



TWO-STEP TRANSESTERIFICATION OF CALOPHYLLUM INOPHYLLUM OIL: OPTIMIZATION AND REACTION KINETICS

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ABSTRACT

Calophyllum inophyllum oil is a non-edible oil, which the plant is widely available in Indonesia, with a very high free fatty acid content of around 30% or acid value of $60 \text{ mg KOH}\cdot\text{g}^{-1}$. Two-step transesterification comprised hydrochloric acid-catalyzed esterification and sodium hydroxide-catalyzed transesterifications was conducted in batch processes. The first step esterification was carried out with molar ratio of methanol to oil of 35:1, hydrochloric acid concentration of 15 wt.%, and stirring speed of 500 rpm for 3 h reaction time at $60 \text{ }^\circ\text{C}$. This esterification reduced the acid value of Calophyllum inophyllum oil from $(59.97 \pm 2.71) \text{ mg KOH}\cdot\text{g}^{-1}$ to $(5.33 \pm 0.71) \text{ mg KOH}\cdot\text{g}^{-1}$. In second step transesterification, response surface methodology, a central composite design, was utilized to optimize reaction conditions which maximized biodiesel yield and minimized acid value. The optimum conditions included molar ratio of methanol to oil of 11.95, sodium hydroxide concentration of 1.26 wt.% for 1.52 h reaction time at $50 \text{ }^\circ\text{C}$ were established. At these optimum conditions, the maximum biodiesel yield of $(84.90 \pm 0.31) \%$ and minimum acid value of $(0.303 \pm 0.015) \text{ mg KOH}\cdot\text{g}^{-1}$ were achieved which were comparable with predicted values. The second step of transesterification was the second-order reaction with reaction rate constant of 0.047 to $0.180 \text{ (M}^{-1}\cdot\text{min}^{-1}\text{)}$ at 30 to $50 \text{ }^\circ\text{C}$. The activation energy of $54.53 \text{ kJ}\cdot\text{mol}^{-1}$ was obtained.

Keywords: Two-step transesterification, calophyllum inophyllum oil, biodiesel, free fatty acid content, central composite design.

INTRODUCTION

Recently, the world oil reserves are running low. Until the end of 2013, world oil reserves were recorded in the value of 1687.9 billion barrels. If there are no sources of new oil reserves, the oil will be consumed in just 53.3 years [1]. Nevertheless, until the end of 2014, petroleum was still the most dominant fuel used. Based on data collected by the International Energy Agency (IEA), 40.7% of world fuel consumption derived from petroleum [2]. This consumption is predicted increasing continuously in line with population growth and increasing the world income per capita [3].

In Indonesia, diesel fuel is the second most consumed petroleum fuel. In 2012, 37% petroleum consumption came from diesel fuel [4]. As other derived petroleum products, diesel fuel is a non-renewable fuel with the limited reserves. Hence, the alternative fuel source is required to substitute diesel fuel or to be mixed with it. Biodiesel is one of this alternative fuels.

Biodiesel is composed some fatty acid alkyl esters derived from vegetable oils or animal fats. Biodiesel has some advantages than petro-diesel, which are renewable fuel, biodegradable, non-toxic, lower greenhouse gas emissions, and higher flash point. The most selected method to produce biodiesel is transesterification, which is the reaction between triglyceride contained in vegetable oils or animal fats and short-chained alcohol in the presence of catalyst [5].

Nowadays, biodiesel is produced from edible oils which led higher cost in its production and vied as consumed food. Usage of non-edible oils could be the problem-solving to reduce the cost of biodiesel fuel and they are not consumed as foods. One of non-edible oils with large abundance in Indonesia is Calophyllum

inophyllum oil. This oil could be obtained by extracting oil from its seeds. Calophyllum inophyllum seeds have high oil content of 40 to 70% [6]. This oil content is higher than oil content in soybean, sunflower, and canola seeds. However, Calophyllum inophyllum oil has very high free fatty acid content which is able to disrupt transesterification with alkaline (base) catalyst, since saponification could take place to produce soap instead of biodiesel [5, 6]. To overcome high free fatty acid content, transesterification catalyzed with acid catalyst could be applied [7]. Another method to produce biodiesel from high free fatty acid content is two step transesterification which comprised of acid-catalyzed esterification as the first step and followed by alkaline-catalyzed transesterification as the second step [8, 9].

