

Transesterification of palm oil using sodium silicate base catalyst from geothermal sludge

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Abstract. The use of solid base catalysts in biodiesel synthesis is becoming more preferable because of their superiority over homogeneous catalysts. In the present work, a strong base catalyst of sodium silicate synthesized from silica-rich geothermal sludge was used in a transesterification of palm oil with methanol. The catalyst was calcined at 400°C for three hours with a temperature ramp of 20°C/min. The transesterification was carried out at varying temperature in the range of 50 - 70°C for 60 minutes with a methanol-palm oil molar ratio of 8.8:1. The catalyst-palm oil ratio was varied in the range of 1 - 5% (w/w). In order to investigate kinetics of reaction, at a certain interval of time samples were taken consecutively during the reaction. Experimental results showed that the sodium silicate was very active in the transesterification of palm oil with methanol. Reaction temperature at 60°C was sufficient to reach a conversion level as high as 93% in a relatively short reaction period. Meanwhile, the high conversion was still achievable with the use of 1 % (w/w) catalyst. In addition, a lumped model of reaction kinetics was adequate to approach the experimental data with a calculated activation energy of 15.73 kcal/mole. Results of the present work suggested that sodium silicate synthesized from local resources of geothermal sludge would become potential solid base catalyst in biodiesel synthesis.

1. Introduction

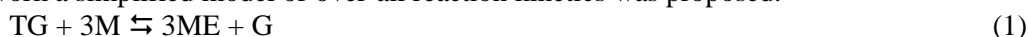
In the last few years, a lot of efforts have been done to search potential renewable energy in order to find solution for the depletion of crude oil which is at the moment still the main source of energy. Among various types of renewable energy sources, biodiesel is one of the interests due to the availability of its raw material i.e. vegetable oil, animal fat, algae, etc. The use of homogeneous base catalysts of NaOH and KOH is very common to produce biodiesel through transesterification of triglycerides with alcohol. The process is already well developed and commercially implemented [1-3]. Even though, high conversion is achievable at a moderate condition, the process still faces problematic separation and purification and it requires intensive energy that causes high production cost [4]. In addition, the need to use inexpensive feed-stocks that might contain high concentration of free-fatty acids and water can lead to saponification that further restraints purification process [5].

As an alternative to homogeneous base catalyst, solid base catalysts for transesterification have drawn a lot of interest. The use of solid catalysts can ease separation/purification of the product, avoid formation of soap and therefore, reduce separation cost that eventually leads to a more competitive biodiesel prices [6]. Several solid base catalysts for transesterification have been investigated including earth alkaline oxides such as calcium oxide [7, 8] and calcium methoxides [9], Mg-Al hydrotalsite [10, 11], K₂CO₃/ γ -Al₂O₃ [12], TiO₂-MgO [13], Zr-La oksid [14], Eu₂O₃/Al₂O₃ [15], La/ β zeolite [16], Na/NaOH/ γ -Al₂O₃ [17], etc. Even though these catalysts are found active in the transesterification of different kinds of triglycerides, the activity is generally less than that of homogeneous catalysts so that a longer reaction time is needed to reach high reaction conversion.



Alkali type catalysts of sodium silicates have also been studied and used as solid base catalysts in biodiesel synthesis. Commercial sodium silicates can be thermally treated and used as catalysts in transesterification of soybean and rapeseed oils both in sub-critical and atmospheric conditions [18-21]. Calcination temperature during pretreatment was found affecting the activity of the catalyst. It was found that the optimum activity was reached from calcination at 400°C for 2 hours [20]. In transesterification of soybean oil with methanol, the catalysts could serve a maximum yield of nearly 100% after 60 minute reaction at 60°C with the use of 3% (w/w) catalyst, 7.5:1 methanol-oil molar ratio and at constant agitation of 250 rpm. Meanwhile, similar catalyst used in transesterification of rapeseed oil with methanol resulted in a maximum yield of 99.6% under optimized conditions of 3% (w/w) sodium silicate, 9:1 methanol-oil molar ratio, 60 min reaction time, 60°C reaction temperature, and 250 rpm stirring rate [19]. The reaction mechanism of soybean-methanol transesterification was studied by Guo, et al.[21]. They concluded that calcined sodium silicate was more active as proton donor in the reaction. The activity of sodium silicates synthesized from commercial amorphous silica and sodium hydroxide in transesterification of corn oil with methanol was investigated [22]. It was found that temperature rise during pretreatment had significant effect on the catalyst activity. The catalyst calcined at 400°C with a temperature ramp of 20°C/min could lead to the maximum conversion of corn oil by about 96%. In our other works, we synthesized sodium silicates from silica rich geothermal sludge and used it as a catalyst in transesterification of corn oil with methanol [23].

