J Amer Oil Chem Soc (2007) 84:399–404
DOI 10.1007/s11746-007-1042-8

ORIGINAL PAPER

Transesterification Kinetics of Soybean Oil for Production of Biodiesel in Supercritical Methanol

Huayang He · Shiyao Sun · Tao Wang · Shenlin Zhu

Received: 16 May 2006 / Accepted: 24 January 2007 / Published online: 28 February 2007

Abstract A kinetic study on soybean oil transesterification without a catalyst in subcritical and supercritical methanol was made at pressures between 8.7 and 36 MPa. It was found that the conversion of soybean oil into the corresponding methyl esters was enhanced considerably in the supercritical methanol. The apparent activation energies of the transesterification are different with the subcritical and the supercritical states of methanol, which are 11.2 and 56.0 kJ/mol (molar ratio of methanol to oil: 42, pressure: 28 MPa), respectively. The reaction pressure considerably influenced the yield of fatty acid methyl esters (FAME) in the pressure range from ambient pressure up to 25 MPa (280 °C, 42:1). The reaction activation volume of transesterification in supercritical methanol is approximately –206 cm^3/mol. The $P\Delta V^{\neq}$ term accounts for nearly 10% of the apparent activation energy, and can not be ignored (280 °C, 42:1).

Keywords Apparent activation energy · Activation volume · Biodiesel · Kinetics · Pressure · Supercritical methanol · Soybean oil

Introduction

The transesterification reaction of vegetable oil with supercritical methanol without a catalyst provides a new way of producing biodiesel fuel and was recently reported by Saka [1, 2], Madras [3], Demirbas [4, 5] and He [6]. Compared to conventional transesterification processes catalyzed by acid and alkali catalysts, there are several outstanding advantages of the supercritical method. It was reported that the transesterification reaction in supercritical methanol was completed in several minutes, while the conventional catalytic transesterification takes several hours. It was believed that the two phase oil and methanol mixture could be converted into a single phase under supercritical methanol conditions due to the great decrease in methanol's dielectric constant [1]. As a result, the good contact between the oil and alcohol greatly increases the rate of reaction. In addition, the supercritical alcohol is expected to act as an acid catalyst to accelerate thereaction [7]. The high reaction temperature and reaction pressure of the supercritical condition also help to accelerate the transesterification reaction. Because the transesterification reaction under supercritical conditions does not require catalysts, the purification of the products after transesterification in supercritical methanol is much simpler and more environmentally-friendly compared to conventional catalytic processes in which all the catalyst and saponification products have to be removed from the biodiesel fuel [2].

Some researchers have reported the kinetics of both acid and alkali-catalyzed transesterification reactions. Freedman [8], Noureddini [9] and Darnoko [10] studied the effects of the alcohol type, the molar ratio of alcohol to oil, the type and amount of catalyst, the mixing of reactants and the reaction temperature for the conventional transesterification of the vegetable oil. Diasakov [11] reported the kinetics of a non-catalytic transesterification reaction of soybean oil processed at

---

H. He · S. Sun · T. Wang · S. Zhu (✉)
State Key Laboratory of Chemical Engineering,
Department of Chemical Engineering,
Tsinghua University, Beijing 100084, China
e-mail: zhusl@tsinghua.edu.cn

220–235 °C. Recently, Saka et al. [2] reported the kinetics of transesterification of rapeseed oil to biodiesel fuel in supercritical methanol without using any catalyst. They studied the effects of the molar ratio and reaction temperature on methyl ester formation and proposed a simple model for the kinetics of the transesterification reaction.

In this work, the kinetics of transesterification of soybean oil in supercritical methanol without any catalyst was investigated. The effects of temperature and pressure on the transesterification reaction rate and apparent activation energy were reported. The reaction activation volume and its effect on the apparent activation energy were also determined.

Experimental Procedures

Materials

Soybean oil (edible grade, average molecular weight: 846) was purchased from Shanxi province, China. Anhydrous ethanol (Analytical Reagent) and *n*-hexane (Analytical Reagent) were supplied by Beihua Fine Chemical Co., Beijing. Esters of palmitic, heptadecanoic, stearic, oleic and linoleic acids (GC grade) were supplied by Sigma.

Transesterification Method

As depicted in Fig. 1, the transesterification reaction was carried out in a reaction apparatus consisting of a 200 ml reactor equipped with a stirrer and a heater, an oil bath, a preheater, a condenser and a separator. The reactants were preheated in the oil bath, then heated and maintained at the reaction temperature in the reactor. The reaction pressure was controlled using a pressure regulator.