Some research works had been investigated to produce biodiesel from Calophyllum inophyllum oil with different free fatty acid contents and various catalyst types. The heterogeneous-catalyzed transesterification of Calophyllum inophyllum oil were reported by Arumugam and Ponnusami [10]. The maximum oil conversion of 96.82% was obtained with 16:1 molar ratio of methanol to oil, 3 wt.% catalyst concentration for 3 h at 80°C . Ong, *et al.* [11] used phosphate acid to remove gum in Calophyllum inophyllum oil with 29.65% free fatty acid content. This pre-treatment oil was esterified with sulfuric acid catalyst followed by transesterification with sodium hydroxide. These processes could reduce the free fatty acid content to be lower than 2% with high oil conversion of 98.92%. One step transesterification of 15% free fatty acid content Calophyllum inophyllum oil with heterogeneous sulphonated carbon catalyst during 5 h reaction time could convert oil to biodiesel with 99% purity [12]. Two step transesterifications of this oil has



been investigated using sulfuric acid [13, 14, 15] continued by transesterification with potassium hydroxide [13, 15] and sodium methoxide [14].

In this research work, two step transesterification was carried out using hydrochloric acid as acid catalyst in the first step, followed by sodium hydroxide – catalyzed transesterification as the second step. In the second step transesterification, response surface methodology, a central composite design, was utilized to optimize reaction conditions which maximized biodiesel yield and minimized acid value.

METHODOLOGY

ANOVA and regression analysis

In this experiment, the first step of esterification was conducted at constant of reaction variables. Meanwhile, in the second step, the transesterification tests were conducted according to a full 2^4 factorial design. In this design of experiment, there were four independent variables (factors) included molar ratio of methanol to oil (7:1 to 15:1), catalyst concentration of sodium hydroxide (1.0 wt.% to 2.0 wt.%), reaction temperature (40 °C to 60 °C), and reaction time (1 h to 2 h), while responses of biodiesel yield and acid value were predicted by response

surface methodology (RSM), a central composite design was selected. Second-order polynomials were used to describe the response surface for biodiesel yield and acid value,

$$Y = \beta_0 + \sum_{j=1}^k \beta_j x_j + \sum_{j=1}^k \beta_{jj} x_j^2 + \sum_{i < j} \sum_{j=2}^k \beta_{ij} x_i x_j \quad (1)$$

where Y is predicted response, β_0 is intercept coefficient, β_j is linear coefficient, β_{jj} is quadratic coefficient, β_{ij} is interaction coefficient, x_i and x_j are independent factors, k is number of independent variable. Table-1 shows the experimental design of second step of Calophyllum inophyllum oil transesterification.

Portable Statgraphics Centurion 15.2.11.0 statistical software (by StatPoint Inc.) was employed to estimate responses of dependent variables and to determine the interaction between factors, the effects, coefficients, standard deviation of coefficients and other parameters of the model equations. By fitting the experiment data to construct the second-order polynomials using multiple regressions, the response surface graph and contour plot can be obtained to determine the optimum condition of experiments.

Table-1. Experimental design of the second step of Calophyllum inophyllum oil transesterification, the observed and predicted yield as well as acid value.

