

Methanolysis of Mixed Crop Oils (*Hevea brasiliensis* and *Jatropha curcas* L.) into Biodiesel: Kinetics Study

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Abstract

In this study, the methanolysis of mixed crop oils (*Hevea brasiliensis* and *Jatropha curcas* L.) was investigated. Due to the oils contain high impurities, a particular pre-treatment of which was carried out. For alkali-catalyzed methanolysis, few parameters (such as: molar ratio, catalyst percentage, and reaction time) were studied. The results showed that the methanolysis optimum conditions were 5.5 of molar ratio, 0.9% w/w of catalyst, and 60 minutes of reaction time with the highest yield of 98.9%. The kinetics study indicated that first order reaction mechanism with reaction rate constant and activation energy were $1.5 \times 10^{-2} \text{ minute}^{-1}$ and $23.93 \text{ KJ} \cdot \text{mol}^{-1}$ respectively. As fuel, the physicochemical properties of biodiesel met the standard values required by ASTM D6751.

Keywords

Biodiesel, Methanolysis, *Hevea brasiliensis*, *Jatropha curcas* L.

1. Introduction

The reliance scenario of modern civilization and transport system on the non-renewable fuels changes periodically. It is due to various efforts by various parties in searching for new resources of environmental-friendly fuel. The critical threats to the environment and energy security of the world resulted from the rapidly growing demand for transport fuel and industrialization [1]. Owen *et al.* [2] reported that only 50% of the usual energy demand can be supplied until ten years forward with current liquid fuel reserve. On the other hand, the current global fuel utilization increased significantly compared to 1990s. Decline of

available oil reserves and more stringent environmental regulations have generated interest in discovering alternative energy sources among researchers [3] [4].

Non edible crop oils are suitable feedstock for biodiesel production since they are not competitive with the food supply chain. Some countries, such as USA have used edible oils from soybean and corn oils as fuel feedstock; Europe has been utilizing rapeseed oil, while Indonesia and Malaysia are using palm oil. It is due to the reason that these countries produced a huge quantity of those edible oils. However, the biodiesel has not yet been more competitive to those from fossil fuel since the current production of biodiesel is not more economical than that of fossil based diesel, which appears to be the primary hindrance in preventing from its more widespread application. Besides, the current global production of crop oil and fat is not sufficient to replace liquid petroleum derived fuel use [5]. Therefore, blending between crop oils with petroleum based diesel is required to solve the lack of fuel sources as well as from green feedstock or fossil based raw material.

Biodiesel is produced by two steps of methanolysis process, in which the methyl group of an ester is replaced through interaction between the triacylglycerol of oil or fat with methanol. The transformation of crop triglycerides into methyl ester (ME) occurs in the presence of a catalyst. The catalyst can be an alkali, acid or enzyme, and its type depends on the properties of feedstock and conditions of the reaction [6] [7].

Darnoko and Cheryan [8] revealed that the study on the methanolysis kinetics provides the parameters that can be utilized to predict the extent to which the reaction has occurred at any time under certain operating conditions. The mechanism of reaction was postulated to occur via three steps irreversible elementary reaction involving glycerides compounds to form intermediates and the final product, methyl ester and glycerol [9].

The objective of this experimental work is to produce biodiesel from the mixed non edible oils (*Hevea brasiliensis* and *Jatropha curcas* L.). The kinetics study on the methanolysis is conducted to determine the reaction order, reaction rate constant and activation energy. The physical and chemical properties of biodiesel should be analyzed prior to be applied into a diesel engine. As reported by Morón-Villarreyes *et al.* [10], some characteristics of biodiesel were analyzed according to ASTM D6751. Through this mixed crop oils based biodiesel production; the qualities of biodiesel were able to be escalated to meet the requirement of diesel engine application.

2. Material and Methods

The *Hevea brasiliensis* and *Jatropha curcas* L. oils were produced from the seeds extracted that was collected from local estates. Methanol, potassium hydroxide, sulphuric acid, phenolphthalein, iso propil alcohol, sodium hydroxide solution (0.1N) and phosphoric acid were purchased from the supplier. Three neck flat bottom flask (500 ml) was used as the acid pre-treatment and methanolysis

reactor. Hot plate with magnetic stirrer, graham condenser, and other related glass wares were utilized in this process.

