Non Catalytic Transesterification of Vegetables Oil to Biodiesel in Sub-and Supercritical Methanol: A Kinetic’s Study

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Abstract

Non catalytic transesterification in sub and supercritical methanol have been used to produce biodiesel from palm oil and soybean oil. A kinetic study was done under reaction condition with temperature and time control. The experiments were carried out in a batch type reactor at reaction temperatures from 210 °C (subcritical condition) to 290 °C (the supercritical state) in the interval ranges of temperature of 20 °C and at various molar ratios of oil to methanol. The rate constants of the reaction were determined by employing a simple method, with the overall chemical reaction followed the pseudo-first–order reaction. Based on the results, the rate constants of vegetables oil were significantly influenced by reaction temperature, which were gradually increased at subcritical temperature, but sharply increased in the supercritical state. However, the rate constants of soybean oil were slightly higher than that of palm oil. The activation energy for transesterification of soybean oil was 89.32 and 79.05 kJ/mole for palm oil. Meanwhile, the frequency factor values of both oils were 7.25x10⁶ and 3.91x10⁵ min⁻¹, respectively. The rate reaction for both of oil were expressed as \(-r_{TG} = 7.25x10^6 \exp(-89.32/RT)C_{TG}\) for soybean oil, and \(-r_{TG} = 3.91x10^5 \exp(-79.05/RT)C_{TG}\) for palm oil. © 2013 BCREC UNDIP. All rights reserved

Keywords: Biodiesel; kinetic; transesterification; vegetables oil; sub- and supercritical methanol

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1. Introduction

To the present, the world energy relies on the fuels derived from non-renewable crude fossil oil [1]. Biodiesel is a promising alternative energy to be developed as a replacement for diesel oil due to the limited resources of the fossil fuel and the environmental concern [2-4]. Biodiesel researches have been intensively conducted because it has many advantages, specifically, it is environmental friendly as it is produced by renewable materials, such as vegetable oils, animal oils, algae and used...
cooking oil. Moreover, biodiesel has a tremendous potential in reducing pollutants and carcinogenic agents in other words it produces lower emissions. Currently, biodiesel is generally produced by conventional methods using homogeneous base catalyst [5, 6]. In this process, however, free fatty acids contained in triglycerides (mainly free fatty acid content >0.5%) react with the catalyst to produce un-desired saponification products. The process also requires a complex purification steps to eliminate saponified product as well as catalyst, eventually resulting in the lower yield of biodiesel. Furthermore, this conventional process also needs high production cost and energy consumption [7-9]. Some researchers are challenged to do research in finding alternative methods or more efficient technology process for biodiesel production in order to overcome that problem.

Transesterification with heterogeneous catalysts is the most promising alternative to produce biodiesel from vegetable oils, since it is able to overcome the weaknesses of the homogeneous catalysts used [1,2,4,8-11]. Heterogeneous catalytic process is expected to be an effective process and provide a minimal impact on the environment. Calcium oxide (CaO) which supported by γ-alumina catalyst has been used by Zabeti et al. [10] for transesterification of palm oil. Their study consisted of the optimization of methyl ester product. The optimal condition was obtained at the molar ratio of 1:12, the amount of catalyst 6% (wt %) and reaction temperature of 65 °C. Asri et al. [4] conducted transesterification of palm oil with commercial grade CaO in a batch reactor with methanol reflux condition, at 65 °C and 7 h reaction time with 6% catalyst [4]. The low yield of biodiesel (64.95%) was obtained. In their next study, Asri et al. [11] synthesized a double promoted catalyst which was supported by γ-alumina (CaO/KI/γ-alumina). At the same conditions with the previous work [4], within 5 h reaction time, yield of biodiesel increased sharply to 95%. However, this process required relatively longer reaction time (5 h) and high amount of catalyst used (6 wt% to palm oil).

