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KINETICS OF BIODIESEL PRODUCTION FROM WASTE COOKING OIL THROUGH MICROWAVE-ASSISTED TRANSESTRIFICATION REACTION

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ABSTRACT

Kinetics parameter is required to determine the production of biodiesel in certain circumstances. This study aims at determining the kinetics parameters of biodiesel production through transesterification assisted by microwaves. This research was conducted using used cooking oil derived from street vendors of fried around the University of Lampung. The chemicals used are methanol (technical) and NaOH (pa). The study was conducted with a molar ratio of 1: 4 and with a combination of three levels of temperature (45°C, 50°C and 55°C) and a five-level of reaction time (2 minutes, 3 minutes, 4 minutes, and 5 minutes). Results showed that the highest biodiesel yield amounted to 66.8% at the time of 6 minutes and a temperature of 55°C. The result of the calculation produces the value of the reaction rate constant (k), which increases with temperature, ie. 0.0609 per minute at a temperature of 45°C, 0.047 per minute at 50°C, and 0.0291 per minute at 55°C. The calculation resulted that the value of activation energy (E_a) of 63.94 kJ/mol with a value for the collision frequency constant (A) was 8.38(10^9) per second.

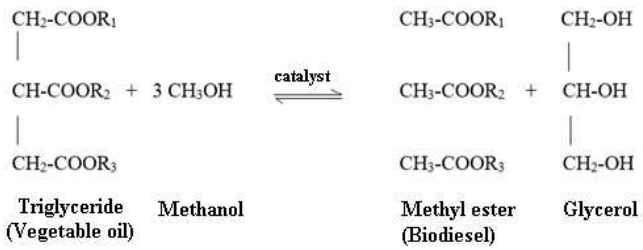
Keywords : biodiesel, microwaves, waste cooking oil, yield, reaction rate, activation energy.

I. INTRODUCTION

Fulfillment of energy derived from petroleum has received a very serious attention. Not only because of the greenhouse effect resulting from CO2 emissions it produces, but also because of the world's petroleum reserves are getting limited. The depletion of petroleum reserves is marked by the surge of crude oil prices in the world market [1]. This situation has caused researchers and the government think hard in preventing energy scarcity. One effort to reduce the need for transportation fuels is to create alternative fuels, such as biodiesel and bioethanol and look for other sources of renewable energy. Biodiesel is one type of fuel produced from vegetable oil or animal fat through a process called transesterification with the help of alcohol and catalyst [2].

Indonesia is one of the tropical countries that has various types of biodiesel raw materials, including palm oil, waste frying oil, rubber seed oil, jatropha curcas, and so on. Biodiesel production potential from palm oil reached 438,876 thousand barrels, cooking oil 45,515 thousand barrels, and rubber seed oil 3,989.7 thousand barrels. Using biodiesel for supplement Indonesia will be able to overcome the energy crisis until the year 2101 [3.

Biodiesel is generally made through a transesterification reaction using an alkaline catalyst. This reaction is faster to form methyl esters (biodiesel) than the esterification reaction using acid catalyst [1, 4]. In addition to biodiesel, the reaction will also produce a by-product of glycerine [5]. This by-product can be utilized for other purposes, such as cosmetic ingredients, soap and others [6]. According to Hikmah and Zuliyan [7] the transesterification reaction of triglycerides to methyl esters can be presented as follows:



Temperature is an important parameter in the reaction. However, heat transfer in the conventional transesterification reaction is slow due to convection and conduction. The microwave applications can accelerate the heat transfer process because microwaves can propagate through the liquid so that the heating process will take place more effectively and the biodiesel process can be done in a shorter time [8]. The use of microwaves in biodiesel production can convert waste frying oil into biodiesel faster, when compared to conventional methods [9].

The reaction kinetic analyses the rate of chemical reaction. Reaction rate is the change of reactant or product concentration over a unit of time. Kinetics of transesterification reactions are required to predict the reaction results at a given time and condition. The purpose of this study is to determine the effect of temperature and reaction time in biodiesel production and to determine kinetic parameters for transesterification of used cooking oil assisted by microwaves.

