Methanolysis of Coconut Oil: The Kinetic of Heterogeneous Reaction

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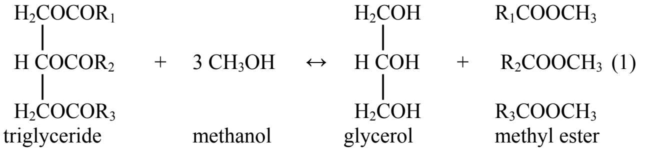
Abstract—**In order to have an easier catalyst separation process, at the end of methanolysis reaction, solid material K_3PO_4 which was insoluble in liquid mixture, was used as catalyst. The reaction was performed in a three necked glass reactor, equipped with a mechanical stirrer, a reflux condenser, a thermometer and a heating mantle. To investigate the optimum reaction conditions and to examine the heterogeneous kinetic model, the methanolysis were done at various degree of mixings, methanol to oil equivalent ratios, catalyst concentrations and reaction temperatures.**

By using a large excess methanol, the experimental data agreed with the second order irreversible heterogeneous catalytic model. The chemical reaction rate constant was significantly affected by temperature, while the mass transfer coefficient was influenced by the degree of mixing.

Index Terms— **coconut oil, heterogeneous, kinetic, methanolysis**

I. INTRODUCTION

Biodiesel has been defined as the monoalkyl esters of long-chain fatty acids derived from renewable materials, vegetable oils or animal fats, for use in diesel engine. The process to produce biodiesel is called transesterification or alcoholysis, is the displacement of alcohol from an ester (glycerol from triglyceride) by another alcohol (for instance methanol, so the process also called methanolysis). The methanolysis reaction is represented by :



$$\begin{array}{ccccccc} H_2COCOR_1 & & & & H_2COH & & R_1COOCH_3 \\ | & & & & | & & \\ H\,COCOR_2 & + & 3\,CH_3OH & \leftrightarrow & H\,COH & + & R_2COOCH_3 \\ | & & & & | & & \\ H_2COCOR_3 & & & & H_2COH & & R_3COOCH_3 \\ \text{triglyceride} & & \text{methanol} & & \text{glycerol} & & \text{methyl ester} \end{array} \quad (1)$$

In this reaction, a catalyst is needed in order to improves the reaction rate. Conventionally, alkaline metal alkoxides are the most effective methanolysis catalyst compared to the acidic catalyst. Sodium alkoxides are the most efficient catalyst used for it, although KOH and NaOH can also be used (Meher, et.al., 2006). Methanolysis occurs faster in the presence of a alkaline catalyst than that catalysed by the same amount of acid catalyst. For this reason and also because alkaline catalysts are less corrosive to industrial equipment than acid catalyst, most commercial biodiesel productions conducted with alkaline catalyst. The mechanism of potassium hydroxide catalysed methanolysis is started by mixing KOH in methanol to form methoxide,

$$CH_3OH + KOH \rightarrow CH_3OK + H_2O \qquad (2)$$

Then, on mixing the oil with the methoxide solution, consecutive reactions occure to produce diglyceride, monoglycerid and mono alkyl ester. In the presence of moisture and free fatty acids in the oils, soap are formed from the reaction of alkaline and the oil, that lower the oil yield and favor emulsion between glycerol and the oil (Bikou, 1999; Ma and Hanna, 1999; jorneytoforever, Rahayu et.al, 2005). Emulsion is also favored by the presence of unreacted mono and di glycerides. Therefore, a long settling time is needed for the separation of the two emulsioned phases, glycerol phase and ester (and unreacted oil) phase. So that, acid catalysts are used only if the vegetable oil contains high free fatty acid (> 5 %). However, as the acid or alkaline relatively high soluble in the methanol and then presence in the ester and glicerol phases, it has some drawbacks, such as, to remove the catalyst at the end of reaction, it needs neutralization process, with the consequence that the catalyst is not reusable and the difficulty in the recovery of a pure glycerol. In order to reduce the cost of purification, heterogeneous catalysts, solid acid catalyst (Kiss, et.al., 2006) and solid alkaline catalyst, such as metal oxides K_2CO_3 and Na_2CO_3 (Schuchardt et.al., 1998) were investigated. The methanolysis of rapeseed oil by trisodium phosphate catalyst, which slightly soluble in methanol, obtained limited unwanted waste product and reduced the difficulty in separation process (Filippis et.al, 2005). This paper investigate the factors affecting the rate of the methanolysis of coconut oil, by using potassium phosphate catalyst and introduce the kinetic equation for heterogeneous model. The coconut tree is the most natural resource available in the westside of Yogyakarta, Indonesia.