A calculated amount of soybean oil was pumped into the reactor by a high pressure pump and heated gradually through the oil bath and preheater to a predetermined temperature. An appropriate volume of methanol was then inserted into the reactor in the same way over several seconds to start the reaction. The reaction mixture (the molar ratio of methanol to oil was 42:1) was stirred for the desired time at the reaction temperature (210–280 °C) and pressure (0–36 MPa).

Samples (1 mL) were taken from the reactor at various intervals, and were immediately immersed in an ice bath to quench the reaction. The samples were vacuum distilled at 50 °C to remove the methanol completely and allowed to settle for 20 min to separate the oil phase (crude ester) and the glycerol phase. The mass fraction of FAME in the glycerol phase was not more than 1.5% [12] under ambient conditions. Due to the ultra low solubility of FAME in the glycerol phase, the amount of ester in the glycerol layer was ignored in this study.

Analysis

The crude methyl ester was analyzed using a GC (Hewlett-Packard 6890) equipped with an HP-INNOWAX capillary column (30 m × 0.15 mm) and a flame ionization detector. The carrier gas was nitrogen. A 4-μL aliquot of the upper oil phase (crude ester) was mixed with 300 μL *n*-hexane and 100 μL internal standard solution (heptadecanoic acid methyl ester *n*-hexane solution). The prepared samples (1 μl) were injected into the column in the oven at 220 °C. After an isothermal period of 4 min, the GC oven was heated at 10 °C/min to 230 °C, and held for 7.5 min. The injector temperature and detector temperatures were 300 and 320 °C, respectively.

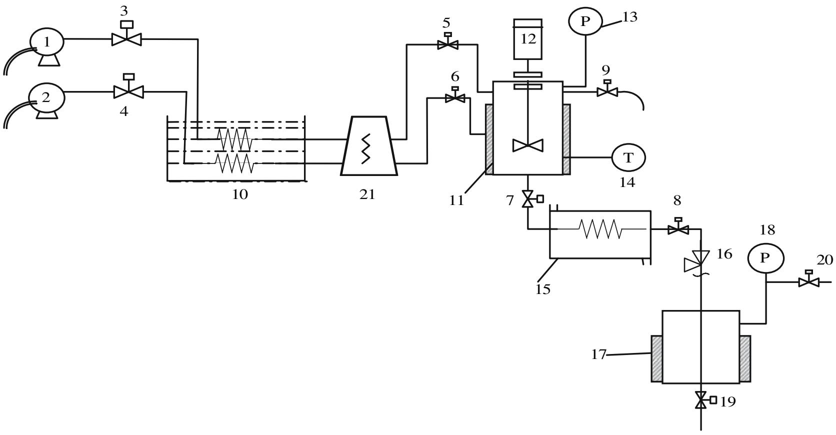

Fig. 1 The high pressure and high temperature reaction apparatus. *1,2* High-pressure pump; *3,4,5,6,7,8,9,19,20* Valve; *10* Oil Bath; *11* Reactor and heater; *12* Stirrer; *13* Manometer; *14* Thermometer; *15* Condenser; *16* Pressure regulator; *17* Separatory funnel; *18* Manometer; *21* Preheater

The methyl ester yield was calculated by the following expression:

$$\text{yield} = \frac{m_{\text{actual}}}{m_{\text{theoretical}}} \times 100\% \approx \frac{C_{\text{esters}} \times n \times V_{\text{esters}}}{m_{\text{oil}}} \times 100\%$$
$$\approx \frac{C_{\text{esters}} \times n \times V_{\text{oil}}}{m_{\text{oil}}} \times 100\% = \frac{C_{\text{esters}} \times n \times V_{\text{oil}}}{\rho_{\text{oil}} \times V_{\text{oil}}} \times 100\%$$
$$= \frac{C_{\text{esters}} \times n}{\rho_{\text{oil}}} \times 100\%$$

In the expression, two approximate calculations were made. First, we think all FAME was in the ester phase as described above. Second, because the density of esters (0.88 g/cm^3) is very close to the oil (0.89 g/cm^3), the total volume of oil phase was considered to be esters. Where, both m_{actual}[g] and $m_{\text{theoretical}}$[g] are the mass of methyl ester; m_{oil}[g] is the mass of vegetable oil used in the reaction; C_{ester}[g/ml] is the mass concentration of methyl ester, which was determined by GC; n is the dilution multiple of methyl ester; ρ_{oil}[g/ml] is the density of vegetable oil; V_{esters}[ml] and V_{oil}[ml] are the volumes of crude ester layer and vegetable oil, respectively. In the experiments, the five FAMEs: palmitic (C16:0), stearic (C18:0), oleic (C18:1), linoleic (C18:2) and linolenic (C18:3) acids methyl ester (Cm:n: m is the number of carbon atoms; n is the number of double bonds) were analyzed.

