

## Vapor–liquid equilibria of triglycerides–methanol mixtures and their influence on the biodiesel synthesis under supercritical conditions of methanol

SANDRA GLIŠIĆ<sup>1</sup>, OSCAR MONTOYA<sup>2</sup>, ALEKSANDAR ORLOVIĆ<sup>1\*#</sup> and DEJAN SKALA<sup>1</sup>

<sup>1</sup>Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, P. O. Box 3503, 11120 Belgrade, Serbia and <sup>2</sup>Department of Chemical Engineering, National University of Columbia, Bogota D. C., Avendida Carrera 30 No 45-03, Columbia.  
(e-mail: orlovic@tmf.bg.ac.yu)

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*Abstract:* The non-catalytic synthesis of biodiesel (fatty acids methyl esters) from triglycerides and methanol proceeds at elevated pressures above 100 bar and temperatures above 523 K. Kinetic investigations of the system revealed an unusual behavior of the reaction rate constant with increasing temperature and pressure. In order to explain this phenomenon, the phase behavior of the triglycerides–methanol mixture was investigated. The phase equilibria of the binary system sunflower oil–methanol were measured at different temperatures between 473 and 503 K, and a range of pressures between 10 and 56 bar. The experimental data were correlated using the Peng–Robinson, Soave–Redlich–Kwong and Redlich–Kwong–Aspen equations of state and different mixing rules. The best results were obtained with the RK–ASPEN equation of state and the Van der Waals mixing rule (VdW), which were then used to calculate the distribution of the phases at pressures and temperatures usual for the non-catalytic synthesis of biodiesel under high pressures. The obtained data indicated a strong influence of the phase equilibria on the reaction kinetics.

*Keywords:* vapor–liquid equilibria, high pressure, supercritical conditions, binary interaction parameters, biodiesel synthesis.

### INTRODUCTION

The main advantages of the application of biodiesel fuel in internal combustion engines are: its renewability, its biodegradability, better quality exhaust gas emissions and the fact that it does not contribute to a rise in the level of carbon dioxide in the atmosphere.<sup>1</sup> These facts have led to increased interest in the production and application of biodiesel fuel worldwide. The conventional process of biodiesel synthesis proceeds with

\* Corresponding author.

# Serbian Chemical Society active member.

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the use of a homogeneous catalyst, either an alkaline or acid one, which necessitates downstream separation and purification units.<sup>2</sup> A catalyst-free process conducted under supercritical conditions offers an opportunity of a much simpler separation and purification of the obtained products (both biodiesel and glycerol). Extensive work has been done on supercritical synthesis in recent years, with the focus on: transesterification of rapeseed oil in supercritical methanol,<sup>3</sup> the influence of the reaction temperature and methanol/oil ratio on the reaction yield,<sup>4</sup> potential applicability of different alcohols<sup>5</sup> and the effects of water on the reaction yield.<sup>6</sup> The kinetics of a non-catalytic process was investigated by Diasakou *et al.*<sup>7</sup> under subcritical methanol conditions (493 and 508 K at 55 and 62 bar, respectively) and the results of this study indicated low reaction rates under these conditions (10 h for complete conversion of triglycerides in a batch reactor). The kinetic study of Kusdiana and Saka<sup>8</sup> was performed under subcritical and supercritical methanol conditions (temperatures of 473–773 K and pressures 70–1050 bar) and results indicated a significant increase of the reaction rate with pressure and temperature. The authors reported a break of the Arrhenius plot in the region between 543 and 573 K, which was attributed to the increased hydrophobic nature of methanol and the better solubility of triglycerides under these conditions. These results also indicate that the phase equilibria of the system play an important role in the reaction mechanism and kinetics of the non-catalytic synthesis.

The phase equilibria of similar binary systems, such as triglycerides–propane or triglycerides–CO<sub>2</sub>, were investigated by several research groups. Among them, noticeably, De la Fuente *et al.*<sup>9</sup> studied the phase equilibria of binary mixtures of sunflower oil with propane and ethane. The experimental data were correlated using the SRK EOS along quadratic mixing rule. Straver *et al.*<sup>10</sup> reported experimental data of near critical propane with tristearin for temperatures between 300 and 460 K and pressures up to 160 bar in order to determine the low critical end point (LCEP) and upper critical end point (UCEP) for this mixture. Weber *et al.*<sup>11</sup> correlated data for systems of triolein, tripalmitin, tristearin–CO<sub>2</sub> and tristearin–propane. For systems containing CO<sub>2</sub>, they found that better results are obtained with the Mathias–Klotz–Prausnitz mixing rule (MKP) and that for systems containing propane, a simple Van der Waals (VdW) mixing rule could be used. Bottini *et al.*<sup>12</sup> studied the capability of the group contribution equation of state (GC–EOS) to calculate vapor–liquid equilibria of supercritical alkane–vegetable oils mixtures. Florusse *et al.*<sup>13</sup> represented experimental equilibria data for the system dimethyl ether–tripalmitin using GC–EOS as well (temperatures between 275 and 450 K and pressures up to 1200 bar).