It is well known that supercritical methanol is an environmental friendly process for transesterification of vegetable oil without catalysts [12]. This method is very promising process to overcome the problems of using homogeneous catalyst. Supercritical methanol process has several advantages, including: being eco-friendly, the product is very easy to be separated because it is a catalyst free process. The reaction is very fast (Kusdiana and Saka [7] noted that at 350 °C under 30 Mpa with molar ratio of oil to methanol 1:30, the 95 % conversion of rapeseed oil to biodiesel was achieved only in 4 min). In addition, this process is able to overcome the weaknesses of diffusion problems in the process using heterogeneous catalysts, because at supercritical state, dielectric constant of methanol decreases resulting in hydrophobic nature of the system. As the result, the two phase’s nature of oil and methanol turns into mutually soluble phases. Furthermore, at the supercritical methanol condition, the presence of water is not effecting the conversion of oil into biodiesel. The existence of water in supercritical methanol condition enhances the formation of methyl ester and esterification of free fatty acids simultaneously in one stage [6]. Thermal stability of biodiesel from various vegetable oils in supercritical methanol has been studied between 270 °C/17 MPa and 380 °C/56 MPa by Imahara et al. [5]. They recommended that the supercritical methanol at temperature lower than 300 °C with a pressure higher than 8.09 Mpa, is appropriate to obtain the maximum yield and thermal stability of biodiesel.

Some researchers studied the kinetics of transesterification reaction with homogeneous (acid / base) catalyst; heterogeneous catalyst and catalyst-free on supercritical methanol. Freedman et al. [13] reported the transesterification reaction of soybean oils and other vegetable oil with alcohol. They stated that in transesterification reaction there are three steps wise reactions with intermediate formation of diglycerides and monoglycerides resulting in the production of 3 mol of methyl esters and 1 mol of glycerol. Diasakou et al. [14] studied the effect of reaction conditions (493 K , 5.5 MPa and 508 K, 6.2 MPa) and molar ratio of methanol- soybean oil (6, 12, 21) on the reaction rate constants and the composition of methyl ester (ME) in the reaction mixture [14]. Kusdiana and Saka [7] investigated the influence of the molar ratio of methanol- rapeseed oil (3.5, 4.5, 6, 21 and 42), reaction temperatures (473-773 K), and pressures 7-105 MPa on the formation of methyl ester [7]. Dasari et al. [15] examined the kinetics of transesterification of soybean oils in batch type steel reactor (SUS 316). They studied the effect of catalyst surface area on the rate of reaction methanol (MeOH) at 393, 423, and 453 K. They also examined the reactivity of higher alcohols such as ethanol and isopropanol. Minami and Saka [6] studied the kinetics of hydrolyses and esterification of methyl for biodiesel production in two steps supercritical methanol process. This process involves hydrolyses of triglyceride into fatty acid in subcritical water. The methyl esterification of fatty acid along with the existing free fatty acid into FAME was
conducted in supercritical methanol process. With this two steps method, the operating reaction condition can be reduced into moderate reaction conditions (270 °C/7-20 MPa) which significantly lower than one step process (350 °C/20-50 MPa). Dosin et al. [16] observed the kinetics of transesterification reaction of ethyl acetate with methanol using magnesium oxide solid base catalysts. The experiment was conducted in the perfectly stirred reactor, and as the results, the reaction rate constant for the transesterification reaction has been obtained. Joelianingsih et al. [3] studied kinetics of catalyst free transesterification reaction in a unstirred reactor at atmospheric pressure. They found that the rate constant of the total system increased with reaction temperature, while the activation energy and the frequency factor values were 31 kJ and 4.2, respectively. Stamencovic et al. [17] studied methanolysis kinetics model of the Sunflower oil using calcium hydroxide catalyst. The methanolysis process was performed at moderate temperature (60 °C), methanol-oil ratio 6:1 and the different ratio of catalysts (from 1 to 10 w% of oil). The reaction kinetic was modeled by a simple model. They reported that the overall chemical reaction kinetics follow single pseudo first order reaction, where the beginning of the reaction was controlled by mass transfer triglyceride (TG) and then followed by chemical reaction region in the later period. Although the kinetics' studies of non-catalytic transesterification in supercritical methanol have been studied by various researchers, however, only Song et al. [18] studied the transesterification kinetic of palm oil. In their study, they employed relatively high temperature and pressure (350 °C and 30 MPa), which was similar to Kusdiana and Saka experimental conditions [7]. In those extreme conditions, the thermal stability of biodiesel is very crucial. As reported by Imahara et al. [5.], that biodiesel, especially unsaturated poly-fatty acid methyl ester very susceptible to the denaturation. For example methyl oleate (18:1) was stable at 270 °C and 17 MPa, but gradually became unstable at 300 °C and 19 MPa and slightly decomposed with increasing the exposure of time, and eventually only 75 wt% methyl linoleat was recovered after 40 min exposure of time. The kinetic study of transesterification of soybean oil in supercritical methanol was conducted by Diasakau et al. [14]. Their experiments were performed in subcritical methanol (at 220 and 235 °C and pressure 55 and 62 bar, respectively). We have carefully searched through different search engines and literature, and we found that the kinetic study of catalyst free transesterification of palm oil and soybean oil in sub-and supercritical methanol is still scarce. In order to obtain kinetic data over a wide range of temperature and pressure, more studies on the kinetics aspects of the transesterification reaction of palm oil and soybean oil is still required. These kinetics data are very valuable for the design, industrial operation and optimization of the process.