The initial free fatty acid (FFA) content of the mixed crop oils was 22.6% w/w. The mixing of crop oils was carried out by 50% of its volume. Under this high FFA patronage, the mixed crop oils had to be treated via acid pre-treatment process to reduce the FFA level up to less than 1.0% w/w as pre-requisite of alkali catalyzed methanolysis feedstock.

The treated of mixed crop oils was reacted under various specified parameters such as molar ratio (5 - 6), percentage of catalyst (0.8 - 1.0)% w/w, and time of reaction (40 - 60) minutes. The whole reaction processes were undertaken at the fixed temperature of 60°C. The schematic of biodiesel production process is as indicated in **Figure 1**.

In order to identify the hydrocarbon compounds and analysis of the kinetics data. Gas chromatography analysis was performed using capillary column Rtx-5MS 30 m × 0.25 mm ID, 0.25 µm with helium at 137.7 ml/minute as a carrier gas and 1:100 of split ratio.

The entire physical and chemical properties (such as: density, kinematic viscosity, flash point, saponification number, acid value, iodine value, calorific value, moisture content, and pour point) analysis were carried out using ASTM D6751 [7].

3. Results and Discussion

The production of ME compound from the treated mixture crop oils of *Hevea brasiliensis* and *Jatropha curcas L.* was conducted under methanolysis process by varying some affecting parameters such as molar ratio of non-edible triglycerides to methanol, percentage of catalyst loading, and time of reaction. Based on the stoichiometry of reaction, one mole of triglycerides requires three moles of methanol to produce three moles of ME and one mole of glycerol as shown in **Scheme 1**. In this study, the molar ratio of triglycerides to methanol was selected from 5 to 6 as shown in **Figure 2**. The excess methanol was required to force the reaction to the production side. Meanwhile, the percentage of catalyst loading, from 0.8 to 1.0% w/w was selected. **Figure 2** indicates that the yield of ME at various concentration of catalyst diverged significantly, in particular from 0.8% w/w to 0.9% w/w of catalyst loading.

Although, the methanolysis reaction continued further by increasing the catalyst concentration up to 1.0% w/w, it did not show a particular change on the yield of ME, even at the highest molar ratio of triglycerides to methanol was utilized. In contrast, at lower catalyst loading (0.8% w/w) and molar ratio of triglycerides to methanol (5:1), the methanolysis reaction was slightly slower indicated by lower production of ME compound (94.6%).

In **Scheme 1**, A is triglycerides, B is methanol, C is ME and D is glycerol.

Nevertheless, in this experimental work, the highest yield of ME compound obtained was 98.9% under the optimal process condition such as molar ratio of triglycerides to methanol (5.5), and percentage of catalyst loading (0.9% w/w).

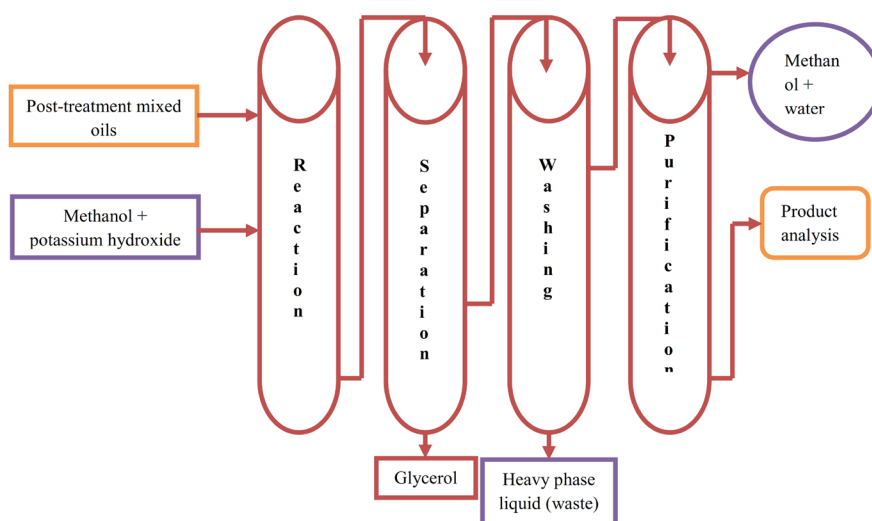
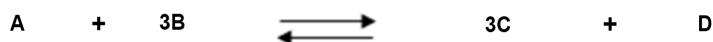


Figure 1. Schematic of biodiesel production process.