II. MATERIALS AND METHODS

A. Materials and Equipment

Materials used in this experiment include waste frying oil (WFO), methanol (technical grade), NaOH (p.a), and aquades. Waste oil is obtained from fried stuffs traders around the University of Lampung. The WFO is filtered using a tea strainer to separate solid particles. Characteristic of WFO and biodiesel to determine the acid number, free fatty acid content, and fatty acid composition is conducted in the Lab. of Agricultural Product Processing, Faculty of Agriculture, University of Lampung. The tools used in this research are microwave oven, spatula, burette, analytical balance, pycnometer glass for mass type analysis, condenser, small mixer with 300 rpm for stirring, Erlenmeyer, beaker glass, thermometer, rubber bulb, spatula, falling ball viscometer to measure the viscosity of the resulted biodiesel.

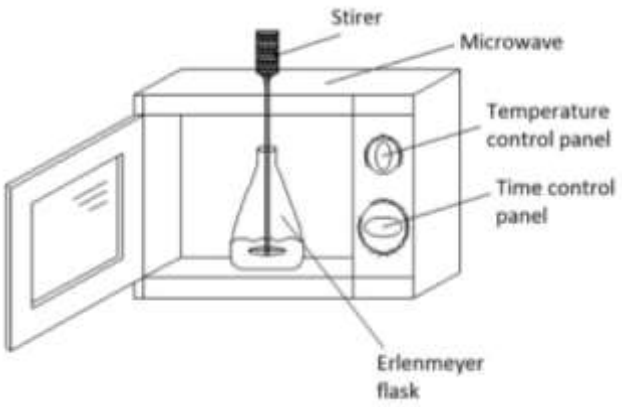


Fig. 1 Biodiesel processing with the aid of microwave.

B. Experimental Design

The treatments in this research are temperature variation and duration of heating. Each consists of three levels for temperature (45, 50, and 55°C) and five for duration (2, 3, 4, and 5 min). The process of biodiesel synthesis with the help of microwave is shown in Fig. 1. The transesterification reaction uses a molar ratio between WFO and methanol of 1: 4. The process of biodiesel production begins with the preparation of a methoxide solution by mixing 0.5 g NaOH into 18 ml of methanol and stir it until all NaOH particles dissolve. This solution is then poured into a 500 ml Erlenmeyer flask that has been filled with 100 ml of cooking oil. The flask is then fed into the microwave in the very middle position. The microwave is turned on for a pre-setting time and the power intensity is adjusted to achieve the desired reaction temperature. At the same time the mini mixer is turned on to stir the WFO.

The reaction result is allowed for 24 hours to rest. Biodiesel is separated from glycerol and washed several times until it is clean (marked by clean wastewater). The yield of biodiesel is calculated using the following equation:

$$\text{Yield} = \frac{\text{Mass of biodisel after washing (g)}}{\text{Mass of WFO (g)}} \times 100\% \quad (1)$$

C. Analysis

Kinetics of transesterification reaction refer to Kusdiana and Saka [10]. In this case, transesterification is considered to be a first order reaction and is a function of non-biodiesel concentration (uME) and reaction

temperature. The uME components include triglycerides, diglycerides, mono-glycerides, and unreacted free fatty acids (FFA). The reaction rate is expressed as:

$$\text{Rate} = -\frac{d[uME]}{dt} \tag{2}$$

$$-\frac{d[uME]}{dt} = k\,[uME] \tag{3}$$

At a time $t = 0$ uME concentration is [uME$_0$] and at $t = t$ is [uME$_t$], where [uME$_o$] > [uME$_t$]. Integration of Eq. (2) from uME$_0$ to uME$_t$ and $t = 0$ to $t = t$ produces:

$$-\int_{uME_0}^{uME_t} \frac{d[uME]}{[uME]} = k\int_0^t dt \tag{4}$$

$$-\ln\left(\frac{[uME_t]}{[uME_0]}\right) = kt \tag{5}$$

Assuming that before a reaction occurs, biodiesel component in the WFO can be neglected, it follows that:

$$\frac{[uME_t]}{[uME_0]} = 1 - \text{Yield} \tag{6}$$

The plot of Eq. (5) with t as abscissa and the negative value of natural logarithm of [uME$_o$]/[uME$_t$] as an ordinate can be used to determine the value of the reaction rate constant k at a certain temperature. Values of this constant at different temperatures are then used to determine the value of the global activation energy (E_a) of the transesterification reaction using the Arrhenius equation:

$$k = A\exp(-E_a/RT) \tag{7}$$

or

$$\ln(k) = \ln(A) - (E_a/\text{R})\left(\frac{1}{T}\right) \tag{8}$$

where A is constant for molecular collision frequency, R is ideal gas constant (8.314472 J/mol.K), and T is the absolute temperature.

III. RESULTS AND DISCUSSION

A. WFO Characteristics

Table 1 shows the characteristics of used cooking oil used in this study. It is seen that the cooking oil is quite viscous with high viscosity (61.75 cSt). But the cooking oil has free fatty acid content or FFA (free fatty acids) is quite low (1.43%), so the process of making biodiesel can be performed through direct transesterification reaction.

Table 1. Font sizes for papers characteristics of used cooking oil used in this study

Parameter	Value
Density (g/ml)	0.912
Viskosity (cSt) 30°C	61.75
FFA (%)	1.43
Acid number	0.7199
Fatty acids:	
Methyl Laurate	0.75
Methyl Myristate	1.58
Methyl Palmitate	42.84
Methyl Linoleat	12.43
Methyl Oleat	35.71
Methyl Stearat	5.15
Unknown	1.54

B. Biodiesel Yield

Table 2 shows the yield of biodiesel resulting from a combination of treating the temperature and duration of the reaction. The resulting biodiesel has a density of between 0.86 - 0.87 g/ml (according to SNI), and viscosity 3,79 - 5,53 cSt (according to SNI). The results showed that the higher the temperature of the higher the biodiesel yield produced. Likewise, the longer the reaction time the higher the yield of biodiesel. The highest yield was produced at 55°C and 6 minutes (66.77%). This non-optimum yield is due to several factors, such as the quality of methanol and NaOH, and the molar ratio used.

Table 2. The yield of biodiesel

T (°C)	Time (Min)	Yield (%)	$-\ln\frac{[uME_t]}{[uME_0]} = -\ln(1-\text{Yield})$
45	2	33.44	0.41
	3	33.45	0.45
	4	38.15	0.51
	5	47.78	0.59
50	2	38.29	0.40
	3	42.84	0.50
	4	44.95	0.53
	5	47.84	0.55
55	2	34.40	0.42
	3	35.33	0.44
	4	36.34	0.46
	5	45.65	0.51

Based on the theory the longer the reaction time, the possibility of contact between substances the greater so that will result in a large conversion [11]. Biodiesel yield is also influenced by the ratio of triglycerides to methanol and oven power intensity. Majid [12] found the ratio of triglyceride concentration to methanol which resulted in optimum biodiesel conversion was 1: 6. They also report initially that biodiesel yields will increase with greater power and heating time, but when optimum heating power and time has been reached, the biodiesel yields will decrease.

C. Reaction Rate (k)

Based on the data in Table 2, the rate constant of the reaction can be calculated by making the plot as given in Fig. 2, where the rate constants constant is a linear line gradient. The results show that the higher the reaction temperature the reaction rate constant will increase. This happens because with the higher reaction temperature, the reaction rate is also increasing [13]. Salamah [14] states that the higher the temperature, the movement rate of each molecule will be faster, so that the frequency of collisions between molecules will be faster, so that the frequency of collisions between molecules will increase and the reaction becomes faster. The relation data between reaction temperature and reaction rate constant are shown in Table 3.