In this study, the vapor–liquid equilibria of the system triglycerides (sunflower oil)–methanol was measured at different temperatures and pressures (473–503 K and 30–56 bar), and correlated with the Peng–Robinson (PR), Soave–Redlich–Kwong (SRK) and Redlich–Kwong–Aspen (RK–ASPEN) equations of state. Van der Waals, Adachi–Sugie (AS) and Mathias–Klotz–Prausnitz (MKP) mixing rules were used along the above equations of state to correlate the experimental data. Since the binary

mixture triglycerides–methanol is a reactive system, the experimental data were collected under pressure and temperature conditions which correspond to very low reaction rates. The phase equilibria of the system were predicted around the kinetic transition temperature region (543–573 K) using the most appropriate equation of state in order to explain the significant increase of reaction rate which occurs in this narrow temperature region.

### EXPERIMENTAL

Methanol was purchased from Merck and food grade sunflower oil was supplied by a local producer ("Servo Mihalj").

The high pressure equipment (Ernst Haage), shown in Fig. 1, was used according to the static-analytic method and the experiments were carried out by bringing the system to equilibrium conditions. Different amounts of methanol and sunflower oil were introduced into the high-pressure vessel (volume 2 dm<sup>3</sup>, height/diameter ratio 3.78), followed by heating the system to the desired temperature (the temperature was measured with a thermocouple K- type, with an accuracy of  $\pm 1$  K). The pressure depended on the initial amount of the components and was measured with an accuracy of 0.2 bar. Once the system had reached the desired conditions ( $T, P$ ), the mixture was stirred at 400 rpm for half an hour in order to equilibrate the phases. After that, the stirrer was stopped and the phases were allowed to settle for an additional half an hour in order to facilitate the elimination of drops from the vapor phase and bubbles from the liquid phase. The vapor phase sample was taken from the top of the vessel (vessel cover outlet) through the upper sampling valve and the liquid phase sample was taken from the vessel bottom outlet through bottom sampling valve. Both samples were cooled with appropriate heat exchangers to ambient temperature prior to further processing. The low solubility of triglycerides in the vapor phase demanded relatively large samples, which were typically 50 ml at ambient conditions. Due to the large vessel volume (2 dm<sup>3</sup>) and slow sampling (10 min), there was no change of the system pressure and temperature and, consequently, the system phase equilibria remained undisturbed by the sampling procedure. Once the samples of both phases had been withdrawn from the vessel, gravimetric analysis was applied. In the first step methanol was evaporated and subsequently the triglycerides content present in both the liquid and vapor phase was determined gravimetrically using a high precision analytical balance. The reproducibility of the method was tested by repeating the experiment twice for each pair of pressure and temperature conditions and the average deviations of the experimental data were: 3.09 % for the liquid phase and 0.15 % for the vapor phase.

The main problem in the determination of the triglycerides–methanol phase equilibria is the reaction between the components. In order to collect representative and reasonably accurate phase equilibria

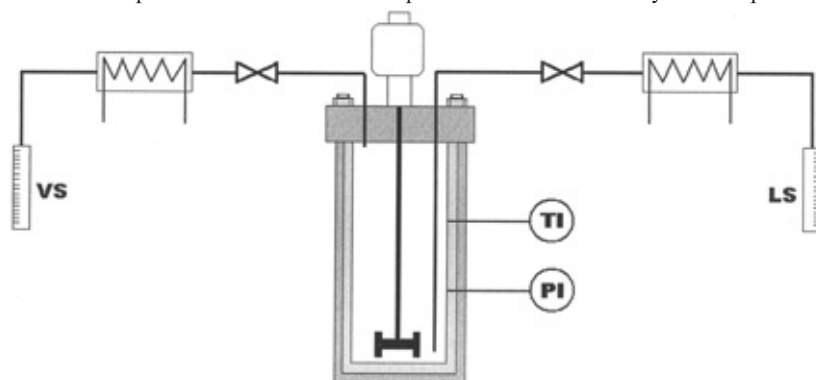


Fig. 1. Schematic representation of the experimental set-up (LS – liquid sampler, VS – vapor sampler, TI – temperature indicator, PI – pressure indicator).

