

Biodiesel Production from Ceiba Pentandra Oil via Transesterification in Situ: Kinetics Study & Characterization

*¹Azhari Muhammad Syam, ²Ishak Ibrahim, ³ Jalaluddin, ⁴Bustami, ⁵Zulfikar

ABSTRACT--Biodiesel, as biodegradable and alternative fuel which is obtaining a great attention compared to fossil-based fuel for diesel engine application. Many crop oils have been used as raw material of biodiesel. In this study, Ceiba Pentandra oil is identified as potential crop for biodiesel feedstock. The method of biodiesel production has been extensively studied by many researchers. Thus, the aim of this research work is to investigate the kinetics study of Ceiba Pentandra glycerides which is converted into alkyl esters compounds under alcohol and alkaline condition via transesterification in situ, and characterization of biodiesel. The results of this work showed that the path way of reaction follows the first order reaction. The values of reaction rate constants between 0.34-0.45 min⁻¹. The reaction activation energy is 34.36kJ mol⁻¹. The effect of temperature on the reaction path way is indicated by high value of activation energy of reaction.

Keywords--ceiba pentandra, biodiesel, kinetics study

I. INTRODUCTION

In consideration of fossil-based oil reserves and the environmental concerns have caused the biodiesel as the chosen fuel for diesel engine application. Edible oils are being used as the feedstock of biodiesel. Present scenario, using non-edible oils as the green feedstock is supported for avoiding food supply competition [1-5].

The selection of non-complicated and cheap technology for producing biodiesel from edible oil is aim at alleviating production cost and maintaining low customer price. For that reason, transesterification process is chosen among whole the current applied ways for biodiesel production. Based on the stoichiometry mechanism, one mole of triglycerides and three moles of methanol is required by transesterification process to produce three moles of methyl esters and one mole of glycerol. However, excess of methanol is necessary to maintain the reaction proceeds to product side (Eq. 1).

Go et al. (2016) [6] stated that transesterification reaction in situ usually takes place while extraction of seed and/or the products simultaneously occurs. In certain cases, extraction and transesterification reaction may actually occur sequentially. Nevertheless, through these processes biodiesel could be produced with fewer overall production steps [7].

¹* Department of Chemical Engineering, Universitas Malikussaleh, Lhokseumawe, Indonesia, armuh@yahoo.com

² Department of Chemical Engineering, Universitas Malikussaleh, Lhokseumawe, Indonesia

³ Department of Chemical Engineering, Universitas Malikussaleh, Lhokseumawe, Indonesia

⁴ Department of Informatics Engineering, Universitas Malikussaleh, Lhokseumawe, Indonesia

⁵ Department of Mechanical Engineering, Universitas Malikussaleh, Lhokseumawe, Indonesia

In terms of catalyst, homogeneous alkali catalysts such as hydroxide and methoxide compounds are commonly utilized. However, during the chemical reaction occurred in presence of alkali with moisture will reduce conversion of triglycerides to methyl esters. Therefore, it is essential to minimize the effects which resulted in the reaction unable to convert the reactant completely into product [8]. One of which is also due to a high content of free fatty acid (FFA). Another method that can be applied without considering the level of FFA namely heterogeneous-catalysed transesterification, but, this process is too expensive.



where TG, MeOH, ME, and GL are triglycerides, methanol, methyl ester, and glycerol, respectively. To overcome the reaction process form non-benefit products (such as: soap), a feedstock without FFA content is used. Otherwise, saponification reaction would occur and cause the complicated of product separation and high catalyst consumption [9-10].

The objectives of this study are to determine the parameters of reaction kinetics such as reaction rate constant, reaction order, and Arrhenius activation energy at various temperatures of reaction, and characterize the biodiesel properties.

