

Kinetic approach of methanolysis of triglycerides at supercritical conditions

Sandra Glisic*, Dejan Skala

Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, POB3503, 11120, Belgrade, Serbia, sglisic@tmf.bg.ac.yu

ABSTRACT

The synthesis of biodiesel represents challenge for many researchers in the World requesting as main task determination the most economical and at the same time environmentally acceptable technology of production. Application of supercritical alcohols (methanol and ethanol) for biodiesel production seems that completely fulfils both tasks. However, the process optimisation is usually based on detailed and proven knowledge of process kinetic in this case the kinetics of supercritical alcoholysis.

Investigation of supercritical methanolysis of triglycerides and determination of kinetic parameters has been the object of several articles published in the last ten years. Most of them suggested the first order kinetic model for representing reaction of vegetable oil and methanol under supercritical condition. Unfortunately, such simple model did not explain the experimental data thoroughly. A literature review was summarised in this study and on the basis of experimental data published by several authors [1-3] the new kinetic model was proposed and tested. This study indicated that better results could be obtained if triglyceride conversion is assumed to be the first order reversible reaction depending on concentration of triglycerides and glycerol for forward and reverse reaction, respectively. The proposed model not only better fits the experimental data for triglyceride conversion but also gives a new starting point for advanced investigation of phase arrangement for such complex mixture and analysis of equilibrium between existing phases under supercritical condition.

INTRODUCTION

Alcoholysis of triglycerides is usually described as a three step consequent reversible reactions [4-6]. In each step of this complex reaction one mol of methanol react and one mol of methyl esters is obtained. The most relevant papers related to subcritical or supercritical methanolysis and mainly to kinetic investigation assumed a simple first order irreversible reaction as an acceptable kinetic model for representing the supercritical methanolysis of vegetable oil [1-3, 7-10].

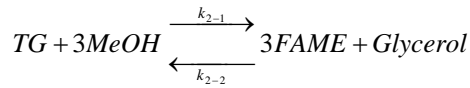
Saka and Kusdiana [3] were analyzed the kinetic of supercritical alcoholysis, assuming that one stoichiometric equation and kinetic expressed by the first order reaction could satisfied experimental data without taking into account complex reaction scheme in which diglycerides and monoglycerides are also products of consecutive-parallel reaction between methanol and oil. The reaction rate constant in temperature interval from 200 to 500 °C was also determined. They indicated that almost same value of activation energy (E) valid for subcritical and supercritical region, but, the pre-exponential factor (A) in equation which define the influence of temperature on reaction rate constant ($k=A \cdot \exp(-E/RT)$) is significantly different changing its value (increases) during transition from subcritical to

supercritical region. Some other authors related the change of frequency factor with density of methanol.

Tabe et al. [11] analyzed reaction between methanol and oil as kinetic mechanism represents by three step irreversible and pseudo first order reactions, and found that reaction rate constants are: $k_{MG} > k_{DG} > k_{TG}$. The subscripts MG, DG and TG of reaction rate constants represent the reaction in which monoglycerides (MG), diglycerides (DG) and triglycerides (TG) are consumed, respectively. All three constants increase with temperature increase. The same results was obtained by Disakou et all [12], analysing the methanolysis of vegetable oil and determination of reaction kinetic at subcritical conditions (220 – 235 °C).

MATERIAL AND METHODS

In this study, the experimental data of triglyceride conversion and yield of FAME (fatty acid methyl esters) at 230-280 °C was used for detailed analysis [1]. The kinetic of methanolysis of triglyceride was assumed according to summarised stoichiometric equation:



being the reversible and second order reaction. For closed system of constant volume the mole balance which represents the change of concentration of triglyceride could be expressed by equation:

$$-\frac{dC_{TG}}{dt} = k_{2-1}C_{TG}C_{MeOH} - k_{2-2}C_{FAME}C_{Glycerol}$$

and in the case

$$C_{MeOH} \gg C_{TG}; C_{FAME} > C_{GL}$$

It can be defined as pseudo first order reversible reaction:

$$-\frac{dC_{TG}}{dt} = k_1C_{TG} - k_2C_{Glycerol}$$

Integral equation of mole balance, i.e. the solution of above differential equation with initial condition $C_{TG}(0) = C_{TG0}$ for $t=0$, expressed in the form of degree of conversion of triglyceride: $X_{TG} = [1-(C_{TG}/C_{TG0})]$ is in the form :

$$X_{TGe} \ln\left(\frac{X_{TGe}}{X_{TGe} - X_{TG}}\right) = k_1 \cdot t$$

where, X_{TGe} is equilibrium degree of conversion of triglyceride.