This study focuses on the kinetic of catalyst free transesterification of palm oil and soybean oil into biodiesel in sub and supercritical methanol at moderate operating conditions (210-290 °C and 4-12 MPa). Palm oil was used due to the abundant availability of this vegetable oil in Indonesia [19]. The used of soybean oil as the feed stock in this study due to a lack of information about the kinetics data on the transesterification of this vegetable oil.

2. Materials and Methods

2.1. Materials

Palm oil and soybean oil as the raw materials were provided by Wako pure chemicals Co., Japan. Free fatty acid content on both of palm and soybean oils were less than 0.005%. Meanwhile, the un-saponifiable matters were less 1.5% Analytical grade of methanol, hexane, and methyl esters standard (methyl palmitate, methyl stearic, methyl linoleic, methyl linoleic and methyl oleic) were also supplied by Wako pure chemicals Co., Japan. The purity of methanol and hexane were 99.8% and 98.5%, respectively and used without further purification.

2.2. Uncatalyzed transesterification in sub and supercritical methanol

Uncatalyzed transesterification of palm and soybean oils in sub and supercritical methanol was carried out in a batch type reactor (stainless steel SUS 304, AKICO Co., Japan). The reactor system consists of an electric furnace (ISUZU Co, Ltd., model NMF-13AD), a stainless steel SUS 304 of reactor (8.8 ml of capacity, 300 °C of maximum temperature, 30 MPa of pressure) and a temperature controller. First of all, the temperature of the heating furnace was adjusted to the desired temperatures (210-290 °C). The reactor was firstly charged with the mixture of vegetable oils and methanol in certain molar ratio oil to methanol, then the reactor was inserted to the electric furnace. The effect of different operational parameters (reaction temperature, reaction time and molar ratio oil to methanol) on the yield of biodiesel and conversion of palm oil was studied. After reaching the set point of temperature, at which point the reaction was kept until the time of
reaction was achieved, the reaction pressure was measured. Afterwards, the reactor was removed from the electric furnace and immersed in a water bath for cooling in order to stop the reaction. The treated liquid was discharged from the reactor into a sampling bottle. Then some amount of water was added into the solution mixture for diluting the excess of methanol. Subsequently, the solution mixture was centrifuged to separate it into two phases. The top phase was FAME (biodiesel) and a small amount of un-reacted oil. The bottom phase consisted of methanol, water and glycerol. Biodiesel was analyzed by gas chromatography-flame ionization detector (GC-FID) (Gas Chromatography GC-14B, Shimadzu, Japan) equipped with a HP-Innowax capillary column (30 m x 0.250 mm x 0.25 mm). The oven temperature was programmed as follow: initial temperature of 210 °C was hold for 9 min, increased to 230 °C at 20 °C/min interval for 20 min, then increased to 250 °C at 20 °C/min interval for 5 min. The injector and detector temperatures were controlled at 250 and 300 °C, respectively. The injection volume was 1 ml. The carrier gas was helium and the makeup gas was hydrogen. The analyses of biodiesel can be used to determine the yield % of biodiesel and the conversion of palm oil, which was defined as follows [2, 8]:

\[
\text{Yield of biodiesel (\%) = } \frac{w \text{ of biodiesel} \times \text{biodiesel conc}}{\text{weight of oil}} \times 100
\]

\[
\text{Conversion of oil (\%) = } \frac{(\text{weight of biodiesel} / \text{W of oil}) \times \text{biodiesel conc.}}{(\text{weight of oil} / \text{W of oil}) \times 3} \times 100
\]

where, W of biodiesel is actual weight of biodiesel produced from the experiment (mg). W of oil is weight of oil used in the experiment (mg). Meanwhile, biodiesel conc. is the content of methyl ester in the product analyzed by GC. The factor 3 in the equation (2) indicates that each molecule of triglyceride produced three molecule of methyl ester.

3. Results and Discussion

3.1. Effect of molar ratio of oil to methanol on conversion of soybean oil

The molar ratio of oil to methanol is one of the most important variables that affecting the conversion triglyceride into FAMEs (biodiesel). Stoichiometrically, transesterification reaction requires three moles of methanol to react with one mole of triglyceride and produce 3 moles of FAME and one mole of glycerol. Since it is an equilibrium reaction, an excess of methanol will increase the yield of biodiesel by shifting the equilibrium to the right side. Generally, in the conventional process, the molar ratio of oil to methanol is 1:6. As reported by Encinar et al. [20] in conventional commercial process with alkaline catalyst that the yield of methyl esters increase with the increase of molar ratio of oil to methanol. The optimum condition was 1:4.05 to 1:5.67. Beyond that ratio, glycerol as by product will be difficult to be separated. If the ratio is less than that mentioned before, the reaction is incomplete [20]. However, in the transesterification using heterogeneous catalysts, a larger ratio of oil to methanol is required [2, 21]. Kim et al. [2] reported that the optimum molar ratio of methanol to vegetables oil in refluxed methanol with heterogeneous base catalyst was found to be 1:9. They also stated that the excess added methanol had no significant effect on the yield of biodiesel [2]. Xie & Li [21] stated that the optimum molar ratio of soybean oil to methanol to produce methyl esters in the reflux temperature with heterogeneous catalyst was approximately 1:15. Song et al. [18] conducted the transesterification of RBD palm oil at 350 °C and 40 MPa for 5 and 10 min at various mole ratios of RBD palm oil to methanol. They found that the contents of FAMEs increased drastically with an increasing of mole ratio of RBD palm oil to methanol up to 30 mole ratio and then constant for further increasing of mole ratio.

Saka & Kusdiana [12] studied the effect of molar ratio of methanol to rapeseed oil in the range of 3.5 to 42. They noted that for molar ratio

![Figure 1. Conversion of soybean oil (%) as function of molar ratio of soybean oil to methanol, at 290 °C and 30 min of reaction time](image-url)
of 42, almost complete conversion was achieved with 95 % yield of biodiesel. Whereas, for lower molar ratio of 6 or less, incomplete conversion was apparent with the lower yield of biodiesel was obtained.

