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Kinetics of Palm Oil Transesterification Using Double Promoted Catalyst CaO/KI/γ- Al_2O_3

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Abstract. Double promoted catalyst (CaO/KI/γ-Al_2O_3) was used as the catalyst for transesterification of palm oil into biodiesel. The experiment was carried out in a batch reactor consisting of a three-neck glass flask (500 ml capacity) equipped with a reflux condenser, thermometer and magnetic stirrer. Kinetic study was carried out with methanol under reflux conditions at different temperatures (35-75°C) and different times of reaction (1-7 hours). The effects of temperature and time of the reaction on the conversion of palm oil into biodiesel and reaction rate constants were investigated. The results showed that the conversion and rate constants of reaction increased with the increasing of the reaction temperature. The highest conversion of 97% was obtained at 65°C and 5 hours of reaction time. Meanwhile, the activation energy and the frequency factor were 15.47 kJ/mol and $1.22.10^2$, respectively.

Keywords: *double promoter; kinetic study; refluxed methanol; transesterification.*

1 Introduction

At present, over 80.3% of worldwide energy demand is supplied by fossil fuel oil, while 57.7% of the amount is used in the transportation sector [1-3]. Meanwhile, global diesel oil consumption is estimated to reach 934 million tons per year [2,4]. On the other hand, petroleum reserves are limited and the World Energy Forum predicts that they will eventually run out in less than 10 decades if new oil deposits are not found anymore [2,5]. Renewable energy systems seem a particularly promising solution to overcome these problems in order to secure the world's energy supplies and to reduce greenhouse gas emissions (GGE) [2,3,6]. Renewable energy sources such as solar energy, wind energy, hydro energy and energy from biomass and waste have been successfully developed and are used in different countries to replace fossil fuels [2]. However, from these renewable resources, biomass and waste still need to be developed further. Biodiesel is one of the potential alternatives for diesel oil because it comes from renewable materials and is produced from local raw

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materials such as vegetable oil, animal fat, algae, and waste cooking oil [6,7]. Moreover, it can be naturally degraded and is non-toxic [3,6].

Biodiesel as an alternative diesel fuel is a mixture of fatty acid alkyl esters commonly produced by transesterification between ester (triglyceride) and alcohol. Methanol is preferred and widely used as a reactant to produce biodiesel, due to its low cost and availability [2,6,8]. Currently, biodiesel is being produced via transesterification of vegetable oil using homogeneous catalysts [6,9]. However, the conventional process has several weaknesses. The two main problems are that the homogeneous catalyst cannot be reutilized or regenerated and separation of catalyst from the biodiesel product is technically difficult thus increasing the operational cost [6,8,10,11].

To solve these problems, researchers have begun focusing on utilization of solid catalysts. Solid catalysts have several advantages, such as being easy to recover from the mixture [12], high purity of glycerol as byproduct [13], cheaper and more environmentally friendly compared to conventional catalysts. Alkaline-earth metals, for example KI/Al_2O_3 [14], $NaOH/\gamma\text{-}Al_2O_3$ [15], Mg-Al hydrotalcite [16] have been studied as heterogeneous catalyst for biodiesel production. Only calcium oxide has shown considerable catalytic activity on the transesterification of soybean oil or palm oil with refluxing methanol [17-19]. However, the catalytic activities of most of them are not as impressive as those of homogeneous catalysts. This study focused on using double promoted catalyst $CaO/KI//\gamma\text{-}Al_2O_3$ in order to improve the activity of the catalyst. Furthermore, the kinetic study of solid catalysts is still very scarce. Only a few researchers have examined the kinetics of transesterification catalyzed by solid catalysts [20-22] and all of them only investigated the kinetics of single promoted catalysts. The kinetics data are crucial for designing the industrial operation and optimization of the process.

Therefore, in the present work, the kinetics of palm oil transesterification into biodiesel with refluxing methanol was studied using double promoted $CaO/KI/\gamma\text{-}Al_2O_3$ catalyst. The main goals were to investigate the influence of temperature and time of the reaction on palm oil conversion and rate of transesterification constant. The kinetics data were investigated in order to develop a kinetic model of palm oil transesterification.

2 Materials and Methods

2.1 Materials

Analytical grade γ-alumina as catalyst support was purchased from Merck, Germany. Commercial grade CaO and KI were also supplied by Merck. Meanwhile, commercial grade acetic acid and methanol were provided by local supplier Brataco-Chem. Refined palm oil was purchased on the local market. The palm oil consisted of 0.26% lauric acid, 1.01% myristic acid, 10,93(%) linoleic acid, 45.96% oleic acid, 3.64% stearic acid, and 38.20% palmitic acid (wt. %) and was used without further purification.