II. MATERIAL AND METHODS

2.1 Material

Ceiba Pentandra seed was collected from local plantation. The chemicals employed were methanol (99.8% purity), sulphuric acid (95-98% purity), isopropanol (99.7% purity), phenolphthalein (1%), and potassium hydroxide (85% purity). The equipment was three neck flask as batch reactor, graham condenser, thermometer, hot plate completed with magnetic stirrer, separating funnel, oven, gas chromatography, and other glass wares.

2.2 Method of transesterification in situ

The fine powdered *Ceiba Pentandra* seed was immersed in Erlenmeyer flask with reactant by certain ratio of seed to reactant volume. In situ process of transesterification was without prior extraction of seed. It refers to the direct use of seed and allowing the transesterification reaction takes place within the matrix solid [11]. The mixture is treated by supplying heat at stipulated temperatures until 60 min. Once the reaction was commenced, the samples of kinetics were collected into vial based on the stipulated times (such as: 0, 2, 5, 9, 14, 20, 30, 40, 50, and 60 min). Thus, the rest of reaction product was allowed into separation funnel to settle down for 120 min.

2.3 Kinetics study

The collected samples of *Ceiba Pentandra* methyl esters were stored for kinetics study. The samples were then prepared for Gas Chromatography (GC) injection. Whole obtained data were plotted in the graph of kinetics order.

2.4 Analytical procedure

GC analysis was performed for identifying the hydrocarbon compounds such as fatty acids and methyl esters. The separation is carried out by using capillary column Rtx-5MS 30m x 0.25mm ID, 0.25 μ m with helium at 137.7 ml/min as a carrier gas and 1:100 of split ratio.

III. RESULTS AND DISCUSSION

The *Ceiba Pentandra* seed oil is used as feedstock in the study on conversion rate of alkyl esters compounds. The molar ratio of MeOH to ceiba pentandra seed oil was fixed at 8, the catalyst amount was 1.4% w/w under various reaction temperatures. The collection of samples was carried out at intervals time (from 0 to 60 min). Finally, the reaction order, the reaction rate constant and activation energy was determined through the kinetics equations.

To plot analysed data and to measure the effects of reaction temperature and time, the prepared samples were further analysed for study of kinetics on *Ceiba Pentandra* TG becomes ME [12].

3.1 Constant of reaction rate

Kinetics model of first order reaction of *Ceiba Pentandra* oil was showed in Figure 1. The amount of ME product may be used to determine reaction rate constant based on reaction time interval.

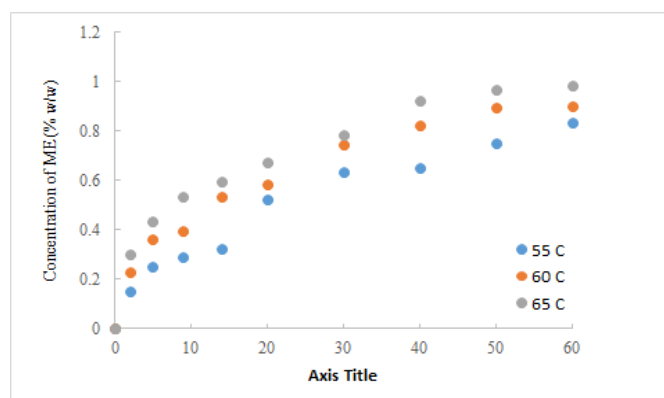


Figure 1: Plot of first order kinetics model for *Ceiba Pentandra* oil to ME

Syam et al. (2016) [10] reveals that the order of reaction plays an important role in determining reaction rate constant. The correct order would be shown by the linear graph of rate equation. Once a graph method is applied to determine order of reaction, the reaction rate constants were calculated from the graph slope. The equation (2) represents the reaction rate at any reaction time.

$$r = \frac{dC}{dt} = k[C] \quad (2)$$

where k, r, C and t denote the overall reaction rate constant, rate of reaction, concentration of product and time of reaction. However, in this study, transesterification in situ of *Ceiba Pentandra* glycerides with MeOH

under catalyst KOH to methyl esters compounds was occurred in a medium rate due to the extraction of oil takes place simultaneously with chemical reaction.