data, it was necessary to avoid pressure and temperature conditions which favor the reaction, but which could still serve for the intended calculation of the phase equilibria at high pressures and temperatures. According to the results of Diaskou *et al.*<sup>7</sup> after 30 min at 493 K and 55 bar, the conversion of triglycerides is around 30 % and the yield of fatty acids methyl esters is 15 % of the theoretical yield. Our HPLC measurements indicated 8.45% of fatty acids methyl esters (FAME) in the sample treated at 473 K and 20 bar for 30 min, and 23.80 % of FAME in the sample treated at 513 K and 63 bar for 30 min. In order to minimize the influence of the reaction products (diglycerides, monoglycerides and methyl esters) on the binary sunflower oil–methanol equilibria, the following pressure and temperature regions were selected for the experimental phase equilibria measurements: 473–503 K and 29–56 bar.

## RESULTS AND DISCUSSION

### *Correlation of experimental data*

Sunflower oil is composed mainly of triolein (17.7 %wt) and trilinolein (72.8 %wt), with minor contents of tripalmitin (6.4 %wt), tristearin (2.9 %wt) and other triglycerides (0.2 %wt). However, to simplify the problem, it is convenient to represent the complex composition of sunflower oil with a pseudo component. In this case, the selected pseudo component was triolein and non trilinolein, since it is the components for which more thermodynamic data is available in the literature.<sup>11</sup> The critical constants of the pure components are needed for the calculation of  $a(T)$  and  $b(T)$ , but these constants are not available for compounds such as fats, since they are chemically unstable and decompose at high temperatures. For this reason the Gani Method<sup>14,15</sup> was used to estimate the critical properties of triolein, as this method offers better results for high molecular weight molecules such as triglycerides.<sup>16</sup> The critical properties and other parameters of the pure components are listed in Table I.

TABLE I. Equation of state parameters for the pure components

	$M/\text{kg kmol}^{-1}$	$T_c/\text{K}$	$P_c/\text{bar}$	$\omega$
Methanol	32	512.6	80.09	0.565
Triolein <sup>a</sup>	884	977.88	3.34	1.978

<sup>a</sup>Parameters calculated by the Gani method<sup>15,16</sup>

The Soave–Redlich–Kwong (SRK),<sup>17</sup> Peng–Robinson (PR)<sup>18</sup> and Redlich–Kwong–Aspen (RK–ASPEN)<sup>11</sup> EOS were used to correlate the experimental data. The correlations were carried out using PE 2000 developed by Pfohl, Petkov, Brunner<sup>19</sup> and the ASPEN Properties Tool.<sup>20</sup> The equations of state are given by expressions (1) to (8).

### *Peng–Robinson EOS*

$$P = \frac{RT}{V - b} - \frac{a(T)}{V^2 + 2bV - b^2} \quad (1)$$

with

$$a_i(T) = 0.45724 \frac{R^2 T_c^2}{P_c} [1 + (0.37464 + 1.54226\omega - 0.266992\omega^2)(1 - \sqrt{T_r})]^2 \quad (2)$$

$$b_i = 0.0778 \frac{RT_c}{P_c} \quad (3)$$

*Soave–Redlich–Kwong EOS*

$$P = \frac{RT}{V-b} - \frac{a(T)}{V^2 + bV} \quad (4)$$

with

$$a_i = 0.42747 \frac{R^2 T_c^2}{P_c} [1 + (0.48 + 1.574\omega - 0.176\omega^2)(1 - \sqrt{T_r})]^2 \quad (5)$$

$$b_i = 0.08664 \frac{RT_c}{P_c} \quad (6)$$

*Redlich–Kwong–Aspen EOS*

$$P = \frac{RT}{V-b} - \frac{a(T)}{V^2 + bV} \quad (7)$$

with

$$a_i = f(T, T_{ci}, P_{ci}, \omega_i, \eta_i) \text{ and } b_i = f(T_{ci}, P_{ci})^{20,21} \quad (8)$$

The polar factor  $\eta$  was set to zero for both methanol and triglyceride.

*Mixing rules*

The Van der Waals, Adachi–Sugie and Mathias–Klotz–Prausnitz mixing rules were used along with the PR and SRK EOS, while the VdW mixing rule was used with the RK–ASPEN EOS to correlate the experimental data. These mixing rules are given by Eqs. (9) to (19).