2.2 Transesterification Reaction

Transesterification was carried out in a batch type reactor which consists of a three-neck flask equipped with a reflux condenser. Oil and methanol with a molar ratio of 1:42 were filled into a three-neck flask and subsequntly 6% of catalyst (wt. % to the oil) was added to the reaction mixture. The mixture was refluxed at the desired temperatures (35, 45, 55, 65 and 75°C) and reaction times (1, 2, 3, 4, 5 and 7 h) under stirring at a constant speed using a magnetic stirrer. After that, the solid catalyst was separated from the mixture by filtration. The liquid was placed in a separator funnel and left for 24 hours at room temperature until it split in three layers; the top layer was methanol, the middle was FAMEs and the bottom layer was glycerin. The biodiesel product was analyzed with GC (GC HP 5890) with the following operation conditions: column flow 28 ml/min, initial temperature 125°C, temperature increment 15°C per minute and final temperature 275°C. Analysis of the biodiesel was used to determine the conversion of palm oil according to the following equation [7,15,17]:

$$Conversion\ of\ oil\ (\%) = \frac{\left({}^{wt.of\ FAME}/_{MW\ of\ FAME}\right) x FAME\ conc}{\left({}^{wt.of\ oil}/_{MW\ of\ oil}\right) x 3}\ x100 \qquad (1)$$

where, wt. of FAME is the actual weight of the biodiesel produced from the experiment (mg), wt. of oil is the weight of the palm oil used in the experiment (mg), MW of FAME is the molecular weight of the biodiesel and MW of oil is the molecular weight of the palm oil used in the experiment. Meanwhile, FAME conc. is the content of biodiesel in the product measured by gas chromatography. The factor of 3 in the Eq. (1) indicates that each molecule of triglyceride produced three molecules of methyl ester.

3 Results and Discussions

3.1 Effect of Temperature and Time of Reaction on Palm Oil Conversion

The effects of reaction time on palm oil conversion were investigated by varying the reaction time from 1 to 7 h with 1 h intervals. The transesterification experiment was conducted at 3 different reaction temperatures (45, 55, and 65ºC), while the other conditions, such as molar ratio of oil to methanol and amount of catalyst, were kept constant at 1:42 and 6% (wt. % to the oil). As expected, the conversion of palm oil increased with the increase of reaction time. Figure 1 shows the effect of reaction time on palm oil conversion at three different reaction temperatures (45-65°C with 10° intervals). At the beginning (1-2 h), the palm oil conversion increased gradually, but from 2-4 h the conversion sharply increased with the increase of reaction time. At 4-5, once more a gradual increase of palm oil conversion was obtained.

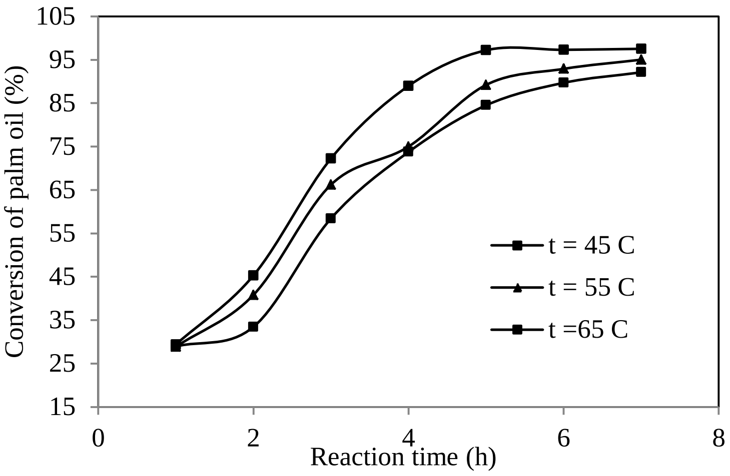

Figure 1 Conversion of palm oil (%) versus time of reaction (h) at various reaction temperatures with oil to methanol ratio 1:42 and amount of catalyst 6%.

Meanwhile, over 5 hours (6-7 h) of reaction time, conversion did not significantly increase. A higher conversion was achieved in a shorter time at higher reaction temperatures. For example, the highest conversion percentages (92 and 95%) were achieved at 45 and 55°C within 7 h. However, a conversion of 97.20% was achieved at 65 °C only within 5 h. The highest conversion percentage of 97.53% was achieved at 65°C within 7 h of reaction time. Therefore, from an economic point of view, a reaction temperature of 65°C and reaction time of 5 h were determined as optimum conditions with 97.20% conversion of palm oil. Meanwhile, Noiroj, *et al.* [23] obtained the highest palm oil conversion percentage of 87.5% at 60°C within 6 hours using KOH/Al_2O_3 catalyst, while they achieved 91.07% conversion within 3 hours using KOH/NaY catalyst. Therefore, it is proven that the rate of transesterification is strongly influenced by temperature and time of reaction.