For this study, the kinetics data was used to develop the first order model based on the increase of ME compound as shown in Figure 1.

$$\int_{C_0}^C \frac{1}{C} dC = k \int_0^t dt \quad (3)$$

$$\ln[C]_{C_0}^C = k[t]_0^t \quad (4)$$

Thus, the reaction rate constant formula can be determined using logarithms

$$kt / 2.303 = \log_{10} \left(\frac{C}{C_0} \right) \quad (5)$$

where C_0 is the initial concentration of ME. For the transesterification in situ of TG, once the plot of first order model is valid, the reaction time versus product concentration should be linier. The reaction rate constant values for ME (k) at temperature (55, 60, and 65) C are shown in Table 1. In this matter, Tapanes et al. (2008) [13] stated that the values of k increased when the temperature was elevated.

The reaction rates are very sensitive with temperature. The kinetics study was suggested in a vessel temperature thermostatically controlled bath. According to Nouredini and Zhu (1997) [14], for elementary irreversible reactions the reaction rates constant proportionally increase with temperature. Therefore, these results prove that the irreversible reaction assumption is valid because the temperatures based reaction rate.

Table 1: Reaction rate constant (k) for transesterification in situ of *Ceiba Pentandra* TG

Temperature (°C)	k (min) ⁻¹
55	0.34
60	0.39
65	0.45

3.2 Arrhenius Activation energy

The reaction rate constant (k) depends on temperature as the Arrhenius equation as shown in equation (6).

$$\log_{10} k = (-E^\ddagger / 2.303RT) + \log_{10} A \quad (6)$$

where T and R is temperature and the universal gas constant. E^\ddagger is Arrhenius activation energy. In this term, k is determined from the slope of graph. The frequency factor, A was the intercept of graph. The plot of reaction rate constant values versus temperatures is shown in Figure 2. The Arrhenius activation energy for transesterification in situ is as shown in Table 2.

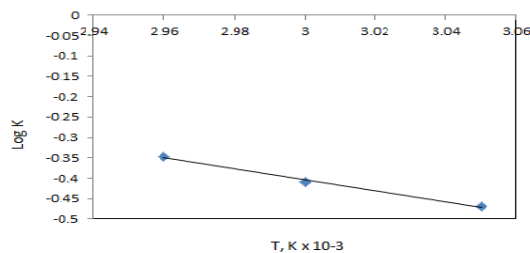


Figure 2: Arrhenius activation energy plot

Activation energy which was determined for each step of the reaction mechanism, with considering the pre-step is common for all of the reactions. The reaction scenario is described as follows. In the first step, the reaction passes through an initial complex and after a transition state with low activation energy forms the intermediate compounds as the main product [15]. In further step, the intermediate compounds dissociate via a second transition state with higher activation energy leads to the methyl esters and glycerol. This phenomenon was considered that the intermediate compounds break off to form final product may play a key role in alkaline-catalysed reaction of TG.

Table 2: Activation energy of transesterification in situ of *Ceiba Pentandra* glycerides to ME

Reaction	E [‡] (kJmol ⁻¹)
TG → ME	34.36

3.3 Characterization of biodiesel

Due to *ceiba pentandra* biodiesel as fuel for diesel engine application, it should meet the standard quality of International specifications. In this study, some characterization of *ceiba pentandra* biodiesel (such as: density, viscosity, pour point, cloud point, flash point, iodine value, acid number and moisture content) are analysed using ASTM method as shown in Table 3. Entire biodiesel properties comply with the values of standards specification.