*Van der Waals*

$$a = \sum_{i=1}^N \sum_{j=1}^N x_i x_j a_{ij} \quad (9)$$

$$b = \sum_{i=1}^N \sum_{j=1}^N x_i x_j b_{ij} \quad (10)$$

$$a_{ij} = \sqrt{a_i a_j} (1 - k_{ij}) \quad \text{with} \quad k_{ij} = k_{ji} \quad (11)$$

$$b_{ij} = \frac{b_i + b_j}{2} (1 - l_{ij}) \quad \text{with} \quad l_{ij} = l_{ji} \quad (12)$$

To achieve a higher flexibility of the mixing model, some authors, such as Adachi and Sugie<sup>22</sup> and Mathias, Klotz and Prausnitz,<sup>23</sup> have modified the original VdW mixing rule. These modifications are very useful especially when there are no interactions between the species present in the system. The SRK EOS combined with AS mixing was found to correlate well the phase equilibria data of a similar binary system methyl oleate–carbon dioxide at high pressures.<sup>24</sup>

#### *Adachi–Sugie*

$$a = \sum_{i=1}^N \sum_{j=1}^N x_i x_j a_{ij} \quad (13)$$

$$b = \sum_{i=1}^N \sum_{j=1}^N x_i x_j b_{ij} \quad (14)$$

$$a_{ij} = \sqrt{a_i a_j} (1 - k_{ij} - \lambda_{ij} (x_i - x_j)) \quad \text{with} \quad k_{ij} = k_{ji} \text{ and } \lambda_{ij} = -\lambda_{ji} \quad (15)$$

$$b_{ij} = \frac{b_i + b_j}{2} (1 - l_{ij}) \quad \text{with} \quad l_{ij} = l_{ji} \quad (16)$$

#### *Mathias–Klotz–Prausnitz*

$$a = \sum_{i=1}^N \sum_{j=1}^N x_i x_j \sqrt{a_i a_j} (1 - k_{ij}) + \sum_{i=1}^N x_i \left[ \sum_{j=1}^N x_j (\sqrt{a_i a_j} \lambda_{ij})^{1/3} \right]^3 \quad (17)$$

With  $k_{ij} = k_{ji}$  and  $\lambda_{ij} = -\lambda_{ji}$

$$b = \sum_{i=1}^N \sum_{j=1}^N x_i x_j b_{ij} \quad (18)$$

$$b_{ij} = \frac{b_i + b_j}{2} (1 - l_{ij}) \quad \text{with} \quad l_{ij} = l_{ji} \quad (19)$$

#### *RK–ASPEN EOS mixing rule*

The RK–ASPEN EOS is an extension of the SRK EOS and it uses the VdW mixing rule (equations (20) to (23)) for correlating data.

$$a = \sum_{i=1}^N \sum_{j=1}^N x_i x_j a_{ij} \quad (20)$$

$$b = \sum_{i=1}^N \sum_{j=1}^N x_i x_j b_{ij} \quad (21)$$

$$a_{ij} = \sqrt{a_i a_j} (1 - k_{ij}) \quad (22)$$

$$b_{ij} = \frac{b_i + b_j}{2} (1 - l_{ij}) \quad (23)$$

The temperature dependence of the parameters  $k_{ij}$  and  $l_{ij}$  can be obtained with Eqs. (24) and (25).

$$k_{ij} = k_{ij}^0 + k_{ij}^1 \frac{T}{1000} \quad (24)$$

$$l_{ij} = l_{ij}^0 + l_{ij}^1 \frac{T}{1000} \quad (25)$$

Average deviations for both phases were calculated on the basis of the relative root-mean-square deviations (*RMSDr*) defined by:

$$RMSDr = 100 \sqrt{\frac{1}{n} \sum_{i=1}^n \left( \frac{\tau_i^{\text{exp}} - \tau_i^{\text{cal}}}{\tau_i^{\text{exp}}} \right)^2} [\%] \quad (26)$$

where  $\tau$  represents the mole fraction of component  $i$  in the liquid and vapor phase.