Kinetic Model

In the transesterification process of vegetable oil in supercritical methanol, the reactions are as follows:

$$\text{TG} + \text{CH}_3\text{OH} \underset{k_2}{\overset{k_1}{\Leftrightarrow}} \text{R}_1\text{COOCH}_3 + \text{DG}$$
$$\text{DG} + \text{CH}_3\text{OH} \underset{k_4}{\overset{k_3}{\Leftrightarrow}} \text{R}_2\text{COOCH}_3 + \text{MG}$$
$$\text{MG} + \text{CH}_3\text{OH} \underset{k_6}{\overset{k_5}{\Leftrightarrow}} \text{R}_3\text{COOCH}_3 + \text{GL}$$

(TG: triglyceride; DG: diglyceride; MG: monoglyceride; GL: glycerol).

The overall reaction was given by Kusdiana [2]:

$$\text{TG} + 3\text{CH}_3\text{OH} \underset{k_8}{\overset{k_7}{\Leftrightarrow}} 3\text{RCOOCH}_3 + \text{GL}.$$

To get a higher conversion of transesterification in the supercritical methanol, a high molar ratio of methanol to oil is needed, generally more than 40:1. Due to this high molar ratio, the reverse reaction was ignored, and the concentration of methanol can be regarded as invariant. Considering only the forward reaction and assuming the whole reaction as a first order reaction [2], the reaction can be modeled as:

$$\text{TG} + 3\text{CH}_3\text{OH} \xrightarrow{k} 3\text{RCOOCH}_3 + \text{GL}$$

The apparent rate constant of the reaction, k can be given by Eq. 1.

$$-\frac{\text{d}[\text{TG}]}{\text{d}t} = k[\text{TG}] \tag{1}$$

In a practical reaction process, the components of the transesterification reaction mixture are complicated. In this model, the components were grouped into four species: methanol, methyl esters (ME), glycerin (GL) and unesterified compounds (uME) including triglycerides, diglycerides, monoglycerides and unreacted free fatty acids [2]. Therefore, the reaction equation can be expressed as:

$$\text{uME} + \text{CH}_3\text{OH} \xrightarrow{k} \text{ME} + \text{GL}$$

Eq. 1 also can be rewritten to be

$$-\frac{\text{d}[\text{uME}]}{\text{d}t} = k[\text{uME}]. \tag{2}$$

By integrating, it gives

$$\ln[\text{uME}, 0] - \ln[\text{uME}, t] = kt \tag{3}$$

Where, [uME, 0] is the initial concentration of vegetable oil, and [uME, t] is the concentration of unesterified compounds at time t. The apparent rate constant k can be obtained by a linear fit of Eq. 3.

Results and Discussion

Effect of Temperature on the Kinetics of Soybean Oil to Methyl Esters

The effect of reaction temperature on the kinetics of transesterification reactions of soybean oil to methyl esters, was carried out at a constant pressure of 28 MPa. By fitting the experimental data at different temperatures using Eq. 3, a good linear relation between ln[uME, 0]–ln[uME, t] and t was found (Fig. 2) and supports the hypothesis that the reaction could be considered as first order. The apparent rate constants at different reaction temperatures are listed in Table 1 and agree closely to those reported in the literature [2]. For example, the apparent rate constant in this work is

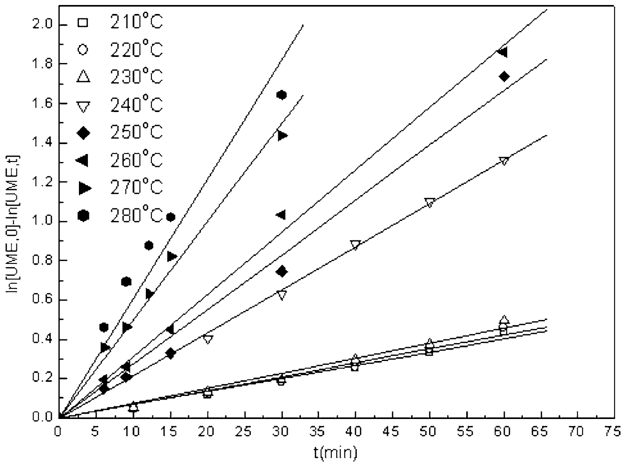

Fig. 2 Plot of ln[uME,0]–ln[uME, t] value of soybean oil to fatty acid methyl esters against reaction time at different reaction temperature (MeOH:SBO = 42:1, Pressure = 28 MPa)