Scheme 1. Overall schematic reaction of methanolysis process.

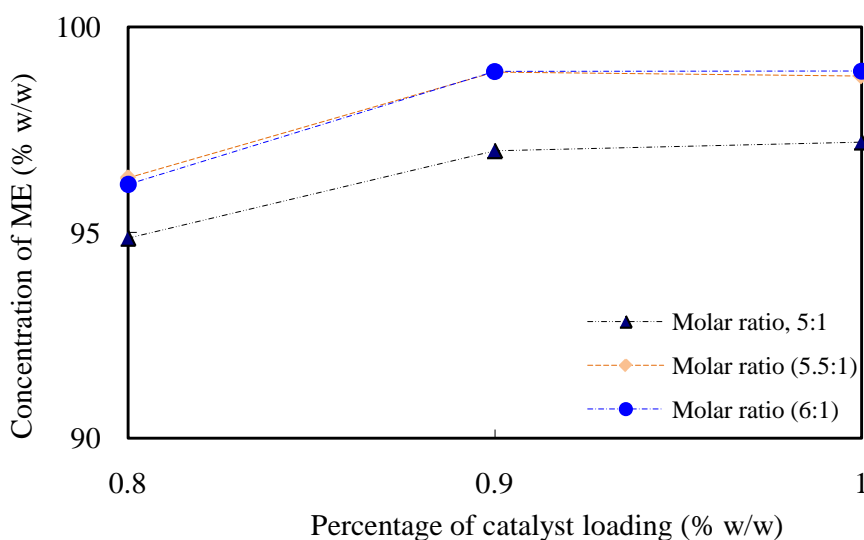


Figure 2. Effect of percentage of catalyst loading on concentration of production of product at various molar ratio.

Figure 3 shows the effect of reaction time on the percentage of ME product at various molar ratio. It can be seen that the rate of methanolysis reaction highly depends on the reaction time. At the first few minutes of reaction time, the reaction was slow due to the mixing and dispersion of the excess reactant with the limited reactant. At shorter reaction time, the percentage of ME compound obtained was also less. Overall, the maximum of ME product yield was obtained at longer reaction time. The similar study reported that the maximum yield of ME compound obtained was 99% at 60 minutes of reaction time, 6:1 of molar ratio

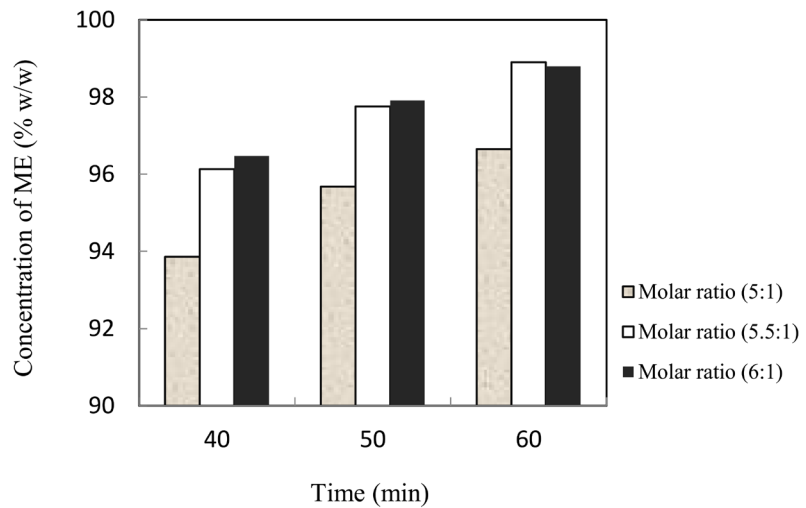


Figure 3. Effect of reaction time on percentage of product at various molar ratio.

and 65°C of reaction temperature [11]. Therefore, the rate of ME conversion is obviously affected by the reaction time.