TABLE II. Experimental phase equilibria data of the system triolein–methanol

<i>T</i> /K	Pressure experimental/bar	Pressure calculated/bar	Methanol mol fraction in liquid <i>x</i> exp	Methanol mol fraction in gas <i>y</i> exp
473	39.7	39.70	0.9744	0.9997
	36.7	36.72	0.9413	0.9998
	34.1	34.10	0.9087	0.9996
	29.2	29.21	0.8540	0.9996
483	45.3	45.22	0.9655	0.9999
	42.5	42.31	0.9557	0.9999
	39.9	39.82	0.9292	1.0000
	31.1	31.13	0.8642	0.9998
493	48.6	48.92	0.9755	0.9997
	48.0	48.00	0.9729	0.9997
	43.5	43.53	0.9569	0.9999
	40.4	40.37	0.9170	0.9999
503	56.0	56.00	0.9849	0.9998
	52.0	51.99	0.9775	0.9999
	38.0	38.01	0.8906	0.9997
	30.0	30.02	0.8207	0.9995

The experimental vapor–liquid equilibria data are shown in Table II. The values of the relative deviation of correlations obtained by the PR, SRK and RK–ASPEN EOS combined with the VdW, AS and MKP mixing rules are shown in Table III. The results indicate that the maximum relative deviation for the liquid phase was 11.85 % and for the vapor phase 0.03 %. From Table III, it can be observed that all mixing rules are appropriate for predicting the composition of the vapor phase with a very small deviation, while the deviation for the liquid phase is always larger. As can be seen from Tables III and IV, the best correlation of the experimental data was obtained using the RK–ASPEN EOS along the VdW mixing rule. Also, the correlation obtained using the PR EOS was slightly better than that with the SRK EOS (Table III). The mixing rule which correlated best the experimental data with the PR EOS was the MKP, while with the SRK EOS it was the AS mixing rule. Fig. 2 shows the investigated isotherms at 473, 483, 493 and 503 K calculated using the RK–ASPEN EOS and the VdW mixing rule.

Table III. The relative deviations of the regressions using the PR, SRK and RK–ASPEN EOS with different mixing rules

EOS	Mixing rule	Relative deviation $x/\%$	Relative deviation $y/\%$
<i>T</i> = 473.15 K			
PR	VdW	1.1749	0.0336
PR	AS	1.1642	0.0336
PR	MKP	1.1638	0.0336
SRK	VdW	1.2637	0.0336
SRK	AS	1.0708	0.0336
SRK	MKP	1.2146	0.0336
RK–ASPEN	VdW	0.0650	0.0179
<i>T</i> = 483.15 K			
PR	VdW	1.0139	0.0123
PR	AS	0.9947	0.0123
PR	MKP	0.9690	0.0123
SRK	VdW	1.1161	0.0123
SRK	AS	1.1063	0.0123
SRK	MKP	1.1126	0.0123
RK–ASPEN	VdW	0.0331	0.0078
<i>T</i> = 493.15 K			
PR	VdW	1.9032	0.0071
PR	AS	1.9939	0.0071
PR	MKP	1.8797	0.0071



Table III. Continued

EOS	Mixing rule	Relative deviation $x/\%$	Relative deviation $y/\%$
SRK	VdW	2.8611	0.0194
SRK	AS	2.8434	0.0194
SRK	MKP	2.8468	0.0194
RK-ASPEN	VdW	0.1531	0.0070
$T = 503.15 \text{ K}$			
PR	VdW	9.0803	0.0194
PR	AS	8.5543	0.0212
PR	MKP	5.6933	0.0187
SRK	VdW	11.8545	0.0312
SRK	AS	11.3275	0.0312
SRK	MKP	11.7651	0.0312
RK-ASPEN	VdW	0.0318	0.0237

