$$T_{MW}^* = \frac{E_a}{R \left[\frac{E_a}{RT} - \ln \left(\frac{k_{MW}}{k_{CH}} \right) \right]}. \quad (7)$$

The calculated values of T_{MW}^* are shown in Table 5. The calculated values of T_{MW}^* are significantly higher than the values of the experimentally measured temperatures in the reaction system and significantly exceed the values of possible measurement errors of T in reaction system, which would be easily detected if they existed. According to this, the significant increase in the rate of the TSMPC in the MWHCC condition compared with the CH condition is not a consequence of the overheating of the reaction system nor due to the existence of hotspots.

The existence of the compensation effect in relation to the heating mode implies that activation of the reacting molecules for the reaction of the transesterification in the presence of the co-solvent is carried out in accordance with the Larssons model of the selective transfer of energy (SET model) [36].

The basic assumptions of the SET model are as follows. First, there exists a possibility of coupling between the set of vibrations of the TG molecules (v_i) with the reaction system (ω_j). The reaction system deduces the set of non-interaction waves that propagate through the reaction mixtures (these waves are formed due to the mutual interaction of the molecules of the reaction mixture. Second, the activated complex for the transesterification is formed via the selective resonant transfer of a certain amount of energy from the reaction system to the resonant vibration of the TG molecule. Third, the value of the transferred energy is

quantized and is determined by the number of the resonant vibration quanta (n), which are exchanged between the reaction system and the resonant vibration of the TG molecule. Finally, the resonant transfer of energy causes the change in the value of the anharmonicity factor of the resonant vibration of the TG molecule. Based on those assumptions, we can calculate the wave number of the vibration in the TG molecule at which SET is carried out from the reaction system to the TG molecule

$$\nu = \frac{T_{ic}}{0.715}, \quad (8)$$

where ν is given in cm^{-1} , and T_{ic} is the isokinetic temperature in K degrees.

The value of T_{ic} can be calculated when the expression for the compensation effect is known in accordance with the study of Linert and Jameson [37]

$$T_{ic} = \frac{1}{R \cdot b}, \quad (9)$$

where b (mol/J) is the slope of the compensation equation (Eq. 6). By substituting the above expression Eq. 9 into Eq. 8, we obtain the expression

$$\nu = \frac{168}{b}, \quad (10)$$

where b is given in mol kJ^{-1} .

Based on the known values of the $E_{a,i}$ and ν , in accordance with Larson's model, the value of the number of resonant vibration quanta (n) can be calculated by using Eq. 14

$$E_{a,i} - RT = h\nu \cdot (1 + nx), \quad (11)$$

where x is the anharmonicity factor. Given that the two variables (n and x) exist in Eq. 24, we need two steps to calculate the n . First, as the value of x is low, the approximate value of n^* should be calculated using Eq. 12

$$n^* = \frac{E_{a,i} - RT}{\nu}. \quad (12)$$

Given that n has to be an integer, the n^* is rounded to an integer value that corresponds to the real value of the n . The value of x is calculated by using Eq. 13 based on the known values of ν , n , and $E_{a,i}$

$$x = \frac{\left(\frac{E_{a,i} - RT}{n\nu} \right) - 1}{n}. \quad (13)$$

Table 6: The values of ν , n , and x for the TG transesterification under the MWHCC and CH conditions.

Variable	CH	MWHCC
ν (cm^{-1})	294	294
n	3	8
x	-0.029	-0.011

The values of ν , n , and x for the TG transesterification under the MWHCC and CH conditions are given in Table 6.

The identical ν values for the transesterification processes under the MWHCC and CH conditions confirm the identical mode of the activation of the TG molecule proposed above. The activation of the TG molecule occurs through the SET of certain quantities of energy from the reaction system to the resonant frequency of the TG molecule with wave number $\nu = 294 \text{ cm}^{-1}$. This frequency corresponds to the out-of-plane C-C-C banding vibration of the TG molecule [38] and leads to the formation of the activated complex as a precursor for the transition of the TG molecules to the ester. The obtained result is also in accordance with the valid model of the mechanism of the activated complex formation for the reaction of the transesterification. The calculated values $n=3$ for CH and $n=8$ for MWHCC are in good agreement with the lower value of the apparent activation energy for the CH. The lower values for $E_{a,CH}$ and $\ln A_{CH}$ compared with the ones for MWHCC is a consequence of the quantum nature of the activation energy (multi excitation) and, therefore, the TG molecule requires a higher number of resonant quanta to overcome the energy barrier for the formation of the activated complex under the MWHCC condition.

The ability of the methanol and catalyst molecules to selectively absorb the microwave field's energy results in the increase in their internal energy, which in turn, leads to the temperature rise in the reaction mixture in the conditions of the thermo-insulation reaction system. Under the MWHCC condition, the constant temperature in the reaction system is maintained by the external controlled cooling using nitrogen vapors. The controlled cooling leads to the redistribution of the reacting molecules through the energy levels. This redistribution maintains the constant ratio as shown in Eq. 14

$$\beta = \frac{dE}{d \ln z}, \quad (14)$$

where z refers to the occupancy degree of the energy levels.

For this reason, the mean value of the internal energy of the reacting molecules increases whereas the relative ratio of the reacting molecules' energy decreases, in comparison with CH. The transesterification reaction also changes the distribution of the reacting molecules through the energy levels of the reaction mixture. In the case when the rate of transesterification reaction is lower than that of the thermodynamically equilibrium achievement, the relative ratio of the activated reactants changes in accordance with the Maxwell-Boltzmann distribution. Under these conditions, the values of E_{aMW} and $\ln A_{MW}$ should be lower than the comparable ones obtained under the CH condition. When the rate of the transesterification reaction is higher than that for thermodynamically equilibrium achievement, the concentration of the activated reactants under the MWHCC condition decreases rapidly, which leads to the redistribution of the reacting molecules with the higher occupation of the energy levels with lower value of the internal energy. Under these conditions, the values of E_{aMW} and $\ln A_{MW}$ are higher than those under the CH condition. Therefore, the higher values of E_{aMW} and $\ln A_{MW}$ in comparison with the CH is a consequence of the complex changes in the shape of the distribution function of the reacting molecules, which are caused by the processes of the thermodynamically equilibrium achievement and transesterification.

4 Conclusion

The rate of the TSMPC under the MWHCC condition is 2.5–3.5 times higher than the corresponding rate under the CH condition. The physicochemical properties of the obtained methyl esters correspond to the properties of the methyl esters required by the EN 14214 standard. The kinetics of the TSMPC under the CH and MWHCC conditions can be adequately described with the kinetic model of the pseudo first-order chemical reaction with respect to the TG concentration. The calculated values of the kinetic parameters under the MWHCC condition are higher than the corresponding values under the CH condition. The kinetic rate-determining step of the alkali-catalyzed TSMPC is a mass transfer of the reactants. The existence of a linear relationship between the values of the kinetic parameters determined for the MWHCC and CH conditions has also been proven.

The activation of the TG molecule for the TSMPC reaction has also been carried out through the SET of a certain

number of resonant photons from the reaction environment onto the resonant vibration mode of the TG molecule (out of plane C-C-C-bending vibrations of the TG molecules).

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