For a different value of conversion of triglycerides in temperature interval from 240 °C to 280 °C the integral equation: $X_{TGe} \ln(X_{TGe}/(X_{TGe}-X_{TG}))$ as a function of time was analyzed. Equilibrium degree of conversion was determined by statistical analysis of experimental data (based on minimal deviation of calculated conversion of triglycerides and experimentally determined for some assumed value X_{TGe}). Based on such analysis the equilibrium degree of conversions (X_{TGe}) were calculated for different temperature, and thus determined the reaction rate constants for forward and reverse reaction (k_1 and k_2) as well as the equilibrium constant ($K=k_1/k_2$) (Table 1).

Arrhenius plot of the forward and reverse reaction rate constant is shown in **Figure 1**. The activation energies for forward and reverse reaction, determined from the slope of the lines as well as pre-exponential factor are given also in **Figure 1**.

From these values one can derive relation between equilibrium constant and temperature:

$$\ln K = -29.96 + 16528/T$$

and used for calculation the equilibrium degree of conversion for other temperature interval used in these studies ($t < 240\text{ }^{\circ}\text{C}$ and $t > 280\text{ }^{\circ}\text{C}$) (**Table 2**). From calculated data, it seems that reversible reaction could be obviously neglected at temperature below $250\text{ }^{\circ}\text{C}$.

Table 1. Kinetic parameter for reversible first order reaction of methanolysis of vegetable oil

t , $^{\circ}\text{C}$	$1000/T$, $1/\text{K}$	X_{TGe}	k_1 , $1/\text{min}$	k_2 , $1/\text{min}$	$K^* = k_1/k_2$
280	1.808	0.950	0.0652	0.00343	19.00
270	1.841	0.970	0.0518	0.001603	32.33
260	1.876	0.982	0.0329	0.000603	54.56
250	1.911	0.990	0.0281	0.000283	99.00
240	1.949	0.995	0.0218	0.00011	199.00

*The equilibrium constant was calculated from the value of the

equilibrium conversion:
$$K = \frac{X_{TGe}}{1 - X_{TGe}} = \frac{k_1}{k_2}$$

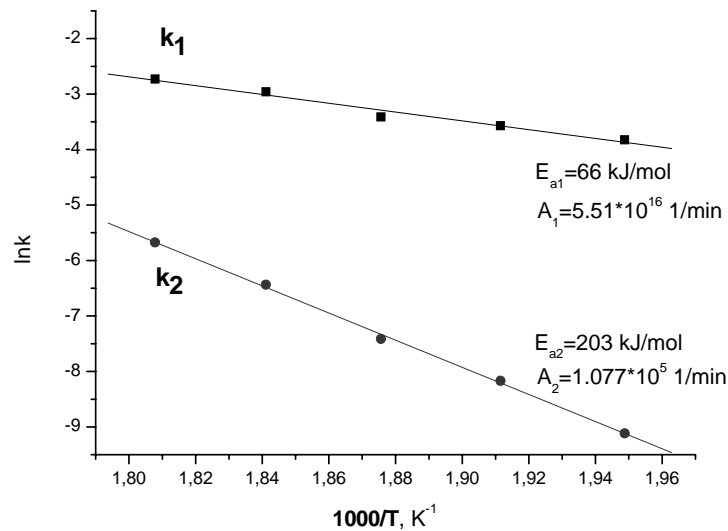


Figure 1. The rate constants of forward and reversible first order reaction as function of temperature

The reaction rate constants calculated on the basis of experimental data published in literature for temperature interval $240\text{--}280\text{ }^{\circ}\text{C}$ [1] were used for simulation and testing some other experimental data of triglyceride conversion [2,3] at subcritical ($t < 240\text{ }^{\circ}\text{C}$) [2] or supercritical condition ($t > 280\text{ }^{\circ}\text{C}$) [3] (**Table 2**). However, at temperature below $240\text{ }^{\circ}\text{C}$ and at temperature higher than $300\text{ }^{\circ}\text{C}$, calculated degree of conversion using integral equation for

the pseudo first order reversible reaction didn't give good prediction as can be seen from **Figure 2**.

