

Pangium edule reinw Biodiesel Production: Kinetics Study and Physicochemical Properties

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Abstract

This paper presents the kinetics study of base-catalyzed *Pangium edule reinw* oil alcoholysis and the characterization of biodiesel product. The acid pre-treatment is required due to the initial free fatty acid content of crude *Pangium edule reinw* oil is 6.7%. Then, transesterification process is carried out under the fixed reaction temperature of 60°C, based on the previous study. The kinetics study of base-catalyzed *Pangium edule reinw* oil alcoholysis is conducted under the three reaction temperatures (50, 55 and 60°C). Determination of physicochemical properties such as density, viscosity, iodine value, acid number, pour point, cloud point, flash point, and moisture content of *Pangium edule reinw* biodiesel is performed using ASTM D6751.

Keywords: *Pangium edulereinw* oil, biodiesel, kinetics study, alcoholysis.

Introduction

The escalating price issue of petroleum based fuel due to more declining reserves of crude oil and the growing environmental concerns have induced the biodiesel attraction as the alternative fuel increasing significantly. Edible and inedible vegetable oils are being used as the feedstock of biodiesel. Nowadays scenario, using inedible oils such as *Jatropha curcas* (Syam, *et al.*, 2012), *Pongamia pinnata* (Rathore and Madras 2007), *Jojoba* (Canoira, *et al.*, 2005), *Madhuca indica* (Ghadge and Raheman, 2005) and *Brassica carinata* (Bouaid *et al.*, 2005) as the second generation feedstock is encouraged for avoiding endless competition with food supply. Besides, it is an effective way to overcome entire the related problems with edible oils.

The selection of a simple and inexpensive technique for producing biodiesel from inedible feedstock is aim at alleviating the production cost and maintaining the lowest customer price. For that reason, alcoholysis (transesterification) is chosen among whole the presently applied ways for biodiesel production. Based on the stoichiometry, the alcoholysis process requires one mole of triglycerides and three moles of alcohol (methanol) to produce three moles of methyl esters and one mole of glycerol. However, excess of alcohol is necessary to maintain the reaction proceeds to the right side (Figure 1). In terms of catalyst, the homogeneous alkali catalysts such as hydroxide and methoxide compounds are commonly used. However, during the alcoholysis in the presence of alkali with water/moisture will reduce the 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 to product (Canakci, 2007). One of which is also due to a high content of free fatty acid (FFA) in feedstock. Another method that can be applied without considering the level of FFA namely heterogeneous-catalyzed transesterification, but, this process is highly cost.

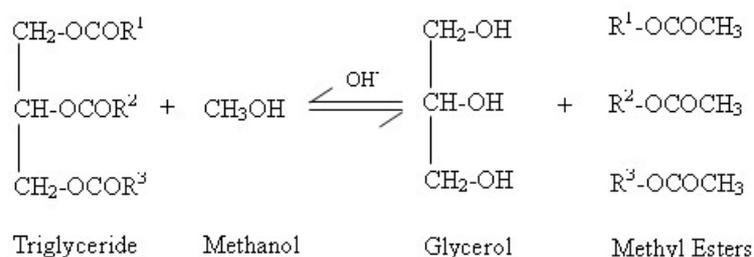


Figure 1. Mechanism of methanolysis overall reaction

To overcome the reaction process forms a less beneficial product (such as: soap), a feedstock post lowering the percentage level of FFA is applied. Otherwise, saponification reaction would occur and cause the difficulty of product separation (Schuchardt, *et al.*, 1997; Syam, *et al.*, 2016).

The objectives of 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. The characterization of *Pangium edule reinw* biodiesel such as density, viscosity, iodine value, acid number, pour point, cloud point, flash point, and moisture content is done according to International Standards of ASTM D 6751.

Experimental Methods

Material

Pangium edule reinw oil was purchased from the local company. 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 batch reactor, graham condenser, thermometer, hot plate completed with magnetic stirrer, separating funnel, oven, gas chromatography, pour and cloud point tester, flash point tester, viscosity & density analyzers, burette, and other glass wares.

Method for acid pre-treatment

The crude oil was heated in the three necks reactor until temperature reached about 60°C. The sulfuric acid (H₂SO₄) catalyst was then poured into reactor simultaneously with methanol at various concentrations as specified previously. Once the reaction has completed, the product was allowed into separation funnel to settle down for 2 h and the methanol water fraction at the top layer was removed. The treated oil was further analyzed on its final value of FFA using conventional titration method.