7.91×10^{-4} s^{-1} at 270 °C, while Kusdiana and coworkers found the rate constant is 7.0×10^{-4} s^{-1} for the transesterification of rapeseed oil in supercritical methanol (270 °C, 12 MPa) [2].

With the apparent rate constants at different temperatures determined, the apparent activation energy for the transesterification reaction was calculated using the Arrhenius formula (Eq. 4).

$$k = k^0 \exp\left(-\frac{E_{\mathrm{app}}}{\mathrm{RT}}\right) \quad (4)$$

As shown in Fig. 3, the ln*k* is non-linear with *1/T* over the temperature range 210–280 °C, which is across the critical temperature of methanol. However, within subcritical temperature region below 239 °C and supercritical temperatures region above 239 °C, good linearity is observed. The main reason for the considerably different apparent rate constants near the critical temperature point are due to the considerable changes in the physical properties of methanol. The properties of the fluid are very sensitive to the change of reaction temperature and pressure near the critical point. ln*k* and *1/T* was correlated by linear fitting at the supercritical state and the subcritical state to obtain the apparent activation energies, respectively. The results are given in Table 2. The apparent activation energy in the supercritical methanol is 56.0 kJ/mol, which is much bigger than that in the subcritical state. The apparent rate constants and apparent activation energies of different FAME were also obtained in the same way, and are shown also in Table 2.

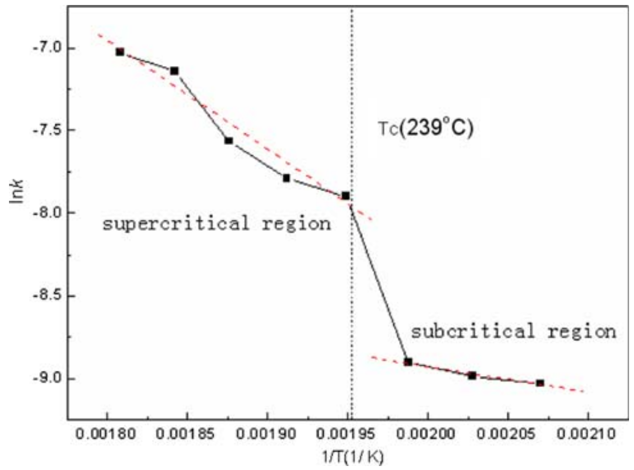

Fig. 3 Plot of ln*k* value of soybean oil to fatty acid methyl esters against 1/*T* (MeOH:SBO = 42:1, Pressure = 28 MPa)

Effect of Pressure on the Kinetics of Soybean Oil to Methyl Esters

The effect of pressure on kinetics of the transesterification of soybean oil to methyl esters in supercritical methanol was experimentally investigated at a constant temperature of 280 °C and a molar ratio of methanol to oil 42:1 with total reaction time 0.5 h. The effect of pressure on yield of the methyl esters was shown in Fig. 4.

Table 1 Apparent rate constant of FAME and soybean oil at different temperatures (pressure = 28 MPa, MeOH:SBO = 42:1)

Temperature (°C)	*k* (s^{-1})					
	C16:0	C18:0	C18:1	C18:2	C18:3	Oil
280	5.49E-4	1.12E-3	8.84E-4	1.41E-3	1.37E-3	8.81E-4
270	4.79E-4	1.08E-3	6.16E-4	1.07E-3	9.20E-4	7.82E-4
260	3.22E-4	8.62E-4	6.03E-4	8.73E-4	5.08E-4	5.25E-4
250	2.44E-4	8.58E-4	5.42E-4	5.55E-4	4.36E-4	4.22E-4
240	2.55E-4	4.54E-4	4.12E-4	4.18E-4	4.04E-4	3.66E-4
230	1.62E-4	1.66E-4	1.42E-4	1.65E-4	1.40E-4	1.33E-4
220	1.52E-4	1.59E-4	1.28E-4	1.51E-4	1.29E-4	1.25E-4
210	1.48E-4	1.49E-4	1.21E-4	1.44E-4	1.23E-4	1.19E-4