Table 2. Testing of different experimental data from literature using calculated values of reaction rate constants

<i>Experimental data</i>	<i>t, °C</i>	<i>K=k₁/k₂</i>	<i>X_{TGe}</i>	<i>k₁, 1/min</i>	<i>k₂, 1/min</i>
Demirbas, 2002 [2]	230	360.99	0.997	0.015	4.59*10 ⁻⁵
	240	190.32	0.995	0.021	1.18*10 ⁻⁴
	250	102.83	0.990	0.028	2.94*10 ⁻⁴
Kusdiana and Saka, 2001 [3]	270	32.13	0.970	0.048	1.64*10 ⁻³
	300	6.53	0.867	0.104	1.73*10 ⁻²

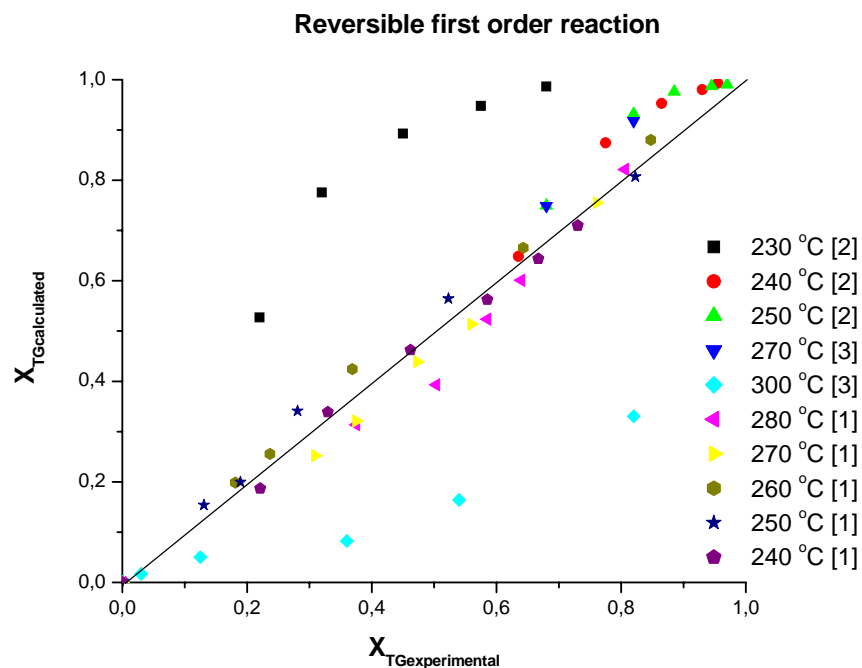


Figure 2. Comparison of calculated and experimental conversion data - the first order reversible reaction of methanolysis of vegetable oil

For assumed first order irreversible reaction as kinetic model a larger deviation between calculated and experimentally determined degree of conversion was obtained. The standard deviation between calculated on the basis of proposed kinetic model and experimentally determined degree of conversion of triglycerides is presented in **Table 3** for different working condition used in [1-3].

Table 3. Comparison of different kinetic model

Standard deviation, x10 ³					
Kinetic model	Temperature, °C				
	280	270	260	250	240
He and Sun, 2007 [1]					
First order irreversible	47.7	32.2	19.3	20.3	12.2
First order reversible	40.6	27.8	20.9	21.3	12.7
Demirbas, 2002 [2]	230	240	250		
First order irreversible	127.5	307.8	277.1		
First order reversible	127.6	308.0	277.6		
Kusdiana and Saka, 2001 [3]	270	300	350		
First order irreversible	48.8	143.5	152.2		
First order reversible	39.3	145.0	150.1		

The main reason for such large deviation between reaction rate constant of forward reaction calculated by Demirbas [2] and Kusdiana and Saka [3] at 230 °C, 300 °C and 350 °C could be explained by different working condition used for investigation of subcritical or supercritical methanolysis of vegetable oil [1-3]. Namely, the reaction rate constant for forward reaction based on data of He and Sun [1] was calculated for 280 bar and some correction of reaction rate constant obviously need to be done taking into account the actual value of methanol density (**Table 4**).

Table 4. Influence of actual density on determined reaction rate constant

<i>t</i> , °C	<i>P</i> , bar	Density at 280 bar, mol/dm ³	Density, mol/dm ³	<i>k_I</i> *, 1/sec	<i>k_I</i> , this study 1/sec	<i>k_I</i> / <i>k_I</i> *
230 [2]	90	18.46	15.16	8.0 * 10 ⁻⁴	2.5 * 10 ⁻⁴	0.31
240 [2]	98	17.92	13.86	4.0* 10 ⁻⁴	3.5 * 10 ⁻⁴	0.87
250 [2]	105	17.35	11.96	5.0 * 10 ⁻⁴	4.7 * 10 ⁻⁴	0.94
270 [3]	120	16.08	8.28	7.0 * 10 ⁻⁴	8.0 * 10 ⁻⁴	1.14
300 [3]	140	13.82	6.09	7.1 * 10 ⁻³	1.73 * 10 ⁻³	0.24
350 [3]	190	9.12	4.96	17.8 * 10 ⁻³	5.35 * 10 ⁻³	0.30