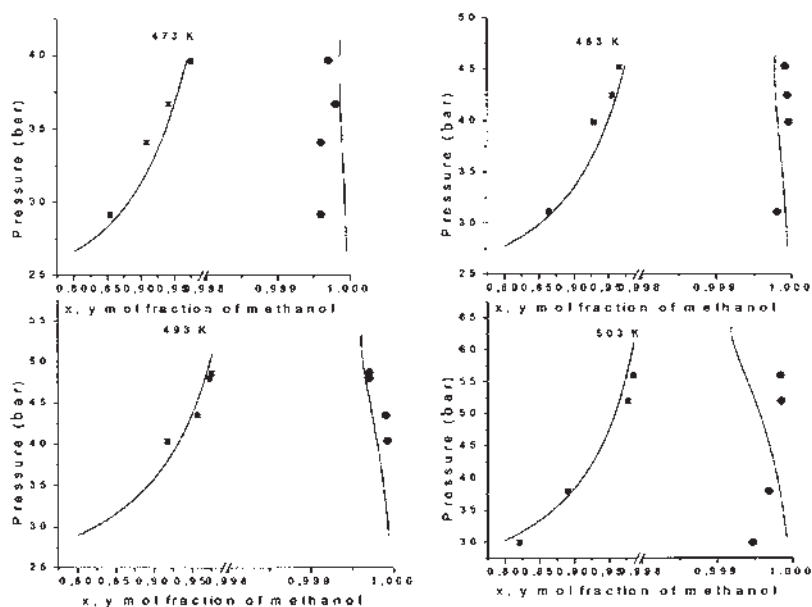


Fig. 2. The experimental data and isotherms obtained with the RK-ASPEN EOS along the VdW mixing rule (■ liquid phase experimental data; ● vapor phase experimental data).

The values of the binary interaction parameters over the investigated temperature range are shown in Tables V (for RK-ASPEN) and VI (for PR-MKP and SRK-AS).

The phase behavior of a reactive system involving supercritical fluids can play an important role in the course of the reaction and the overall conversion. For example, a significant influence of phase equilibria on dibenzyl ether pyrolysis in supercritical toluene was demonstrated by Wu *et al.*<sup>25</sup> In order to investigate the influence

of phase equilibria of triglycerides–methanol mixture on the biodiesel synthesis at high pressure and temperature, the RK–ASPEN EOS with optimized binary interaction parameters (Table V) and Eqs. (24) and (25) were used to perform a flash calculation at the temperatures, pressures and methanol/triglycerides ratio used by Kusdiana and Saka in their kinetic investigation.<sup>8</sup> Fig. 3 and Table VII give the values of the pseudo first order kinetic constant<sup>8</sup> along with the distribution of the phases in the system as predicted by the RK–ASPEN EOS. As can be seen, the Arrhenius plot consists of two branches, an upper and a lower one, with a transition region from 543 to 573 K between them (Fig. 3). The flash calculation indicated the presence of only vapor phase at the high reaction rates (upper branch), while the first two points of the lower branch corresponded to liquid phase conditions and the third point to vapor phase conditions (Fig. 3). This significant increase in the reaction rate constant when going from the liquid phase reaction to the vapor phase reaction can be attributed to a change of the reaction mechanism. A reaction mechanism change when going from subcritical to supercritical reaction conditions was reported for the similar reaction of ester hydrolysis by Krammer and Vogel,<sup>26</sup> who explained this phenomenon by the modified structural properties of water under supercritical conditions. High reaction rates were found at higher temperatures and lower densities of the supercritical water, since under these conditions water consists of small clusters and gas-like molecules as the result of the absence of hydrogen bonding. Structural investigations of subcritical and supercritical methanol have revealed a similar behavior of methanol above its critical point.<sup>27,28</sup> The results of these investigations can be summarized by the following: the number of hydrogen bonds decreases with increasing temperature and pressure as in the case of water, below a density of 0.3 mol/dm<sup>3</sup>, supercritical methanol exists dominantly in the monomeric form, between 0.3 and 15 mol/dm<sup>3</sup>, supercritical methanol exists in monomeric – dimeric structural forms equilibria, increasing temperature at a constant reduced density results in a shift of the structural equilibria to smaller species, and above 15 mol/dm<sup>3</sup>, the presence of hydrogen bonding shifts the methanol structure equilibria to larger aggregates.

TABLE IV. The experimental and calculated vapor–liquid using the PR, SRK and RK–ASPEN EOS along the most appropriate mixing rules

T/K	P/bar	Methanol mol fraction in liquid				Methanol mol fraction in vapor			
		$x_{\text{exp}}$	$x$			$y_{\text{exp}}$	$y$		
			RK–ASPEN	SRK–AS	PR–MKP		RK–ASPEN	SRK–AS	PR–MKP
473	39.68	0.9744	0.9745	0.9652	0.9623	0.9997	0.9998	1.0000	1.0000
	36.72	0.9413	0.9414	0.9417	0.9331	0.9998	0.9998	1.0000	1.0000
	34.09	0.9087	0.9095	0.9195	0.9175	0.9996	0.9998	1.0000	1.0000
	29.2	0.8540	0.8548	0.8702	0.8700	0.9996	0.9999	1.0000	1.0000
483	45.28	0.9655	0.9655	0.9623	0.9621	0.9999	0.9998	1.0000	1.0000
	42.48	0.9557	0.9554	0.9541	0.9441	0.9999	0.9999	1.0000	1.0000