3.2 Kinetic Analyses

Theoritically, transesterification reactions are equilibrium reactions consisting of three steps, as represented by Eqs. (2)-(4) [24,25]:.

$$\text{Triglyceride} + \text{ROH} \rightleftharpoons \text{Diglyceride} + \text{RCOOR}_1 \tag{2}$$

$$\text{Diglyceride} + \text{ROH} \rightleftharpoons \text{Monoglyceride} + \text{RCOOR}_2 \tag{3}$$

$$\text{Monoglyceride} + \text{ROH} \rightleftharpoons \text{Glycerol} + \text{RCOOR}_3 \tag{4}$$

However, in real application, the excess of methanol is used to shift the reaction towards the right side. Several studies have indicated that with high methanol content, the reverse reaction is not important and does not influence the forward reaction rate [7,19,25]. Diasakaou, *et al.* [25] have proposed the following mechanism of transesterification of vegetables: TG reacts with methanol to produce diglyceride (DG), which subsequently reacts with methanol (MeOH) to produce monoglyceride (MG). Finally, MG reacts with MeOH to produce methyl ester (ME) and glycerol (GL). At each reaction step, one molecule of methyl ester (ME) is produced for each molecule of MeOH consumed. The kinetic mechanism can be represented by the following equations:

$$TG + MeOH \xrightarrow{k_2} DG + ME \tag{5}$$

$$DG + MeOH \xrightarrow{k_1} MG + ME \tag{6}$$

$$MG + MeOH \xrightarrow{k_3} GL + ME \tag{7}$$

where k_1, k_2, and k_3 are the reaction rate constants of Eqs. (5), (6), and (7), respectively. Each reaction step is assumed to be first order with respect to each reacting component and irreversible. However, in fact, the desired end products in the transesterification are biodiesel and glycerol, therefore the reaction kinetics analysis in this study used the simpler model proposed by Kusdiana and Saka [26], which ignores intermediate product diglycerides and monoglycerides. Hence the reaction mechanism can be simplified into a single stage and irreversible, as in Eq. (8):

$$TG + 3\,MeOH \xrightarrow{k} 3\,ME + GL \tag{8}$$

Based on Eq. (8), the transesterification reaction rate can be expressed by Eq. (9):

$$-r_{TG} = \frac{-dC_{TG}}{d_t} = k\ [TG]\ [MeOH]^3 \tag{9}$$

where k is the rate constant of the overall reaction of Eq. (9).

Theoretically, the overall rate reaction is 4th order [27]. However, in the application, the reaction was conducted with a high excess of methanol (C_{MeOH} = constant). Therefore, the reaction is assumed to follow pseudo first order reaction kinetics. Hence, the rate reaction can be given by Eq. (10):

$$-r_{TG} = -\frac{dC_{TG}}{dt} = k'[TG] \tag{10}$$

TG concentration is transformed into conversion form by Eq. (11).

$$C_{TG} \ = \ C_{TG0}\ (1 - X_{TG}) \tag{11}$$

Hence, Eq. (10) can be written as Eq. (12):

$$\frac{dX_{TG}}{dt} = k' \ \ (1 - X_{TG}) \tag{12}$$

The rearrangement and integration of Eq. (12) produces Eq. (13), as follows

$$-ln(1 - X_{TG}) \ = \ k't \tag{13}$$

where k, k', t and X_{TG} are kinetic constant of triglyceride (TG), $k[C_{MeOH}]^3$, time of reaction and conversion of TG, respectively. Eq. (13) is used for non catalytic reactions. For catalytic reactions in a batch reactor, Eq. (14) [28] is used:

$$\frac{W\,k\prime}{V} t \ = \ [-ln(1 - X_{TG})] \ \ , \tag{14}$$

where w is weight of catalyst (g). In this work, the synthesized CaO/KI/γ-Al_2O_3 catalyst are in powder form with small particle size (average particle size 10 μm, specific surface area 16.508 m^2/g, pore volume 0.083 cm^3/g and mean pore size 38.21 A°). This catalyst was used to convert palm oil into biodiesel. Due to the very small particle size, the reactant fully penetrates the particle and wets all its surfaces and therefore, the particle is in the diffusion free regime ($M_T < 0.4$). This means either a short pore slow reaction or rapid diffusion, and hence the system is controlled by chemical reaction.