The use of widely available feedstocks as raw material in biodiesel synthesis is crucial. In the present work, sodium silicates synthesized from silica-rich geothermal sludges was further studied as a solid base catalyst in transesterification of palm oil with methanol. The effect of temperature and amount of catalyst on the reaction conversion were investigated in a batch reactor. In addition, in the present work a simplified model of over-all reaction kinetics was proposed.



Assuming that the catalyst is always saturated with methanol and the reaction is reversible, the rate of lumped reaction can be expressed as in eq. (2)

$$-\frac{d[\text{TG}]}{dt} = k_f ([\text{TG}] - 1/K [\text{ME}]^3 [\text{G}]) \quad (2)$$

where k_f is a rate constant of forward reaction and K is an equilibrium constant. Triglyceride is denoted as TG, methyl ester ME and glycerol G. The rate of reaction and equilibrium constants are temperature (T) dependent as expressed in eq. (3) and (4), respectively.

$$k_f = k_o e^{-\frac{E}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right)} \quad (3)$$

$$K = \alpha e^{\beta/T} \quad (4)$$

where E is activation energy, R universal gas constant, T_0 reference temperature, whereas K_0 , α and β are constants.

2. Methodology

Geothermal sludge from PT Geo Dipa Energi in Dieng, Centre Java was initially washed with distilled water, filtered and then dried in an oven at 150°C for 16 hours. The remaining dried material was pulverized to obtain -60 mesh powder fractions so called dry sludge. The dry sludge was underwent silica extraction following procedure developed in the previous works [24]. 10 g silica resulted from the extraction step was slowly added to a solution that was made by dissolving 11.7 g NaOH (99.9%, Merck) in 12 mL distilled water. The solution was continuously stirred at a constant temperature of 60°C while evaporation was taking place to finally form a gel phase. The gel-phase was dried in an oven at 120°C for two hours. The dried substance was then calcined at 400°C with a ramp rate of 20°C/min while the temperature was kept constant for three hours. The resulting dried material was then pulverized for use as a catalyst. The resulting catalyst was used in transesterification of palm oil with methanol. As much as 120 g commercial palm oil in a beaker glass was heated to 60°C. Meanwhile, 158 mL methanol (Merck) (8.8 methanol-palm oil molar ratio) and 6 g sodium

silicate (5% w/w) were placed into a three-neck flask equipped with a mercury sealed stirrer, a thermometer and a condenser. The mixture in the three-neck flask was heated to 60°C at a constant stirring of 410 rpm and was kept at the same temperature for one hour for methanol activation. After that, the preheated palm oil was added to the flask and transesterification started. Samples as much as 5 mL each were taken during the reaction. The samples were centrifuged and the residual oil in the heavy phase was analyzed using standard iodometric method to determine the amount of glycerol produced and total conversion of the triglycerides. The experiments were repeated at varying temperatures of 50, 60 and 70°C; and varying catalyst-palm oil ratios of 1%, 3% and 5% (w/w). The experimental data was then used to verify the proposed kinetics model.

3. Results and Discussion

In the present work, the activity of sodium silicate catalysts in transesterification of palm oil with methanol was studied. The ratio of catalyst-palm oil was varied at 1%, 3% and 5% (w/w) while other parameters i.e. temperature, agitation speed and palm oil-methanol molar ratio were kept constant at 60°C, 410 rpm and 8.8:1, respectively. Figure 1 shows conversion of reaction during the time at various catalyst-palm oil ratios. The conversion increases with time and it approaches about the same high conversion level at prolong reaction time. For all catalyst-palm oil ratios, the conversion can reach as high as ~93% after about 20 minute-reaction. This result is much better compared to that of other sodium containing catalysts such as Na/NaOH/Al₂O₃ as reporter by Lee, et.al.[25]. The experimental results show that the activity of the catalyst is even comparable with NaOH of conventional homogeneous catalyst. In sodium silicates, the sodium is anchored in the silicate frameworks. Transesterification reaction is activated by formation of surface CH₃O⁻ species due to interaction between methanol and sodium on the catalyst surface [21].