TABLE IV. Continued

T/K	P/bar	Methanol mol fraction in liquid			Methanol mol fraction in vapor				
		$x_{\text{exp}}$	$x$	$x$	$x$	$y_{\text{exp}}$	$y$	$y$	$y$
			RK-ASPEN	SRK-AS	PR-MKP		RK-ASPEN	SRK-AS	PR-MKP
39.86	0.9292	0.9293	0.9273	0.9267	1.0000	0.9999	1.0000	1.0000	
31.12	0.8642	0.8647	0.8480	0.8520	0.9998	0.9999	1.0000	1.0000	
493	48.63	0.9755	0.9754	0.9508	0.9579	0.9997	0.9997	1.0000	0.9998
	48	0.9729	0.9730	0.9478	0.9553	0.9997	0.9997	1.0000	0.9998
	43.5	9.9569	0.9570	0.9208	0.9319	0.9999	0.9998	1.0000	0.9999
	40.4	0.9170	0.9198	0.8963	0.9089	0.9999	0.9998	1.0000	0.9999
503	56	0.9849	0.9849	0.9603	0.9621	0.9998	0.9997	1.0000	0.9999
	52	0.9775	0.9775	0.9437	0.9466	0.9999	0.9997	1.0000	0.9999
	38	0.8906	0.8912	0.8256	0.8485	0.9997	0.9998	1.0000	1.0000
	30	0.8207	0.8206	0.6482	0.7420	0.9995	0.9999	1.0000	1.0000

TABLE V. Binary interaction parameters over the investigated temperature range (473–503 K), regressed with the RK-ASPEN EOS and the VdW mixing rule

Parameter	Value
$k_{ij}^0$	0.679953
$k_{ij}^1$	-2.000000
$l_{ij}^0$	-1.217525
$l_{ij}^1$	1.753871

TABLE VI. Binary interaction parameters regressed with the PR EOS along the MKP mixing rule and with the SRK EOS along the AS mixing rule

Temperature/K	Interaction parameters		
	$k_{1,2}$	$l_{1,2}$	$\lambda_{1,2}$
PR-MKP			
473	-0.092131	0.094685	0.021604
483	-0.038109	0.103971	0.111250
493	-0.230635	-0.177136	-0.074614
503	-0.266321	-0.043031	-0.207143
SRK-AS			
473	-0.082066	0.070603	0.010837
483	-0.058790	0.063627	-0.009634
493	-0.205408	-0.062518	0.095507
503	-0.145571	-0.077121	0.037586

TABLE VII. The pseudo first order reaction rate constant, phase distribution of the system and methanol density at the reaction conditions investigated by Kusdiana and Saka<sup>8</sup>

Temperature/K	Pressure/bar	Rate constant/s <sup>-1</sup>	Vapor fraction	Liquid fraction	Density/mol dm <sup>-3</sup>
473	70	0.0002	0	1	18.125
503	90	0.0003	0	1	15.625
543	120	0.0007	1	0	8.281
573	140	0.0071	1	0	6.094
623	190	0.0178	1	0	4.964
658	650	0.0249	1	0	10.678
704	900	0.0503	1	0	11.303
770	1050	0.0803	1	0	10.977

Based on these properties of supercritical methanol, it can be concluded that the vapor phase mechanism is governed by the existence of small methanol species, which react with triglyceride molecules in a manner different from that involving larger methanol aggregates. This can explain not only the low kinetic constant values in the liquid phase, but also the low value of the kinetic constant at 543 K and 120 bar, which corresponds to a vapor phase reaction. The density of supercritical (vapor) methanol under these conditions is 8.281 mol/dm<sup>3</sup>. This is a relatively high value and corresponds to hydrogen bonded structure consisting of

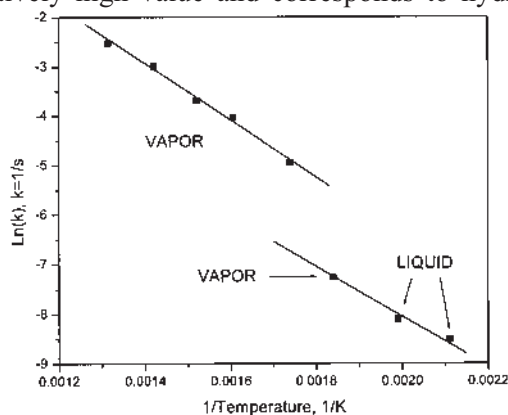


Fig. 3. The pseudo first order reaction rate constant, Arrhenius plot of rapeseed oil transesterification with methanol<sup>8</sup> and phase distribution of the system.

larger molecular aggregates, which is similar to the liquid phase structure (also due to the low reduced temperature  $T_r = 1.06$  under these conditions). High densities of supercritical methanol are also present at 658, 704 and 770 K, but under these conditions, the higher reduced temperatures ( $T_r > 1.28$ ) result in the breakdown of hydrogen bonds and smaller methanol species.