The kinetics study of the transesterification reaction of palm oil with CaO/KI/γ-Al_2O_3 catalyst in refluxed methanol was conducted according to the data for the reaction temperature range of 35-75°C with 10° intervals and reaction times of 1-7 h with 1 h intervals. The conversions of TG (X_{TG}) were calculated from Eq. (1). The rate constant k' for the catalytic reaction was determined from Eq. (14)

with the amount of catalyst w = 6% (wt. % to palm oil) by the fitting of $[-ln(1-X_{TG})]\ vs$ t with the slope of $\frac{W\,k\prime}{V}$ (plot data not shown). A straight line was used to fit the data in order to adopt the first order reaction. Linearity was checked by the coefficient of determination (R^2). Based on the fitting data, the rate constant was obtained for each reaction temperature, as shown in Table 1.

Table 1 Rate of transesterification reaction constant at varied reaction temperatures.

T (°C)	k'(min^{-1})	R^2
35	0.297	0.957
45	0.345	0.980
55	0.402	0.983
65	0.556	0.930
75	0.557	0.939

Table 1 shows that the coefficient of determination (R^2) for each temperature was > 0.9, meaning that the curve at each temperature is a straight line. Thus, the first-order assumption was proven. It can also be seen that the rate constant of the trasesterification reaction was significantly influenced by the reaction temperature. As expected, the value of k' increased with the increase of reaction temperature according to Arrhenius' law [28], as shown in Eq. (15)

$$k = k_o\, e^{-E_a/RT}, \tag{15}$$

where E_a, R, T and k_o are activation energy, molar gas constant (8.314 J/mol K), absolute temperature (K) and the pre-exponential factor, respectively. The data of temperature (°C) and k' in Table 1 were used to determine E_a and k_o, by fitting the reaction rate constant (k') versus the reciprocal absolute temperature (1/T), as shown in Figure 2.

According to Eq. (15), E_a was found to be 15.47 kJ/mol and k_o was $1.22\text{x}10^2$. Meanwhile, the values of k' and E_a for sunflower oil reported by Lukic et al. [21] were 0.12/min and 72 kJ/mol. The k' value from this work (0.556/min) was 4.6 times higher than that of sunflower oil. Also, the E_a value was 1/5 times lower than that of sunflower oil. This indicates that the double promoted catalyst ($CaO/KI/\gamma\text{-}Al_2O_3$) was much more active than the single one (K_2CO_3/Al_2O_3) used by Lukic, *et al*. [21]. The highest conversion percentage of 93% was achieved by Lukic, *et al*. within 1 h. Meanwhile, the highest conversion percentage of 97% was obtained in this work within 5 h. It should be noted that Lukic, *et al.* conducted their experiment in autoclave at high temperature and pressure (120°C and 10 bar).

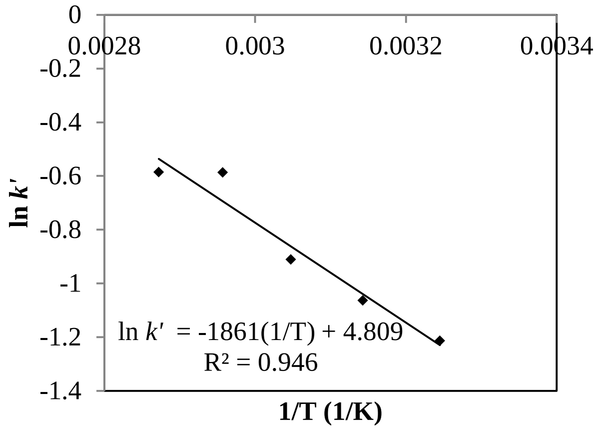

Figure 2 Plot ln *k*′ vs 1/T (1/K) for palm oil transesterification with CaO/KI/γ-Al_2O_3 catalyst in *batch* reactor with refluxed methanol.

4 Conclusions

A kinetics study of palm oil transesterification was conducted in a batch reactor with refluxed methanol using double promoted CaO/KI/γ-Al_2O_3 catalyst. The rate constant of palm oil transesterification was determined by employing a simple method with the overall chemical reaction following the pseudo first order reaction. The results showed that the conversion of palm oil and the rate constant of the reaction were significantly influenced by the reaction temperature. The highest conversion percentage of 97% was achieved at 65°C and 5 h of reaction time. An activation energy (*Ea*) of 15.47 kJ/mol and pre-exponential factor of 1.22 E+2 were obtained, hence the rate constant of palm oil transesterification using CaO/KI/γ-Al_2O_3 catalyst can be expressed as:

$$-r_A = 1.22\,E + 2\,Exp\,(\frac{-15.47}{RT})\,C_A.$$

This proves that CaO/KI/γ-Al2O3 is very promising for use as a catalyst for palm oil transesterification into biodiesel as compared to conventional catalysts.

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