3.1. Kinetics of Methanolysis

In this experimental work, the kinetics of methanolysis reaction involving the mixed crop oil was developed by determining the reaction order, reaction rate constant (k) and Arrhenius activation energy. The reaction order was determined by plotting the experimental data on certain curve of reaction order which was derived from the mathematical equation. The value of k was determined based on the increased amount of the product that occurred in some reaction time intervals or alternatively based on the decreased amount of the limiting reactant [9]. Equation (1) represents the correlation of k with reaction order which is based on the increase of reaction product.

$$\text{rate} = dC_{ME}/dt = k[C_{ME}]^n \quad (1)$$

Figure 4 shows that the experimental data plotted on the first order curve. The correct reaction order would be determined using experimental data in which the rate equation best fitted the linear requirement. Once the reaction order was established through plotting the data, thus, the slope of the linear plot could be used to estimate the k by a simple calculation. In this study, the increase of ME product was selected as the function of k as indicated by Equation (2) to (5).

$$\int_{ME_0}^{ME} \frac{dC_{ME}}{[C_{ME}]} = k \int_0^t dt \quad (2)$$

$$\ln[C_{ME}]_{ME_0}^{ME} = k[t]_0^t \quad (3)$$

$$k = \frac{1}{t} \ln \frac{C_{ME}}{C_{ME_0}} \quad (4)$$

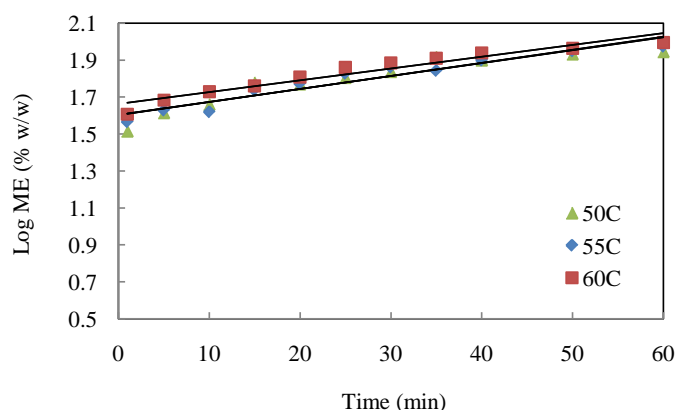


Figure 4. First order kinetics model for mixed crop oils methanolysis at various reaction temperatures.

$$k = \frac{2.303}{t} \log_{10} \left(\frac{C_{ME}}{C_{ME_0}} \right) \quad (5)$$

The value of k for all reaction temperatures are shown in **Table 1**.

The methanolysis reaction of mixed crop oil with methanol was highly affected by the reaction temperatures. This phenomenon was indicated by the increase of k , when the reaction temperature was escalated as shown in **Table 1**. The similar work reported that the increase of k resulted from the elevated reaction temperature. It proved that the k significantly depends on the quantity of heat adsorbed [9].

3.2. Determination of Activation Energy

The Arrhenius activation energy is one of factors that affect the steps of methanolysis reaction as postulated theoretically. Furthermore, the activation energy can be applied in explanation of the reaction scenario as reported by some researchers [12]. They stated that in the first step, reaction passes through an initial complex and after a transition state with low activation energy, it 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 ME and the glycerol. This phenomenon is considered that the tetrahedral intermediate breaks down to form the final product which may play a key role in the methanolysis reaction. **Figure 5** shows the Arrhenius plot between k and reaction temperatures.

In this study, the Arrhenius activation energy of methanolysis process between mixed crop and methanol is calculated based on the **Figure 5**, the results are shown in **Table 2**. The Arrhenius activation energy in this experimental work is comparable to the other similar study as indicated in **Table 2**.