In this work, the effect of molar ratio of soybean oil to methanol on the conversion of soybean oil into biodiesel was studied in the range of 1:12 to 1:42 at reaction temperature of 290 °C and reaction time of 30 min. Reaction was carried out in a batch reactor with sub and super-critical methanol. Figure 1 shows the influence of molar ratio of soybean oil to methanol on the conversion of soybean oil. It is seen that the extent of conversion increased with the increase in the molar ratio of soybean oil to methanol (from 22.5 to 77%). At molar ratio from 1:12 to 1:18, the conversion gradually increased from 22.5 to 27 %. However, at 1:24 of molar ratio, the conversion drastically increased to 75 %. On the other hand, the increasing molar ratio from 1:30 to 1:42 had no significant effect on the conversion of soybean oil into biodiesel. It can be concluded that the higher molar ratio of soybean oil to methanol, the higher conversion of soybean oil was obtained until a certain molar ratio of soybean oil to methanol. Practically, the use of high excess of methanol is not favorable because high energy is required to recover the methanol from the mixture, which is finally increasing the total production cost of biodiesel. In this work, the optimum molar ratio of soybean oil to methanol was 1:24.

3.2. Effect of reaction time and reaction temperature on conversion of vegetable oils

The effect of reaction time on the conversion of oil was observed by varying the reaction time from 10 to 90 min at 10 min intervals. The reaction was carried out at five different reaction temperatures (210, 230, 250, 270 and 290 °C) and molar ratio of oil to methanol was 1:24. As expected, the conversion of oils increased with the increasing of reaction time at all reaction temperatures. Figures 2 and 3 show the effect of temperature on the conversion of soybean and palm oil, respectively. As shown in Figure 2 at the temperature of 210 and 230 °C, the conversion of soybean oil was low and gradually increased with an increase in reaction time. It might be due to the subcritical condition of methanol at 230 °C. At this condition, oil and methanol were not properly mixed, and as the result the reaction run slowly, and eventually the conversion was low. At 250 °C, the conversion was still low. It occurred because the temperature of 250 °C is relatively close to the critical point of methanol, so it is still affected by the stability of supercritical methanol condition. At 270 °C, the conversion didn’t immediately rise and it was still similar as at 250 °C. Nevertheless, the conversion sharply increases to 75 % for 60 min. At 290 °C, the conversion of soybean oil increased dramatically from 0.4 to 75 % for 5 to 30 min. Beyond the 60 min of reaction time, the conversion increased gradually with increasing reaction time. The highest conversion achieved at 270 and 290 °C were 79 and 88.5%, respectively. In supercritical condition, the nature of the mixture of two phase’s oil and methanol easily converted into one phase because dielectric constant of methanol decreases. It can be explained that liquid methanol is a polar solvent and has hydrogen bonding. The degree of hydrogen bonding decreases with the increasing temperature, and the polarity of methanol would decrease in supercritical state. This means that supercritical methanol has a hydrophobic nature with low dielectric constant [12, 14].

The influence of reaction time on the conversion of palm oil at various temperatures is shown in Figure 3. As well as soybean oil, the conversions of palm oil increased with an increase in reaction time at all level of temperatures. However, the conversions gradient of palm oil at subcritical temperature (210 and 230 °C) and at near critical point (250 °C) are much lower than soybean oil.

A significant increase in the conversion of oil into biodiesel occurred at a temperature of 270 °C. At 290 °C, the conversion of palm oil sharply increased from 0.4 to 90% at 10 to 90 min. Around the reaction time of 10 min to 70 min, the conversion of palm oil gradually increased as the increase in reaction time, but the values were relatively lower than those of soybean oil. Moreover, beyond 70 min (70 to 90 min) the
Conversion of palm oil drastically increases from 55 to 90%. It might be due to the higher physical properties of palm oil (mainly viscosity and density). For instance, the viscosity of palm oil is 130 cP and the viscosity of soybean oil is 80 cP. While, the density of palm oil and soybean oil are 0.91 and 0.89, respectively. Thus, it need longer time to achieve the setting temperature.