#### CONCLUSIONS

In this study, the phase equilibria of the triglycerides–methanol binary system was investigated using several equations of state and different mixing rules. Sun-

flower oil was used to represent triglycerides and triolein was used as the pseudo component for the correlation of the experimental data. The results indicate very good correlation of the experimental data with the Redlich–Kwong–Aspen equation of state and the Van der Waals mixing rule. The most adequate mixing rule along the Peng–Robinson equation of state was the Mathias–Klotz–Prausnitz mixing rule, while the Adachi–Sugie mixing rule was the most adequate one for the Soave–Redlich–Kwong equation of state. The results of a flash calculation performed with the Redlich–Kwong–Aspen equation of state and the extrapolated binary interaction parameters indicate the strong dependence of the kinetics of biodiesel synthesis on the phase distribution of the system. High reaction rates could be expected when only the vapor phase is present and when the pressure and temperature correspond to a low density of supercritical methanol. Low density, supercritical methanol is characterized by a structure dominantly composed of the non-hydrogen bonded small species. This specific structure is probably responsible for the difference in the reaction mechanism compared to that found in high density methanol, which is characterized by large molecular aggregates.

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#### LIST OF SYMBOLS

$a$  – Attraction parameter (EOS-parameter)  
 $b$  – Molecular co-volume (EOS-parameter)  
 $k$  – Adjustable binary interaction parameter  
 $l$  – Adjustable binary interaction parameter  
 $\lambda$  – Adjustable binary interaction parameter  
 $n$  – Number of components  
 $P$  – Pressure  
 $T$  – Temperature  
 $x$  – Mole fraction for the liquid phase  
 $y$  – Mole fraction for the vapor phase  
 $\omega$  – Acentric factor  
 $\eta$  – Polar factor

#### *Subscripts*

$c$  – critical point  
 $i$  – index to denote component  
 $j$  – index to denote component

#### *Superscripts*

Calc – calculated  
Exp – experimental

## ИЗВОД

## РАВНОТЕЖА ПАРА–ТЕЧНОСТ ЗА СИСТЕМ ТРИГЛИЦЕРИДИ–МЕТАНОЛ И ЊЕН УТИЦАЈ НА КИНЕТИКУ СИНТЕЗЕ БИОДИЗЕЛА ПОД УСЛОВИМА НАТКРИТИЧНОГ МЕТАНОЛА

САНДРА ГЛИШИЋ<sup>1</sup>, OSCAR MONTOYA<sup>2</sup>, АЛЕКСАНДАР ОРЛОВИЋ<sup>1</sup> и ДЕЈАН СКАЛА<sup>1</sup><sup>1</sup>Технолошко-металуришки факултет, Универзитет у Београду, Карнегијева 4, 11120 Београд и <sup>2</sup>Department of Chemical Engineering, National University of Columbia, Bogota D. C., Avenida Carrera 30 No. 45-03, Columbia

Синтеза биодизела (метил-естара виших масних киселина) из триглицерида и метанола се одвија без присуства катализатора на условима повишеног притиска, изнад 100 bar, и температуре изнад 523 К. Кинетичка испитивања ове реакције су указала на необично понашање константе брзине хемијске реакције са порастом температуре и притиска. У циљу објашњења ове појаве испитивана је фазна равнотежа система триглицериди–метанол на повишеном притиску и температури. Равнотежа фаза бинарног система сунцокретово уље–метанол је испитивана на температурама од 473 до 523 К и притисцима од 10 до 56 bar. Експериментални подаци су корелисани коришћењем Peng–Robinson, Soave–Redlich–Kwong и Redlich–Kwong–Aspen једначина стања уз примену различитих правила мешања. Најбољи резултати корелисања експерименталних података су добијени применом RK–ASPEN једначине стања и Van der Waals-овог правила мешања. RK–ASPEN једначина стања је затим искоришћена за израчунавање фазне равнотеже за бинарни систем триглицериди – метанол на повишеним притисцима и температурама, који су уобичајени за реакцију синтезе биодизела без присуства катализатора. Добијени резултати су указали на значајну зависност кинетике реакције од фазне равнотеже посматраног бинарног система.

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