Figure 1 also shows that catalyst-palm oil ratio influences the early state of reaction conversion. It is evidence that the reaction rate is lower with the use of a lower amount of catalyst. The rate is apparently faster with the use of higher amount of catalyst. However, the use of catalyst-palm oil ratio above 3% (w/w) results in insignificant difference of reaction rate. As seen in the Figure 1, the maximum conversion is already achieved in 10 minutes of reaction. Similar work had been conducted by Guo, et al. (2010) which used commercial sodium silicate treated at 400°C for 2 hours for transesterification of soybean oil at 60°C [20]. They found that the maximum conversion was reached with the use of 3% (w/w) catalyst at 7.5:1 methanol-oil molar ratio and at a constant agitation of 250 rpm.

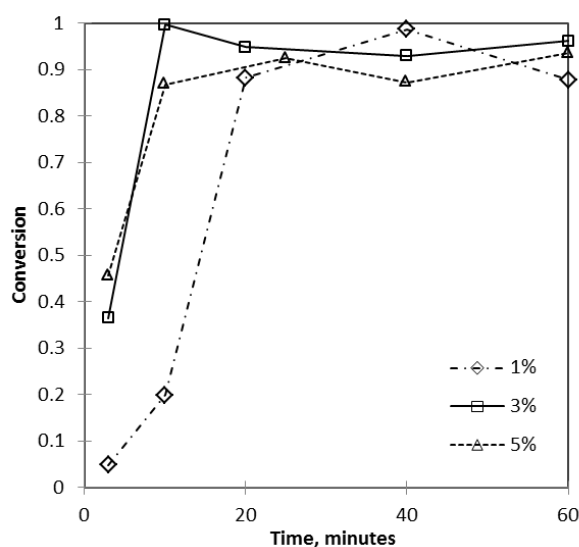


Figure 1. Reaction conversion at various catalyst-palm oil ratios (reaction at 60°C, 410 rpm agitation and 8.8:1 methanol-palm oil molar ratio)

The activity of sodium silicates as strong base catalyst in transesterification of palm oil with methanol is activated by temperature. Figure 2 shows the reaction conversion profile at different reaction temperatures. Even though the conversion always increases with reaction time, the increase has different rate. It is obvious that the rate is faster at higher temperatures to reach the maximum conversion. At high temperatures, interaction intensity among reactant molecules is expected to escalate that increases the reaction rate. However, as seen in Figure 2, different level of maximum conversion is apparently reached at different reaction temperatures. At lower temperatures, the reaction resulted in a maximum conversion at a lower level. This indicates that at the operating conditions used in the current study, transesterification of palm oil with methanol is limited by an equilibrium condition. Since the reaction is endothermic, the level of maximum conversion is expected to be higher at elevated temperatures. As depicted in Figure 2, the average maximum conversions are 0.85, 0.92 and 0.97 at 50°C, 60°C and 70°C, respectively. It is evidence that even though the amount of methanol with a methanol-palm oil molar ratio of 8.8:1 is much larger than its stoichiometric requirement, the reaction is determined not merely by the amount of methanol in the solution. Since the number of active sites on the catalyst surface is limited, only a certain amount of methanol molecules can be adsorbed and the catalyst surface is always saturated by the adsorbed methanol.

Based on the aforementioned maximum conversion levels, reaction equilibrium constant at each temperature can be determined. The relation between the equilibrium constants and temperatures is shown in Figure 3. As expected, the equilibrium constant increases with temperature. This means that the reaction conversion can be maximized at elevated temperatures. This also indicates that the reaction is endothermic so that it requires heating to increase the equilibrium conversion. The relation between equilibrium constant (K) and temperature (T in Kelvin) can be written as in eq. (5).

$$\ln K = 37.804 - \frac{11824}{T} \quad (5)$$

Since the reaction is thermodynamically preferable at high temperatures, the reaction condition is also desirable to increase the rate of reaction. As depicted in Figure 2, at elevated temperatures the maximum reaction conversion is reachable in a relatively shorter reaction time. At high reaction temperatures, a steep conversion change is observable which indicates a fast reaction rate. A certain activation energy level is needed to overcome for the reaction to proceed. As the results, at high temperatures not only the reaction conversion can be enhanced, but duration of the reaction can also be shortened to reach an acceptable reaction conversion.