3.3. Kinetic Analysis

Transesterification is a reaction in which triglyceride (TG), the main component of vegetable oils or animal fats, reacts with short chain-alcohols, preferable methanol (MeOH), to form fatty acid methyl ester (FAME), now popularly known as biodiesel [3, 7, 14]. The mechanism of transesterification of vegetable oils has been proposed by Diasakau et al. [14], in which the thermal transesterification divided into three steps. TG reacts with methanol to produce diglyceride (DG) which in turn reacts with methanol (MeOH) to produce monoglyceride (MG). Finally, MG reacts with MeOH to produce glycerol (GL). At each reaction step, one molecule of methyl ester (ME) is produced for each molecule of MeOH consumed [3, 7, 14]. The kinetics mechanism can be represented by the following equations:

\[ \text{TG} + \text{MeOH} \xrightarrow{k_1} \text{DG} + \text{ME} \]  
\[ \text{DG} + \text{MeOH} \xrightarrow{k_2} \text{MG} + \text{ME} \]  
\[ \text{MG} + \text{MeOH} \xrightarrow{k_3} \text{GL} + \text{ME} \]

Where \( k_1, k_2 \) and \( k_3 \) are the reaction rate constant of equation (3), (4) and (5), respectively. Each reaction step is assumed to be first order with respect to each reacting component. Due to the fact that final products are methyl esters, a simple mathematical model has been defined by ignoring the intermediate reaction of diglyceride and monoglyceride to be one step reaction model as follow [3, 7, 12, 14, 22]:

\[ \text{TG} + 3\text{MeOH} \rightarrow 3\text{ME} + \text{GL} \]  
\[ -r_{\text{TG}} = -\frac{dC_{\text{TG}}}{dt} = k[TG][\text{MeOH}] \]  

Theoretically, the overall conversion follows a forth order reaction [23]. However, practically transesterification reaction was conducted in a huge excess of methanol (\( C_{\text{MeOH}} \) is constant). The reaction could be considered as obeying the pseudo-first order kinetics [7, 13, 23]. Therefore, the rate of reaction can be expressed as:

\[ -r_{\text{TG}} = -\frac{dC_{\text{TG}}}{dt} = k'[\text{TG}] \]  

Since the TG concentration is related to the conversion degree of TG, \( X_{\text{TG}} \):

\[ C_{\text{TG}} = C_{\text{TG}0} (1 - X_{\text{TG}}) \]  

Equation (8) can be transform into the following one:

\[ \frac{dX_{\text{TG}}}{dt} = k'(1 - X_{\text{TG}}) \]  

rearranging and integration Equation (10) gives:

\[ \ln(1 - X_{\text{TG}}) = k' t \]

where \( k \) is the kinetic constant of triglyceride (TG), \( k' \) is \( k[C_{\text{MeOH}}]^3 \).
To correlate the experimental data and quantify the effects of temperature and reaction time, the experimental results were analyzed further in term of reaction kinetics. Kinetic analysis for transesterification of soybean and palm oils was conducted based on experimental data for reaction time of 5 to 90 min, temperature of 210 to 290 °C, and molar ratio of oil to methanol of 1:24. The rate constant $k'$ was determined by equation (11), by fittings of $t$ versus $-\ln (1-X_{TG})$ in order to adopt the first order rate equation. The obtained values of $k'$ at different temperatures were listed in Table 1.

Based on data in Table 1, it is seen that $k'$ values of soybean oil were higher than that of palm oil at all temperatures. At subcritical temperature, $k'$ of both oils were low but it was much higher at supercritical state. For instance, the value of $k'$ at 290 °C was 20 times to the $k'$ value at 210 °C for soybean oil, and about 18.5 times for palm oil. Meanwhile Kusdiana & Saka (2001) obtained that $k'$ of rapeseed oil at 350 °C was increased by factor 85 compared to $k'$ at 200 °C [7]. In general, as expected, the rate constant of transesterification of both oils increased with increasing temperature according to the Arrhenius equation [24]:

$$k' = k_o e^{\frac{E_a}{R T}} \quad (12)$$

$$\ln k' = \ln k_o - \frac{E_a}{R T} \quad (13)$$

where $E_a$ is the activation energy, $R$ is the molar constant of gas (8.314 J/mol K) and $k_o$ is the frequency factor [24].