Table 3. Relation of temperature and reaction rate constant

Temperature T (°C)	1/T (K^{-1})	K ($minute^{-1}$)	ln *k*
45	0.003143	0.059	-2.83
50	0.003095	0.094	-2.36
55	0.003047	0.096	-2.34

D. Activation Energy

The activation energy can show how easy or difficult the reaction is, in theory if a reaction has a smaller activation energy will tend to react more quickly and easily than a reaction with a larger activation energy that tends to react more difficult and longer [15]. The greater the value of the reaction rate constant, the reaction will take place quickly. The faster a reaction allows for large collisions of particle with a relatively short time and lower energy levels so that the balance will be achieved at a faster time.

Based on Eq. (7) then the activation energy (Ea) can be obtained by plotting 1/T as the abscissa versus ln(k) as ordinate. In this case the slope of the linear line is the value of Ea/R. From Table 3, we can make a plot as given in Fig. 3 so it can be used to determine the value of each parameter on the proposed kinetic model. From Fig. 3, we get the following mathematical equations:

$$\ln k = 13.28 - 5101\left(\frac{1}{T}\right) \quad (9)$$

By substituting the above equation in the previous equation, the value of A = 8.38(10^9) s^{-1} and E_a is 63.94 kJ/mol. Therefore the resulting kinetic equation can be presented as:

$$k = 8.38(10^9)\ \exp(-63941/RT) \quad (10)$$

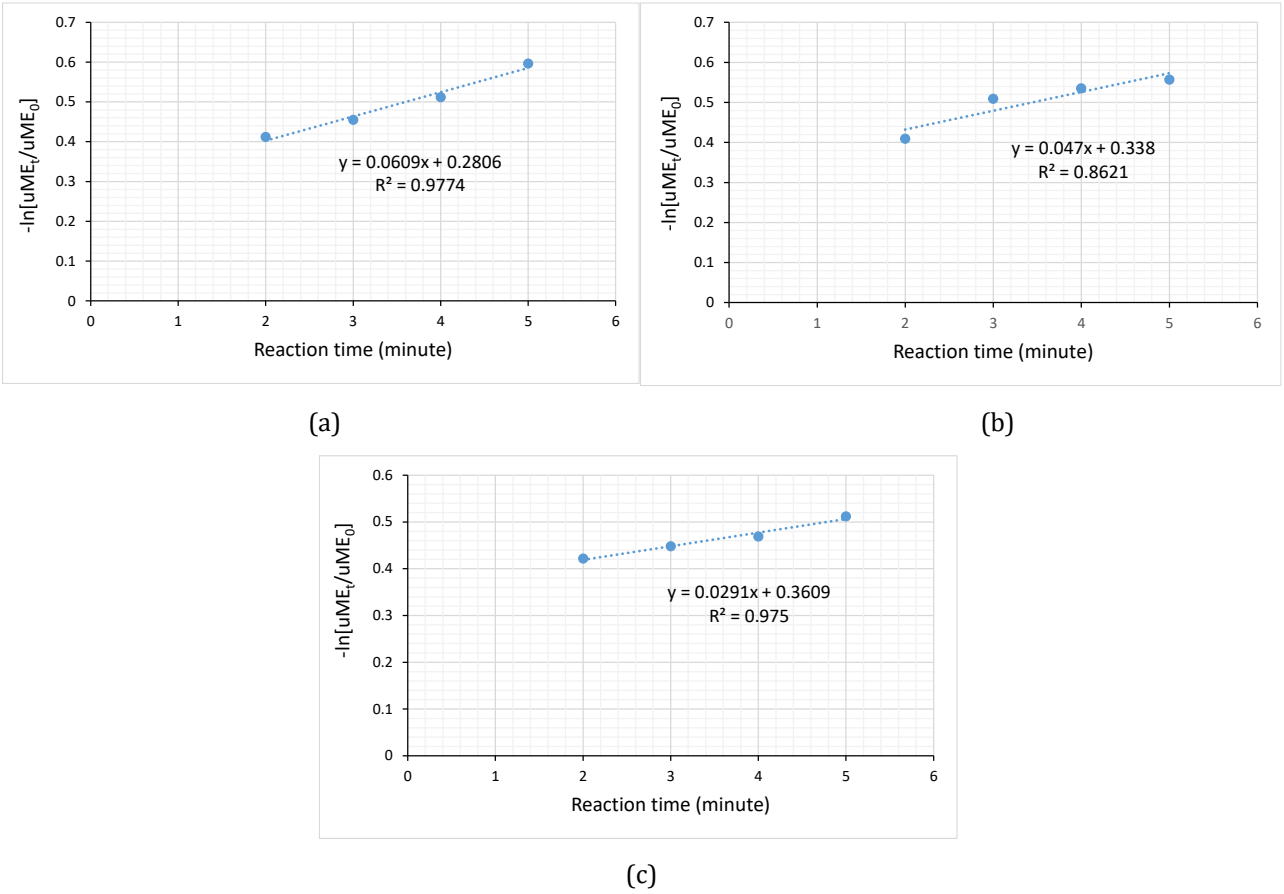


Fig. 2. Relationship of time and –ln[uME$_t$/uME$_0$] at reaction temperature of 45°C (a), 50°C (b) and 55°C (c).

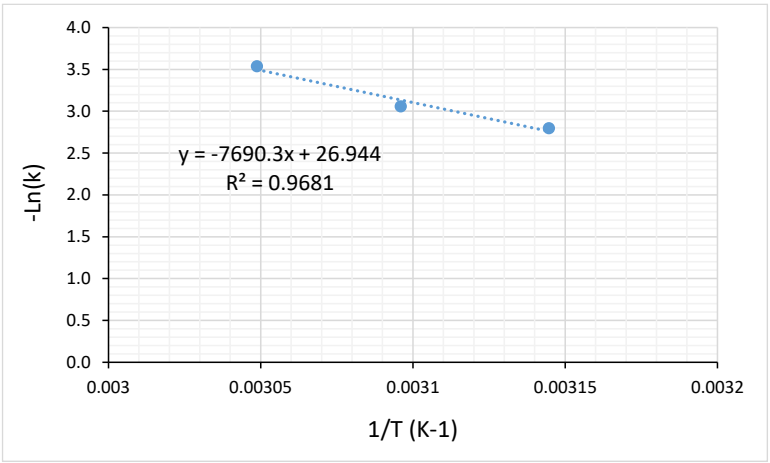


Fig. 3. Plot of 1/T and ln(k)

The activation energy obtained from this study is considerably high when compared to the activation energy of biodiesel production using different oils and heating systems as given in Table 4. This is probably because at the start of the reaction the oil is not preheated to the desired temperature, but starting from the lowest temperature (room temperature). Therefore, the reaction requires a large enough energy to start.

Table 4. Energy activation of biodiesel reactions

Feedstock	Reaction Condition	E_a (kJ/mol)	Reference
UCO	MR 1:4, t = 2-6 min, T 45-55°C, microwave aided	63.94	This work
Kapok seed oil	MR 1:3, t 60 -120 min, T 40, 70, 90°C, conventional.	10.39	[14]
Pongamia oil	MR 1:6, T, 30-70°C, conventional	41. 57	[18]
Cotton seed oil	MR 1:6, T 30 - 70°C, conventional	23. 69	[18]
Jatropha seed oil	MR 1:6, conventional, T 40-60°C	41.94	[16]
Jatropha seed oil	MR 1:9, T 100-140°C, t 120 min (interval 15 min)	17.54	[17]
Nyamplung seed oil	MR 1:6, T 29, 45, 60, 70°C t 0-30 min, conventional	16.25	[19]
Palm oil	MR 1:6, T 30, 40, 60 C, t 10-30 min, static mixing reactor	71.83	[20]

IV. CONCLUSION

The results showed that the yield of biodiesel ranged from 33.45 to 66.77%. The highest yield is at 55°C and reaction time is 6 minutes. The results showed that the higher the reaction temperature the greater the rate of the reaction rate constant (k). The k values were 0.0609, 0.047, and 0.0291 per minute, respectively obtained for temperatures of 45, 50 and 55°C. The value of activation energy (E_a) of transesterification reaction of used cooking oil with the help of microwave is 63.94 kJ/mol.

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