Kinetics Study

The treated oil as feedstock was introduced into the reactor and heated at the specified temperature. The mixture of methanol and catalyst was then added to the reactor at which the reaction was assumed to commence. When the reaction was running, the kinetics samples was provided at every specified times (1, 5, 10, 15, 20, 30, 40, 50, and 60) min. The samples were then prepared for Gas Chromatography (GC) injection. All obtained data were plotted in the graph of kinetics order.

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, 0.25µm with helium at 137.7 ml/min as a carrier gas and 1:100 of split ratio.

Results and Discussion

The *Pangium edule reinw* -based oil were used in the synthesis to investigate the effect of fatty acid methyl esters conversion rate. The molar ratio of methanol to oil was fixed at 6:1, the percentage of catalyst was 1.0% w/w, and the reaction temperatures were varied. The samples were collected at intervals time from 1 to 60 min. The experiments were designed to determine the reaction order, the rate constant and activation energy for the reaction.

To correlate experimental data and to quantify the reaction temperature and time effects, the results were further analyzed for the reaction kinetics of *Pangium edule reinw*-based oil (triglycerides) to be methyl esters. In this matter, the transesterification reaction to be divided into three steps (Diasakou, *et al.*, 1998) as shown in equations (1–3). Triglycerides (TG) react with methanol to produce diglycerides (DG), and then DG reacts to produce monoglyceride (MG). Finally, MG reacts with methanol to produce glycerol (by-product). At each reaction step, one molecule of methylated compounds is produced for each molecule of methanol consumed (Vicente *et al.*, 2006)



In this study, because of the relatively faster rates of intermediate reactions shown in equations (1–3), the reaction is limited by the last reaction as shown in Figure 1. This is called the limiting step reaction and will be the one which control the kinetics of the reaction. Based on those assumptions, a simpler mathematical equation for this reaction can be defined by ignoring the intermediate reactions involving MG.

Determination of Reaction Rate Constant.

Figure 2 showed the first order kinetics model for transesterification of *Pangium edule reinw*-based oil. The reaction rate constant can be determined based on the decrease amount of the limiting reactant that occurs in some reaction time interval or alternatively based on the increased amount of the product, i.e. methyl esters.

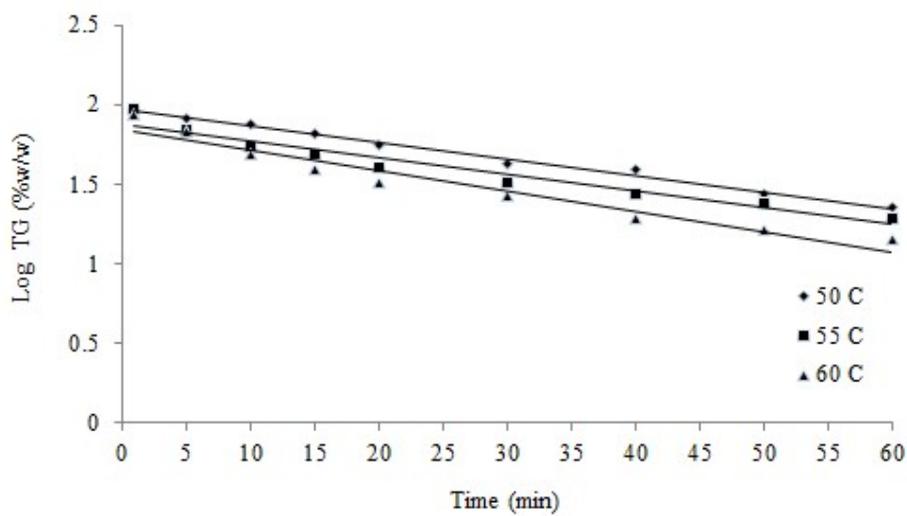


Figure 2. First order kinetics model for transesterification of *Pangium edule reinw*-based oil

The determination of reaction rate constant also depends on the reaction order. Employing experimental data, the correct order would be determined by which function of rate equation best fit the linear requirement. Once the order of reaction was established, the reaction rate constants were estimated from the slope of the linear plot. Based on the overall transesterification reaction scheme as showed in Figure 1, the rate of reaction at any time is given by the equation (4).

$$r = -\frac{d[TG]}{dt} = k[TG] \quad (4)$$

where k , r and t denote the overall reaction rate constant, rate of reaction and time of reaction. However, in this study, the transesterification of *Pangium edule reinw*-based oil with methanol in the presence of potassium hydroxide as catalyst was occurred very rapidly. Therefore, in this work, the negligible of intermediate reactions need to be considered. This phenomenon was proved from the GC chromatograms. In addition, the use of excess methanol will minimize the rate of backward reaction.