3.3. Characterization of Biodiesel

In order to be used for engine application purpose, the physical and chemical properties of mixed crop oil based biodiesel such as density, kinematic viscosity,

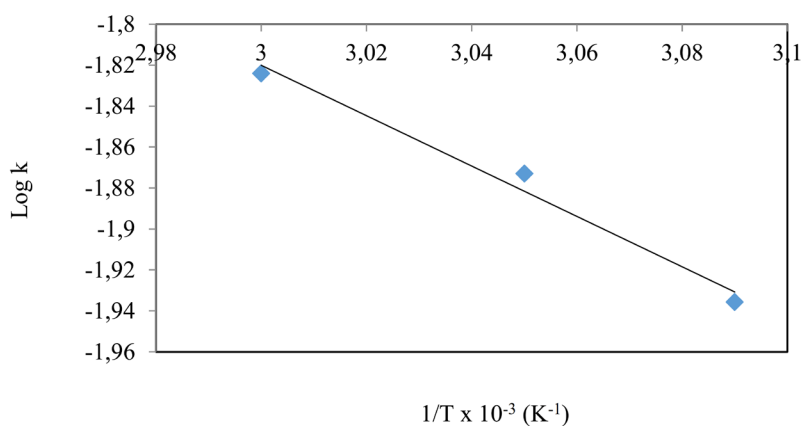
Table 1. Value of k for methanolysis of mixed crop oil.

	Temperature ($^{\circ}\text{C}$)		
	50	55	60
$k, \text{min}^{-1} \times 10^{-2}$	1.16	1.34	1.50
R^2	0.86	0.92	0.93

Table 2. Arrhenius activation energy.

	Activation Energy ($\text{kJ}\cdot\text{mol}^{-1}$)
This study	23.93
Other work	27.38 ^[e]

^e: [9].

**Figure 5.** Arrhenius plot showing the temperature dependency of rate constants.

flash point, saponification number, acid value, iodine value, calorific value, moisture content, and pour point had to be analyzed. The analysis on the characteristics of the biodiesel is shown in **Table 3**. All properties of this biodiesel are compared to other non-edible oils based biodiesel. It can be concluded that through a mixing of these crop oils, it produced biodiesel which has a lower pour point than that of other two non-edible oils based biodiesel. Yet, other properties do not show any significant difference compared to both *Jatropha curcas L.* biodiesel (JC-Bio) and *Hevea brasiliensis* (HB-Bio) properties (**Table 3**).

4. Conclusion

The production of mixed crop oil based biodiesel was carried out under optimum operation condition such as molar ratio of 5.5:1, percentage of catalyst loading of 0.9% w/w, and reaction time of 60 minutes with maximum yield of biodiesel obtained was 98.9%. The kinetics study of methanolysis of mixed crop oil showed that the reaction followed first reaction order, the value of k between 1.16×10^{-2} to $1.5 \times 10^{-2} \text{ minute}^{-1}$. The reaction took place under irreversible

Table 3. Physical and chemical properties of mixed crop oil based biodiesel.

Parameter	Unit	Types of Biodiesel		
		M-Bio	JC-Bio	HB-Bio
Density	kg/m ³	869	866 [13]	881 [17]
Kinematic Viscosity	mm ² /s	4.68	4.33 [13]	5.81 [15]
Flash Point	°C	120	73 [13]	130 [15]
Saponification Number	-	188	185.7 [14]	192 [16]
Acid Value	mgKOH/g oil	0.452	0.738 [13]	0.118 [15]
Iodine Value	g Iodine/100 g	102	99 [13]	132 [16]
Calorific Value	MJ/kg	37	38.72 [13]	36.50 [15]
Moisture Content	%	0.007	0.004 [13]	0.08 [16]
Pour Point	°C	-14	-10 [13]	-8 [15]

mode with Arrhenius activation energy was about 23.93 kJmol⁻¹. The physical and chemical properties of mixed crop oil based biodiesel were compared to other non-edible based biodiesel (JC-Bio and HB-Bio) and from this comparison, the properties of biodiesel meet the specification of standard biodiesel. However, this experimental work produced biodiesel which has lower pour point than that of both JC-Bio and HB-Bio.

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