Table 2 Apparent activation energies (kJ/mol) of different FAME and soybean oil (pressure = 28 MPa, MeOH:SBO = 42:1)

Temperature (°C)	C16:0	C18:0	C18:1	C18:2	C18:3	Oil
210–230	8.93	10.6	16.2	13.6	13.0	11.2
240–280	51.7	48.4	39.0	72.9	74.7	56.0

The experiments showed pressure to significantly influence the yield in the pressure range from ambient pressure to 25 MPa. In the range of pressure below 15.5 MPa, the pressure had a considerable impact on the reaction yields. At 8.7 MPa, the yield of soybean oil methyl ester was only 56.1%. When the pressure was increased to 15.5 MPa, the yield of soybean oil methyl ester increased to 81.7%. From 15.5 to 25 MPa, the influence of pressure on the yield became smaller. The yield increased only about 9% when the pressure raised from 15.5 to 25 MPa. Above 25 MPa, the influence of pressure on yield was negligible. When the pressure increased from 25 to 36 MPa, there was only 1% increase in the yield. Warabi [7] reported that at a temperature of 300 °C, the effect of the reaction pressure does not result in a significant increase in reaction rate when the reaction pressure was higher than 20 MPa. Warabi's conclusion is similar to our results.

The effect of the pressure on the reaction rate could be interpreted with the transition-state theory [13]. According to the transition-state theory, the effect of pressure on apparent reaction rate constant was described as following relationship:

$$\left(\frac{\partial \ln k}{\partial P}\right)_T \cong -\frac{\Delta V^{\neq}}{\mathrm{RT}}. \tag{5}$$

Where, $\Delta V^{\neq}$ is the reaction activation volume, cm^3/mol.

Integrating Eq. 5, we get:

$$\ln k = -\frac{\Delta V^{\neq}}{\mathrm{RT}} P + C_0. \tag{6}$$

Where, C_0 is a constant related with temperature.

Using Eq. 6, $\Delta V^{\neq}$ can be calculated from the rate constants at different pressures.

The relationship of rate constant, temperature and pressure can be expressed in Eq. 7 as:

$$k = k^0 \times \exp\left(-\frac{E^{\neq} + P\Delta V^{\neq}}{\mathrm{RT}}\right) = k^0 \times \exp\left(-\frac{E_{\mathrm{app}}}{\mathrm{RT}}\right). \tag{7}$$

The relationships between the FAME yield from soybean oil and reaction time at four different pressures (12.5, 17, 25 and 32 MPa) are shown in Fig. 5. The apparent rate constants of the transesterification at the different pressures were determined according to Eq. 3. and subsequently used to estimate $\Delta V^{\neq}$ of the transesterification by linear fit of Eq. 6.

The value of $\Delta V^{\neq}$ of the transesterification of the soybean oil is –206 cm^3/mol at 280 °C. The absolute value of $\Delta V^{\neq}$ is so large that it cannot be ignored in the calculation of the activation energy. At 28 Mpa, the value of $P\Delta V^{\neq}$ is –5.77 kJ/mol, which accounts for 10.3% of the apparent activation energy 56.0 kJ/mol at same pressure. The reaction activation volume and

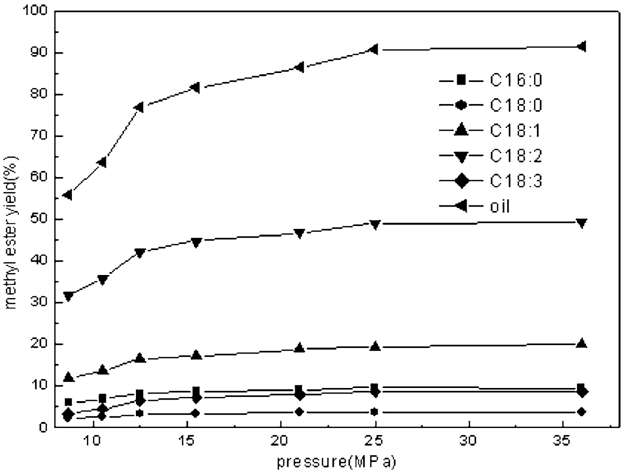

Fig. 4 Effect of reaction pressure on the conversion of soybean oil to fatty acid methyl esters (temperature = 280 °C, MeOH:SBO = 42:1, Time = 30 min)