The best kinetics model for this study appears to be a first order model for the initial stages of the transesterification as shown in Figure 2. In order to test these experimental data, a model was developed based on the kinetics of alcoholysis TG. As prior discussion, it defined the mathematical model for this reaction by ignoring the intermediate reaction of MG. The first order rate is assumed as a function of the concentration of triglycerides. The reaction rate constant can be estimated based on the decreased amount of the limiting reactant in certain reaction interval time. In this study, TG are chosen as the decreased amount of limiting reactant. Therefore, the reaction rate constant can be given by equation (8).

$$-\int_{TG_0}^{TG} \frac{d[TG]}{[TG]} = k \int_0^t dt \quad (5)$$

$$-\ln[TG]_{TG_0}^{TG} = k[t]_0^t \quad (6)$$

$$k = \frac{1}{t} \ln \frac{[TG_0]}{[TG]} \quad (7)$$

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

$$k = \frac{2.303}{t} \log_{10} \left(\frac{[TG_0]}{[TG]} \right) \quad (8)$$

where TG_0 is the initial concentration of TG. For the alcoholysis of TG, a plot of reaction time (t) versus $\log(TG_0/TG)$ should be a straight line if the first order model as equation (9) is valid. Figure 2 shows such plots at temperatures (50, 55, and 60) °C. The slope is $2.303/k$ with the units of min^{-1} . The values of reaction rate constant for TG (k_{TG}) and its corresponding correlation coefficient are shown in Table 1. Thus, other researchers stated that the values of k increased when the temperature was escalated (Om Tapaneset *al.*, 2008). However, if the data is plotted in the second order model, the graph doesn't form a straight line. Therefore, the reaction doesn't match that for second order model. A similar calculation method is applied for determining the rate constant for DG as tabulated in Table 2.

The rates of reaction are very sensitive to change in temperature. It is normally necessary to carry out kinetics experiments in a vessel maintained in a thermostatically controlled bath the temperature. Also, according to other researchers, reaction rates constant almost always increase with temperature for elementary irreversible reactions. Multiple and reversible reactions occasionally exhibit an optimal temperature with respect to the yield of a desired product (Noureddini and Zhu, 1997). Thus, indirectly, these findings prove that our assumption of irreversible reaction is valid since the rate increases with temperatures. Rate constants for the first two reactions increase with temperature for the forward reactions. The kinetics study on rates of reaction for MG could not be performed because it occurs so fast that MG could not be detected on GC chromatogram.

Table 1. Reaction rate constant (k_{TG}) for intermediate reaction of *Pangium edule reinw*-based TG

Temperature (°C)	k_{TG} (min) ⁻¹
50	0.23
55	0.25
60	0.27

Table 2. Reaction rate constant (k_{DG}) for intermediate reaction of *Pangium edule reinw*-based DG

Temperature (°C)	k_{DG} (min) ⁻¹
50	0.15
55	0.16
60	0.18

Determination of Activation Energy.

The dependency of reaction rate constant (k) on temperature follows the Arrhenius equation as shown in equation (9)

$$\log_{10} k = (-E^\ddagger/2.303RT) + \log_{10} A \quad (9)$$

where T is expressed in °K and R is the universal gas constant. The activation energy (E^\ddagger) was estimated from the slope of a plot of $\log_{10} k$ versus $1/T$. In this term, k is equal to k_{TG} and k_{DG} . The frequency factor, A was determined from the y-intercept. The plot is shown in Figure 3 for *Pangium edule reinw* methyl esters synthesis at 50–60 °C. These data were used to determine the Arrhenius energy of activation. The activation energy for the transesterification reaction are comparable with other study as shown in Table 3.