II. THEORY

The derivation of kinetic model is started by introducing heterogeneous reaction mechanism steps (Smith, J.M.,1981):

a. Mass transfer of methanol (A) from methanol phase to oil phase through methanol-oil interface
b. Mass transfer of methanol from oil phase to catalyst surface
c. Mass transfer of triglyceride (B) from oil phase to catalyst surface
d. Chemical reaction of methanol and triglyceride at catalyst surface.

And the rate of each step may be expressed as :

$r_1 = k_L a_c (C_{Ab} - C_A)$ from methanol phase to oil phase (3)

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$r_2 = k_{Ac}a_c\left(C_A - C_{As}\right)$ from oil phase to catalyst surface (4)

$r_3 = k_{Bc}a_c\left(C_B - C_{Bs}\right)$ from oil phase to cat.surface (5)

$(-r_A) = (-r_B) = k_R C_{As} C_{Bs}$ chemical reaction (6)

If $r_1 = r_2 = r_3 = -r_A = -r_B$, then the equation of overall rate in the batch reactor is

$$\left(-r_B\right) = -\frac{dC_B}{dt} = \frac{C_{Ab}C_B}{\left[\dfrac{C_{Ab}}{k_{Bc}a_c} + \alpha C_B + \dfrac{1}{k_R}\right]} \tag{7}$$

with $$\alpha = \frac{1}{k_L a_c} + \frac{1}{k_{Ac}a_c} \tag{8}$$

By multivariable optimization methods, the mass transfer coefficient and reaction rate constant can be evaluated.

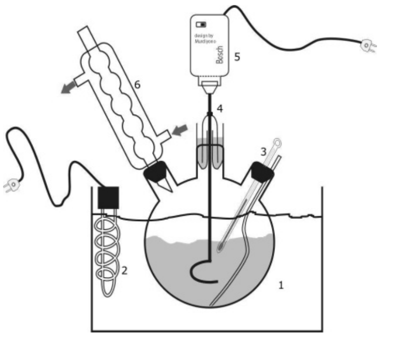
III. EXPERIMENTAL

A. *Materials*

The coconut oil used in the methanolysis process was a refined edible grade oil. The oil was purchased in local market in Yogyakarta, Indonesia. The oil properties were : water content 0.2786 %, saphonification number 253.77, free fatty acid content 0.3478 % (or 0.0062 meq FFA/g oil), density 0.9163 g/mL and viscosity 28.5 cSt at ambient temperature. Methanol used was technical grade (99.5% purity). The methanol density at 30 ^{o}C was 0.785 g/mL. The catalyst $K_3PO_4.7H_2O$ was purchased in local chemical store, Multi Kimia, in Yogyakarta. The spesific gravity of the catalyst was 2.564.

B. *Apparatus*

Methanolysis reactions were carried out in a 500 mL three necks flask equipped with a mechanical stirrer, reflux condenser, thermometer, heating mantle and sampling device.



1. Water bath
2. Heating coil
3. Thermometer
4. Stirrer
5. Motor
6. Reflux condenser
7. Sampling devise

Fig. 1. Diagram of Methanolysis Equipment

C. *Procedure*

The procedure was as follows. Initially, the reactor was charged with 100 mL of coconut oil, then it was heated to the selected temperature. At the same time, but in another flask, certain amount of methanol was charged and heated. When the selected oil temperature was achieved, the catalyst and the hot methanol were added to the hot oil under stirring and heating. The attainment of the selected temperature of the mixture determined the start of the reaction time. The system was maintained under the certain conditions during the reaction. Ten mililitres of sample was taken every 20 minutes until 2 hours. The reaction in the sample was stopped by immersing it in the cold water before the glycerol content was analyzed by periodic acid-iodometric method. At the end of the process, the mixture left was poured into a separating funnel, allowing the glycerol and the catalyst to separate from the biodiesel. The glycerol layer and the biodiesel layer were drained separately and collected prior to purification processes. The catalyst was separated from the glycerol by vacuum filtration.