All data in Table 1 were used to determine the activation energy and the frequency factor by plotting of $\ln k'$ versus the reciprocal of absolute temperature ($1/T$) as shown in Figure 4 and Figure 5 for soybean oil and palm oil, respectively. According to equation (13), the activation energy ($E_a$) was found to be 89.32 kJ/mole and frequency factor was 7,246,289 min$^{-1}$ for soybean oil. While, the activation energy and the frequency factor of palm oil were 79.05 kJ/mole and 391,210 min$^{-1}$, respectively.

As reported by Kusdiana & Saka (2001), the reaction rate constant at 270 °C for rapeseed oil transesterification in supercritical methanol was 0.0007 s$^{-1}$ (0.042 min$^{-1}$) with 69 kJ/mole of activation energy (Ea) and 6936 of frequency factor ($k_o$) [7]. The rate constant of rapeseed oil is about 1.6 times and 5.6 times higher than the values obtained in this experiment for soybean and palm oils, respectively. The activation energies of our experiments were slightly higher than that of the rapeseed oil, i.e. 20 and 10 kJ/mole for soybean oil and palm oil, respectively. It might be due to the higher frequency factor of soybean and palm oils. The frequency factor of soybean oil and palm oil were 1045 and 56 times higher than that of rapeseed oil, respectively. Moreover, in the study by Kusdiana and Saka [7], they used higher molar ratio of oil to methanol (1: 42), while in our

| No | Temperature (°C) | $k'$ soybean oil 1/min | $k'$ palm oil 1/min |
|----|------------------|------------------------|---------------------|
| 1  | 210              | 0.0015                 | 0.0013              |
| 2  | 230              | 0.0042                 | 0.0023              |
| 3  | 250              | 0.0074                 | 0.0044              |
| 4  | 270              | 0.0265                 | 0.0075              |
| 5  | 290              | 0.0305                 | 0.0243              |

Table 1. The values of $k'$ for soybean oil and palm oil at various temperatures

![Figure 5](image-url)  
**Figure 5.** First order reaction rate constant in Arrhenius plot of palm oil in methanol during transesterification reaction

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The rate of transesterification of soybean and palm oils was investigated in this study. The conversion of both oils gradually increased with the increasing reaction time at subcritical methanol. However, in supercritical methanol the conversion was sharply increased with the increasing reaction time. For both oils the optimum molar ratio of oil to methanol was 1:24. The evaluation on the reaction kinetic of both oils were conducted based on a simple model, with the overall chemical reaction followed the pseudo-first–order reaction. As expected, the reaction rate constant of soybean oil and palm oil increased with the increase in reaction temperature, however, the rate constants of soybean oil slightly higher than that of palm oil. At subcritical temperatures, the reaction rate constant was low, but it was much higher at supercritical state (about 20 and 18.5 time for soybean oil and palm oil, respectively). The activation energy was 89.32 kJ/mole and frequency factor was 7,246,289 min⁻¹ for soybean oil. While, for palm oil activation energy and frequency factor were 79.05 kJ/mole and 391210 min⁻¹, respectively. The reaction rate for both of oil were expressed as 

\[ r_T = \frac{N_r}{V(T)} \exp\left(\frac{E_a}{RT}\right) \]  

and 

\[ r_T = \frac{N_r}{V(T)} \exp\left(\frac{E_a}{RT}\right) \]  

**4. Conclusions**

Biodiesel was prepared by non catalytic transesterification of soybean and palm oils with sub and supercritical methanol in a batch reactor. The effect of reaction time, reaction temperature and molar ratio of oil to methanol were investigated. The conversion of both oils gradually increased with the increasing reaction time at subcritical methanol. However, in supercritical methanol the conversion was sharply increased with the increasing reaction time. For both oils the optimum molar ratio of oil to methanol was 1:24.
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