Table 3: Characterization of *ceiba pentandra* biodiesel

Parameters	Unit	Method	Values
Density (15°C)	kg/m ³	ASTM D 40	863
Kinematic viscosity	mm ² /s	ASTM D 445	5.33
Iodine value	-	-	94
Moisture content	% volume	ASTM D 95-05	0.007
Cloud Point	°C	ASTM D 2500	6
Pour point	°C	ASTM D 97	-1
Flash point	°C	ASTM D 93	141

Acid number	mg KOH/g	ASTM D 974	0.68
oil			

IV. CONCLUSIONS

The kinetics of *Ceiba Pentandra* TG and MeOH to methyl esters was investigated. The conversion of TG into methyl esters appeared to be first order up to 60 min of reaction time. The rate constants for the formation of final product of methyl esters were determined at various temperatures. The values of k range from 0.34 to 0.45, respectively. The activation energy for step-wise reaction in transesterification of *Ceiba Pentandra* TG becomes methyl esters is 34.36 kJ/mol.

V. ACKNOWLEDGEMENTS

Authors acknowledged the dean of Engineering Faculty, Universitas Malikussaleh Lhokseumawe, Indonesia for financial support under fundamental research scheme.

REFERENCES

1. Bouaid A., Diaz Y., Martinez M. and Aracil J. 2005 *Catalyst Today* **106** 193
2. Syam A.M., Yunus R., Ghazi T.I.M. and Choong T.S.Y. 2012 *Industrial Crops and Products* **37** 514
3. Rathore V and Madras G 2007 *Fuel* **86** 2650
4. Canoira, L., Alcántara, R., Garcia-Martinez, M.J., Carrasco, J. (2005). Biodiesel from *Jajoba* oil-wax: Transesterification with methanol and properties as a fuel. *Biomass & Bioenergy*, 30: 76-81.
5. Ghadge, S.V., Raheman, H. (2005). Biodiesel production from mahua (*Madhuca indica*) oil having high free fatty acids. *Biomass and Bioenergy*, 28: 601–605.
6. Go, A.W., Sylviana, Ong, L., Tran-Nguyen, P.L., Ismadji, S., Yi-Hus, J. (2016). Developments in in-situ (trans)esterification for biodiesel production: A critical review. *Renewable and Sustainable Energy Reviews*, 60: 284-305.
7. Guldhe, A., Singh, B., Rawat, I., Bux, F. (2014). Synthesis of biodiesel from *scenedesmus* sp. By microwave and ultrasound assisted in situ transesterification using tungstated zirconia as a solid acid catalyst. *Chem Eng Res Des*, 92: 1503-1511.
8. Canakci, M. (2007). The potential of restaurant waste lipids as biodiesel feedstocks. *Bioresour. Technol.*, 98:183–190.
9. Schuchardt, U., Sercheli, R., Vargas, R.M. (1997). Transesterification of vegetable oils: a review. *Journal of Brazilian Chemical Society*, 9: 199-210.
10. Syam, A.M., Rashid, U., Yunus, R., Hamid, H.A., Al-Resayes, S.I., Nehdi, I.A., Al-Muhtaseb, A.H. (2016). Conversion of oleum papaveris seminis oil into methyl ester via esterification process: optimization and kinetic study. *Grasas Y Aceites*, 67: 1-9.
11. Harington, K., D'Arcy-Evans, C. (1985). Transesterification in situ of sunflower seed oil. *Ind Eng Chem Prod Res Dev*, 24: 314-318.

12. Vicente, G. Martinez, M., Aracil, J. (2006). Kinetics of brassica carinata oil methanolysis. *Energy and Fuel*, 20: 1722-1726.
13. Tapanes, N.O., Aranda, D.G., de Mesquita Carneiro, J.W., Antunes, O.A.C. (2008). Transesterification of *Jatropha curcas* oil glycerides: theoretical and experimental studies of biodiesel reaction. *Fuel*, 87, 2286-2295.
14. Nouredini, H., Zhu, D. (1997). Kinetics of transesterification of soybean oil. *Journal of American Oil Chemist Society*, 74: 1457-1463.
15. Syam, A.M., Yunus, R., Ghazi, T.I.M., Yaw, T.C.S. (2009). Methanolysis of *Jatropha* oil in the presence of potassium hydroxide catalyst. *Journal of Applied Science*, 9: 3161-3165.