IV. RESULTS AND DISCUSSION

A. *Effect of Catalyst Concentration*

Usually, the studies on the effect of KOH or NaOH on methanolysis of vegetables oils are done at concentration ranging from 0.5 to 2 % oil weight. Since the content of ion K^+ in K_3PO_4 is less than ion K^+ in KOH, more % K_3PO_4 is needed to catalyze the same amount of oil. So, eeffect of catalyst concentration (% weight of catalyst in the oil) in methanolysis process was studied in four sets of reactions. The reactions were conducted using catalyst ranging from 1 % to 4 %, while the methanol-oil equivalent ratio, temperature and stirring speed were maintained constant and equal to respectively, 6 : 1, 45^{o}C and 600 rpm. The results was summarized in Figure 2

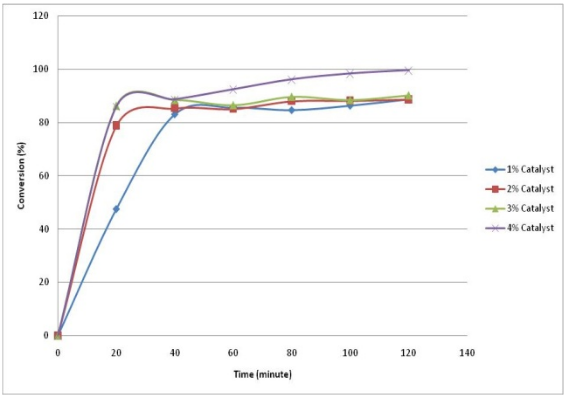


Fig. 2. The effect of catalyst concentration on oil conversion (45 ^{o}C, M=6, N= 250 rpm)

Figure 2 shows, the oil conversion increases at increasing catalyst concentration, especially for the first 20 min reaction time. The methanolysis using 1 % catalyst shows only 50% oil conversion, while 3 and 4 % catalyst show higher values. The conversions are not significantly different for all sets of reactions when the reactions are conducted for more than 40 min. It also shows the tendency of reaction time on achieving equilibrium oil conversion. The higher catalyst concentration needs longer time to reach equilibrium oil conversion, eventhough the conversion is higher. The oil conversion that will fullfill the standard biodiesel is usually more than 95 %. This conversion is achieved by using 4 % catalyst for more than 80 min reaction time. So, 4 % catalyst is the optimum catalyst concentration.

B. *Effect of Reactant Ratio*

Methanolysis is a reversible reaction. In order to shift the reaction to the right, it is necessary to use either a large excess of alcohol or to remove one of the products from the reaction mixture. The second option was prefered, whenever feasible, since in this way, this reaction can be driven to completion. Freedman (1984), Mittelbach and Remschmidt (2004) and Encinar (2005) recommended the ratio of alcohol to oil was at least 3:1, and a molar ratio of 6 : 1 is normally used in industrial processes to obtain oil conversion higher than 98%. Since larger excess methanol needs more energy to recover the unreacted methanol, runs to study the kinetics were conducted with methanol ranging from 150 to 600 % equivalent of oil. Figure 3 shows the results , oil conversions increase on increasing % methanol. However, the conversion are not significantly change when the reaction are conducted with 450 and 600 %. To study the kinetics, the methanolysis was conducted with methanol 450% oil.

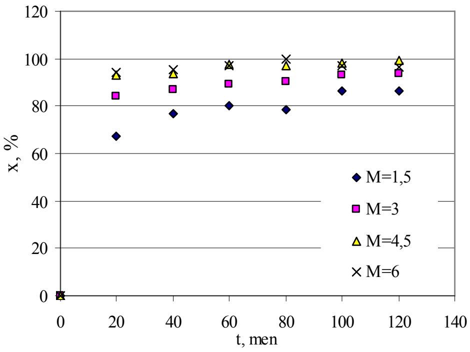


Fig.3. Oil conversion as a funtion of time at various reactant ratio (T=50 °C, C=4 %, N= 500 rpm)

C. *Effect Degree of Mixing*

The effect of stirring speed are studied ranging from 250 rpm to the maximum speed of the equipment. The oil conversions at various stirring speeds are showed at Figure 4. The faster stirring speed, the higher molecule collision frequency, the more reaction occured, then the higher oil conversion achieved. Slower stirring speed needs longer time to reach equilibrium oil conversion. At 250 rpm, the equilibrium conversion was achieved after 60 min, while at 500 rpm or above, the equilibrium starts at 40 min or less. This results show that the rate of reaction is influenced by stirring speed and fulfill the Arrhenius equation. Eventhough, the effect is not significantly showed at stirring speed more than 500 rpm. So, 500 rpm is the optimum stirring speed with maximum equilibrium conversion 99.5 %