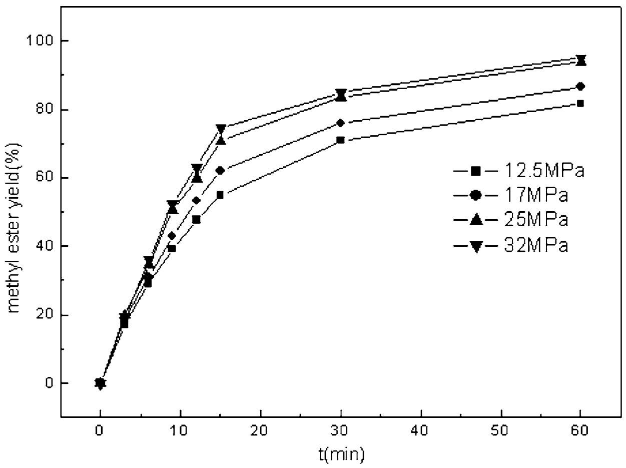

Fig. 5 Plot of methyl ester yield of soybean oil against reaction time at different reaction pressure (temperature = 280 °C, MeOH:SBO = 42:1)

Table 3 Effects of pressure on reaction activation volume and apparent activation energies (temperature = 280 °C, MeOH:SBO = 42:1)

Pressure (MPa)	C16:0	C18:0	C18:1	C18:2	C18:3	Oil
k (s^{-1})						
32	1.17E-03	1.14E-03	1.21E-03	1.01E-03	1.20E-03	1.12E-03
25	8.33E-04	6.59E-04	9.11E-04	1.08 E-03	1.01E-03	7.71E-04
17	6.20E-04	7.01E-04	6.59E-04	5.74E-04	6.04E-04	5.46E-04
12.5	5.13E-04	3.87E-04	4.67E-04	4.96E-04	4.84E-04	4.55E-04
$\Delta V^{\neq}$ (cm^3/mol)						
	–191	–211	–217	–192	–225	–206
$(-P\Delta V^{\neq})/E_{app}$ (%)						
32	11.8	14.0	17.8	9.47	9.64	11.8
25	9.24	10.9	13.9	7.40	7.53	9.20
17	6.28	7.41	9.46	5.03	5.12	6.25
12.5	4.62	5.45	6.96	3.70	3.77	4.60

apparent activation energy for the different FAME in the soybean oil were also listed in Table 3. The results indicate that the pressure has a significant effect on the reaction rate over certain pressure ranges.

References

1. Saka S, Kusdiana D (2001) Biodiesel fuel from rapeseed oil as prepared in supercritical methanol. Fuel 80:225–231
2. Kusdiana D, Saka S (2001) Kinetics of transesterification in rapeseed oil to biodiesel fuel as treated insupercritical methanol. Fuel 80:693–698
3. Madras G, Kolluru C, Kumar R (2004) Synthesis of biodiesel in supercritical fluids. Fuel 83:2029–2033
4. Demirbas A (2003) Biodiesel fuels from vegetable oils via catalytic and non-catalytic supercritical alcohol transesterifications and other methods: a survey. Energy Conv Manag 44:2093–2109
5. Demirbas A (2002) Biodiesel from vegetable oils via transesterification in supercritical methanol. Energy Conv Manag 43:2349–2356
6. He H, Wang T, Zhu S (2007) Continuous production of biodiesel fuel from vegetable oil using supercritical methanol process. Fuel 86:442–447
7. Warabi Y, Kusdiana D, Saka S (2004) Biodiesel fuel from vegetable oil by various supercritical alcohols. Appl Biochem Biotech (115):793–801
8. Freedman B, Butterfield RO, Pryde EH (1986) Transesterification kinetics of soybean oil. J Am Oil Chem Soc 63:1375–1380
9. Noureddini H, Zhu D (1997) Kinetics of transesterification of soybean oil. J Am Oil Chem Soc 74:1457–1463
10. Darnoko D, Cheryan M (2000) Kinetics of palm oil transesterification in a bath reactor. J Am Oil Chem Soc 77:1263–1267
11. Diasakov M, Loulodi A, Papayannakos N (1998) Kinetics of the non-catalytic transesterification of soybean oil. Fuel 77:1297–1302
12. Zhou H, Lu H, Liang B (2006) solubility of multicomponent systems in the biodiesel production by transesterification of *Jatropha curcas* L. oil with methanol. J Chem Eng Data 51:1130–1135
13. Moore W, Pearson RG (1981) Kinetics and mechanism. 3rd edn, Wiley, New York