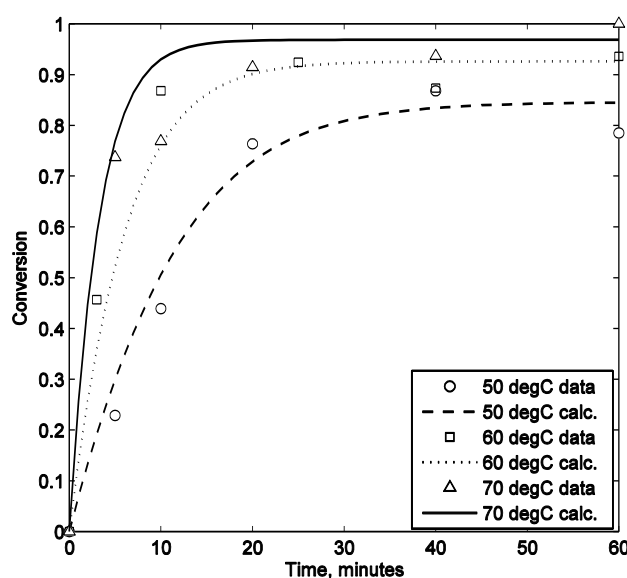


Figure 2. Reaction conversion at various reaction temperatures (5% w/w catalyst, 410 rpm agitation and 8.8:1 methanol - palm oil molar ratio)

Figure 2 also shows results from simulation based on reaction kinetics model proposed in the present work. The model which considers a reversible reaction scheme can apparently simulate the reaction conversion in a good agreement with the experimental. It is clearly indicated that the reaction is activated by temperature. The reaction is faster at higher temperatures with an activation energy of 15.73 kcal/mole. The reaction rate constant (k_f , minutes⁻¹) as a function of temperature (T , Kelvin) can then be expressed as in eq. 6.

$$k_f = 0.1484e^{-7914(1/T-1/333)} \quad (6)$$

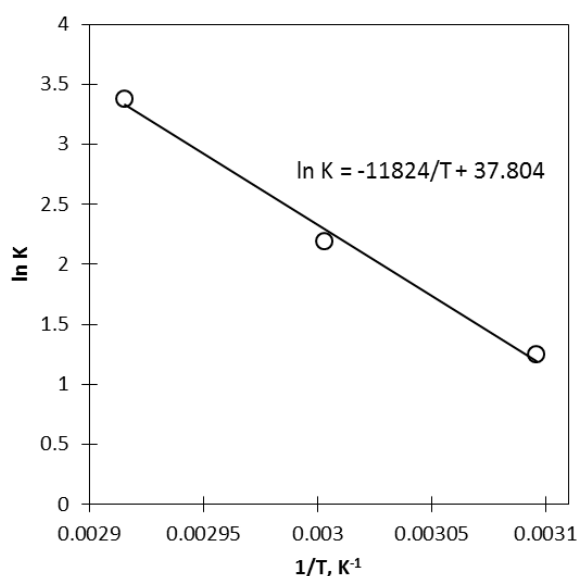


Figure 3. Equilibrium constant (K) at various temperatures (T)

As suggested in the model, even though the amount of methanol is much larger than stoichiometric requirement (8.8 times larger), reaction conversion is still limited by equilibrium condition. Although, the catalyst is always saturated with methanol, it seems that the amount of methanol adsorbed on the surface of catalyst is limited to react with palm oil. This eventually leads to a certain equilibrium reaction conversion which level is determined by reaction temperature.

3. Conclusions

Sodium silicates synthesized from silica rich geothermal sludge used as a solid base catalysts was found very active in transesterification of palm oil with methanol. Even though the amount of methanol in the reaction was much higher than that of its stoichiometric requirement, the reaction was limited by equilibrium which maximum conversion was temperature dependent. The highest conversion level of about 93% could be achieved by the use of as low as 1% catalyst (w/w) in a relatively short period of reaction time. A lumped reversible reaction kinetics model assuming that the catalyst is always saturated with methanol is sufficient to approach reaction conversion profile.

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