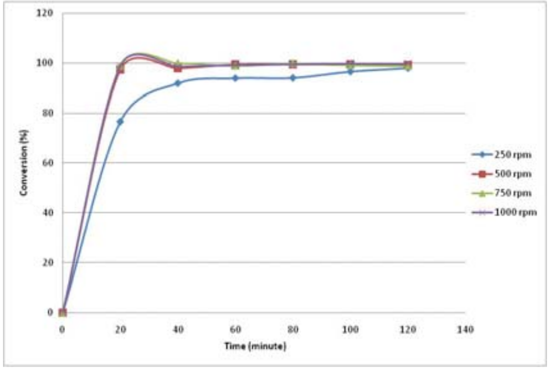


Fig. 4. Oil conversion as a function of time for various degree of mixing (50 °C, M=4.5, C= 4 %)

D. *Effect of Reaction Temperature*

The coconut oil methanolysis results which were conducted at various temperature ranging from 30 to 60°C, are presented on Figure 5. In each run, the catalyst 4 %, stirring speed 500 rpm and methanol 450% are constant. Since after 20 min the oil conversion starts to reach the equilibrium conversion, then to study the kinetics, the samples were withdrawn with period of 5 min. They show, the oil conversion increase at increased temperature.

Table I. Oil conversion as a funtion of time with various reaction temperature (M = 4.5, C=4 %, N= 500 rpm)

Time (min)	Oil Conversion at Temperature			
	30 °C	40 °C	50 °C	60 °C
5	33.2869	57.5193	79.5011	84.7060
10	55.2365	65.8663	87.5031	88.3084
15	66.3232	85.3524	91.3217	91.2110
20	73.2239	98.9065	95.6346	99.3076
60	95.2079	99.6716	99.5348	99.1115
120	99.4059	98.9845	99.1311	99.9602

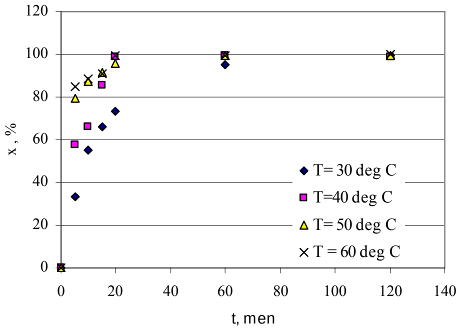


Fig 5. Oil conversion as a funtion of time with various reaction temperature (M = 4.5, C=4 %, N= 500 rpm)

E. *Reaction Kinetics*

By multivariable optimization calculation methods, the reaction rate constant, mass transfer coefficient, and mass transfer resistant of methanol to surface catalyst can be evaluated from oil conversion. The calculation results with SSE less than 2 % are presented on Table II to V

Table II. Mass transfer coefficient and reaction rate constant at various catalyst concentration

C %	α	k_{Bc}.ac	k_R
1	0.0001	1.1449	0.0014
2	0.0001	1.0896	0.0026
3	0.0001	1.0258	0.0038
4	0.0001	0.9966	0.0039

Table III. Mass transfer coefficient and reaction rate constant at various degree of mixing

N. rpm	α	$k_{Bc}.ac$	k_R
250	0.0001	1.0909	0.003
500	0.00005	1.1483	0.0087
750	0.000033	1.2184	0.0111
1000	0.000028	1.2215	0.0107

Table IV. Mass transfer coefficient and reaction rate constant at various catalyst concentration

M	α	$k_{Bc}.ac$	k_R
1.5	0.0001	1.1242	0.0015
3	0.0001	1.0297	0.0034
4.5	0.000072	1.0914	0.0059
6	0.000067	1.0554	0.0065

Table V. Mass transfer coefficient and reaction rate constant at various reaction temperature

Temp	α	$k_{Bc}.a_c$	k_R
30^{o}C	0.000015	1.1400	0.0008
40^{o}C	0.000014	1.1175	0.0015
50^{o}C	0.000012	1.0736	0.003
60^{o}C	0.000011	1.0196	0.0037

The dependency of mass transfer coefficients on catalyst concentration, stirring speed and reactants equivalent ratio are not significantly shown, while the dependency of reaction rate constant on each variable are slightly shown. The results may different if the samples were taken in shorter periodic time before equilibrium achieved.