It was assumed that energy of activation of forward reaction has the same value in subcritical and supercritical region of temperature as already proposed by Kusdiana and Saka [2] and that only influence of density on pre-exponential factor is obviously important. The relation between reaction rate constant, temperature and density could be derived using polynomial non-linear regression:

$$\ln k = \ln A + a \ln \rho + \frac{E_a}{R} \cdot \frac{1}{T} .$$

The values of different parameters and the function which might be used for calculation the reaction rate constant are:

$$k_1 = 1.476 \times 10^6 \cdot \rho^{-0.1173243} \cdot e^{-\frac{93000}{R} \frac{1}{T}} \quad s^{-1} \quad (1)$$

The standard deviation of calculated reaction rate constant on the basis of equation (1) and k_1^* from **Table 4** is 0.0558.

CONCLUSION

In this study the analysis of experimental data [1-3] of degree of conversion of triglyceride which reacts with methanol at subcritical or supercritical condition using proposed kinetic model valid for reversible reaction of first order were performed. Obtained results indicated that better agreement between calculated and experimentally determined degree of conversion could be obtained if first order reversible reaction of triglyceride alcoholysis is assumed but only for temperature interval between 240 °C and 280 °C. The proposed model not only better fits the experimental data for triglyceride conversion but also gives a new starting point for advanced investigation of phase condition for such complex mixture and analysis of equilibrium between existing phases under supercritical condition.

The predicted kinetic model based on assumption that methanolysis of triglyceride in transition region between subcritical and fully observed supercritical region, based on data presented in literature [1] could be used for other temperature but only if specific working conditions, i.e. pressure and temperature which define density of supercritical or subcritical methanol is taking into account for determining corrected value of reaction rate constant.

REFERENCES

- [1] He, H., Sun, S., Wang, T., Zhu, S., Transesterification Kinetics of Soybean Oil for Production of Biodiesel in Supercritical Methanol, *Journal of the American Oil Chemists' Society*, Vol. 84, **2007**, p. 399.
- [2] Demirbas, A., Biodiesel from vegetable oils via transesterification in supercritical methanol *Energy Conversion and Management*, Vol. 43, **2002**, p. 2349.
- [3] Kusdiana, D., Saka, S., Kinetics of transesterification in rapeseed oil to biodiesel fuel as treated in supercritical methanol, *Fuel*, Vol. 80, **2001**, p. 693.
- [4] Freedman B., Butterfield, R.O., Pryde, E.H., Transesterification kinetics of soybean oil. *J. Am. Oil Soc. Chem.* Vol. 63, **1986**, p. 1375.
- [5] Schwab, A.W., Bagby, M.O., Freedman, B., Preparation and properties of diesel fuels from vegetable oils, *Fuel*, Vol. 66, **1987**, p. 1372.
- [6] Ma, F., Hanna, M.A., Biodiesel production: a review, *Bioresource Technology*, Vol. 70, **1999**, p. 1.
- [7] Madras, G., Kolluru, C., Kumar, R., Synthesis of biodiesel in supercritical fluids, *Fuel*, Vol. 83, **2004**, p.2029.
- [8] Silva, C., Weschenfelder, T. A., Rovani, S., Corazza, F. C., Corazza, M. L., Dariva, C., Oliveira, J., Continuous Production of Fatty Acid Ethyl Esters from Soybean Oil in Compressed Ethanol, *Ind. Eng. Chem. Res.*, Vol. 46, **2007**, p. 5304.
- [9] Song, E.-S., Lim, J.-W., Lee, H.-S., Lee, Y.-W., Transesterification of RBD palm oil using supercritical methanol, *Journal of Supercritical Fluids*, Vol. 44, **2008**, p. 356.
- [10] Varma, M. N., Madras, G., Synthesis of biodiesel from castor oil and linseed oil in supercritical fluids, *Industrial & engineering chemistry research*, Vol. 46, **2007**, p.1.
- [11] Tabe, A., D.Kusdiana, E.Minami, S.Saka, Kinetics of transesterification of rapeseed oil by supercritical methanol treatment, 2nd World Conference and Technology Exhibition Biomass for Energy, Industry and Climate Protection, Rome, Italy (**2004**).