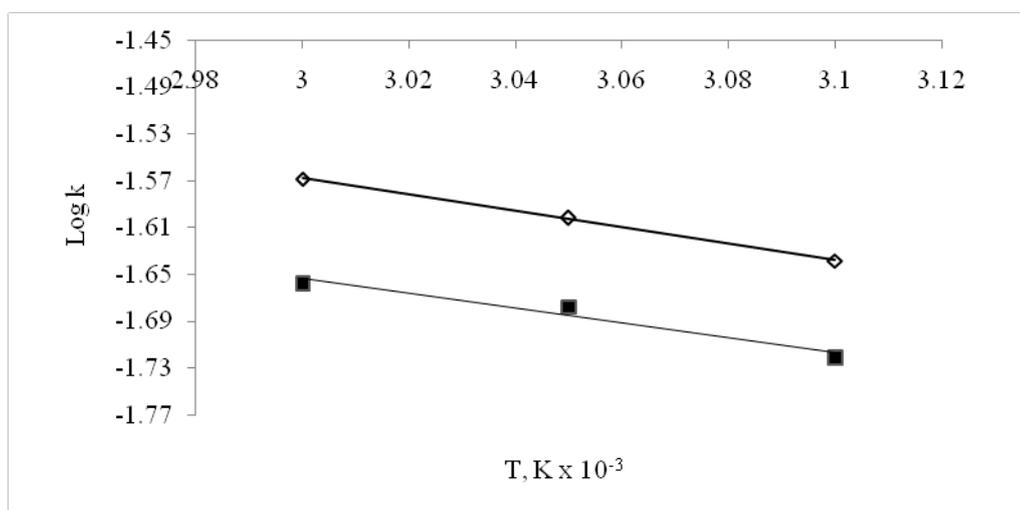


Figure 3. Arrhenius plot showing the temperature dependency of reaction rate constants

Activation energy which was determined for each step of the reaction mechanism, not considering the pre-step is common for all of the reactions. According to Syam *et al.*, (2009), 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 tetrahedral intermediate as the main product. In the next step, the tetrahedral intermediate dissociates via a second transition state with larger activation energy leads to the methyl esters and the glycerol. This phenomenon was considered that the break of the tetrahedral intermediate to form the final product may play a key role in the base-catalyzed transesterification of TG. Furthermore, Nouredini and Zhu, (1997) reported that normally, with multiple reactions, a high temperature favors the reaction of higher activation energy, and a low temperature favors the reaction of lower activation energy. In this study, the experimental data is comparable to other similar work.

Table 3. Activation energy for transesterification of *Pangium edule reinw*-based oil

Step-wise reaction	$E^{\ddagger}(\text{kJmol}^{-1})$	$E^{\ddagger}(\text{kJ mol}^{-1})^a$
TG → DG	19.48	27.38
DG → ME	45.63	46.72

^a Yunus and Syam, (2011).

Characterization of *Pangium Edule Reinw Methyl Esters*.

Since *Pangium edule reinw* methyl esters (biodiesel) as fuel for the diesel engine application, it should fulfil the standard quality of International specifications. In this study, some physicochemical properties of *Pangium edule reinw* methyl esters such as density, viscosity, iodine value, acid number, pour point, cloud point, flash point, and moisture content are analyzed using ASTM method as shown in Table 4. All physicochemical properties comply with the values of standards specification.

Table 4. Physicochemical Properties of *Pangium edule reinw* methyl esters (ASTM D 6751)

Parameters	Unit	Method	Values	Limitation
Density (15°C)	kg/m ³	ASTM D 40	865	–
Kinematic viscosity (40°C)	mm ² /s	ASTM D 445	5.43	6.0 (max)
Moisture content	% volume	ASTM D 95–05	0.008	0.05 (max)
Iodine value	–	PORIM	92	–
Pour point	°C	ASTM D 97	–2	–
Cloud Point	°C	ASTM D 2500	5	–
Flash point	°C	ASTM D 93	143	130 (min)
Acid number	mg KOH/g oil	ASTM D 974	0.75	0.80 (max)

Conclusions

The kinetics of transesterification of *Pangium edule reinw*-based oil and methanol to methyl esters was investigated. The mechanism of reaction is believed to occur via two step-wise irreversible elementary reactions to form intermediates and final product of methyl esters. However, the first reaction is too fast and doesn't control the reaction. The conversion of TG and DG into methyl esters appeared to be first order up to 60 min of reaction time. The rate constants for the formation of intermediate DG and the final product of methyl esters were determined at various temperatures. The values of k_{TG} ranges from 0.23 to 0.27 and the values of k_{DG} are from 0.15 to 0.18, respectively. The activation energy for step-wise reaction in transesterification of *Pangium edule reinw*-based TG and DG with alcohol is 19.48 and 45.63 kJmol⁻¹. The whole physicochemical properties of *Pangium edule reinw* biodiesel meet the diesel engine specification.

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