With α is an overall mass transfer resistant of methanol, Table VIII shows the values of α tends to decrease at increasing temperature. This condition might be caused by increasing viscosity and density at higher temperature, then transfer of methanol into other phase become easier or the mass transfer resistant become smaller.

On the other hand, the resistant to mass transfer of oil slightly increases or relative constant on increasing temperature. According to Arrhenius equation, the reaction rate constant increases at increasing temperature. The proposed equation is

$$k = 40538.2 \exp(-\frac{5358.2}{T}), \frac{g}{meq.\min}$$

The comparation of oil conversion between the experimental results and the predicted values of heterogeneous kinetic model are presented on Figure 6 to 9.

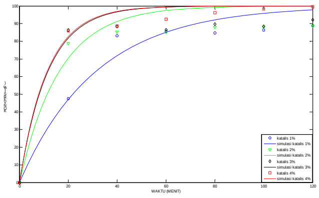


Fig. 6. The comparation of experimental and calculated value of oil conversion at various catalyst concentration

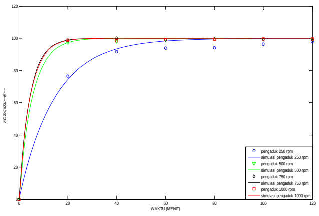


Fig. 7. The comparation of experimental and calculated value of oil conversion at various degree of mixing

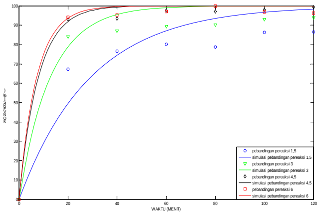


Fig. 8. The comparation of experimental and calculated value of oil conversion at various reactant ratio

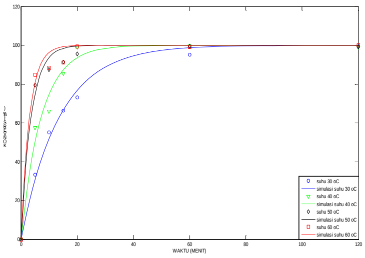


Fig.9. The comparation of experimental and calculated value of oil conversion at various reaction temperature

They are shown, that the plots of experimental oil conversion and predicted oil conversion by using the model are not significantly different, so the second order heterogeneous model is suitable for methanolysis of coconut oil catalyzed by K_3PO_4.

V. CONCLUSION

According to the coconut oil methanolysis results which were conducted at various catalyst concentration, various stirring speed, various methanol/oil equivalent ratio and temperature,

1. The optimum conditions are achieved by using K_3PO_4 catalyst as much as 4 % (wt) of oil, stirring speed of 500 rpm, methanol to oil ratio of 9:2 and reaction temperature of 50^{o}C. At these conditions, 99% of oil was converted within 60 min.
2. By using a large excess of methanol coconut oil methanolysis catalysed by K_3PO_4 agreed with second order heterogeneous kinetic model.
3. The reaction rate constant is affected by all variable conditions especially temperature, while the mass transfer coefficient is more affected by stirring speed.
4. The dependency of reaction rate constant with temperatue is expressed by Arrhenius's equation
5. It is recommended to take samples within shorter periodic time, that the concentration change with time can be observed better before equilibrium condition is achieved.

APPENDIX

C_{Ab} : Methanol concentration in methanol phase, mgeq (g oil)$^{-1}$
C_A : Methanol concentration in oil phase, mgeq (g oil)$^{-1}$
C_{As} : Methanol concentration in catalyst surface, mgeq(g oil)$^{-1}$
C_B : Oil concentration in oil phase, mgeq (g oil)$^{-1}$
C_{Bs} : Oil concentration in catalyst surface, mgeq (g oil)$^{-1}$
k_La_c : Mass transfer coefficient of methanol from methanol phase to oil phase, min^{-1}
$k_{Ac}a_c$: Mass transfer coefficient of methanol from oil phase to catalyst surface, min^{-1}
$k_{Bc}a_c$: Mass transfer coefficient of oil from oil phase to catalyst surface, min^{-1}
k_R : Second order rate of reaction constant, g oil(mgeq.min)$^{-1}$
$(-r_B)$: Oil rate of reaction, mgeq(g oil)$^{-1}$ men^{-1}
t : Reaction time, min

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