Test	A	B	C	D	Yield (Y_{BD})		Acid value (AV)	
	$M_{MeOH}:M_{oil}$	[NaOH] (wt.%)	T (°C)	t (h)	Observed	Predicted	Observed	Predicted
1	11	1.5	50	1.5	85.23 ± 3.11	85.34	0.39 ± 0.08	0.33
2	11	2.5	50	1.5	43.41 ± 1.60	44.47	2.29 ± 0.02	2.28
3	7	2.0	40	1	55.13 ± 2.88	54.24	1.92 ± 0.06	1.87
4	15	1.0	40	2	81.98 ± 2.72	81.41	0.39 ± 0.09	0.44
5	7	1.0	40	2	78.67 ± 3.23	77.44	1.12 ± 0.04	1.10
6	15	2.0	60	1	71.78 ± 1.19	71.88	1.17 ± 0.05	1.15
7	11	1.5	70	1.5	74.90 ± 2.89	76.79	1.15 ± 0.03	1.13
8	15	1.0	60	2	68.61 ± 1.25	68.36	1.23 ± 0.06	1.24
9	11	1.5	50	1.5	84.32 ± 3.12	85.34	0.29 ± 0.07	0.33
10	11	1.5	50	1.5	86.83 ± 2.49	85.34	0.27 ± 0.08	0.33
11	7	1.0	60	2	71.14 ± 1.83	68.06	1.59 ± 0.11	1.54
12	15	2.0	60	2	51.29 ± 1.96	49.36	1.44 ± 0.09	1.42
13	15	2.0	40	2	61.33 ± 1.24	60.09	1.22 ± 0.07	1.18
14	7	2.0	40	2	61.13 ± 1.72	59.86	2.01 ± 0.13	2.00
15	11	1.5	50	1.5	84.97 ± 3.07	85.34	0.35 ± 0.03	0.33
16	3	1.5	50	1.5	62.68 ± 1.27	64.90	1.87 ± 0.02	1.88
17	11	1.5	30	1.5	73.31 ± 2.85	74.20	0.65 ± 0.04	0.68
18	15	1.0	40	1	72.72 ± 1.43	71.64	0.56 ± 0.15	0.43
19	15	1.0	60	1	81.68 ± 1.38	81.30	0.95 ± 0.08	1.00
20	7	2.0	60	1	70.97 ± 1.39	69.89	1.53 ± 0.03	1.51
21	11	1.5	50	2.5	57.60 ± 0.78	61.02	1.19 ± 0.02	1.18
22	7	2.0	60	2	52.85 ± 1.06	52.80	1.79 ± 0.09	1.88
23	15	2.0	40	1	58.45 ± 2.74	59.89	1.06 ± 0.08	1.14
24	11	1.5	50	0.5	68.98 ± 1.46	68.34	0.79 ± 0.03	0.81
25	11	0.5	50	1.5	69.75 ± 1.37	71.47	1.20 ± 0.04	1.22
26	7	1.0	40	1	61.97 ± 1.82	62.25	0.94 ± 0.07	0.99
27	19	1.5	50	1.5	70.29 ± 2.65	70.85	0.85 ± 0.02	0.85
28	7	1.0	60	1	75.47 ± 2.13	75.58	1.21 ± 0.07	1.20



Materials

Calophyllum inophyllum oil was obtained from CV Cahaya Katulistiwa, Bantul, Yogyakarta, Indonesia. The chemicals used in this research included methanol pro analis (p.a.) (>99%), sodium hydroxide p.a. (>99%), hydrochloric acid p.a. (>99%), potassium hydroxide p.a. (85%), phenolphthalein p.a. (>99%) were purchased from Merck, Indonesia, whereas toluene and isopropanol teknis was purchased from JT Baker, Indonesia. The reference standards for fatty acid methyl ester with gas chromatography grade consisted of monoolein, diolein, triolein, and tricaprin along with pyridine, glycerin and N-Methyl-N-trimethyl-silyl-trifluoro acetamide (MSTFA) were purchased from Sigma Aldrich, Indonesia.

Experimental approach

Two step transesterification of Calophyllum inophyllum oil comprised esterification of oil as the first step followed by transesterification of oil as the second step process. These processes were carried out in batch processes.

In esterification, high free fatty acid Calophyllum inophyllum oil was placed in a two neck round-bottom flask and it was heated to 60 °C. Meanwhile, 10 wt.% hydrochloric acid was dissolved in methanol and the mixture was heated to 60 °C. The molar ratio of methanol to oil was 35:1. Then, catalyzed methanol was poured into the oil. The reaction of catalyzed methanol and oil was carried out at 60 °C and it was stirred at 500 rpm. After 3 h reaction time, the esterification was stopped and the mixture was transferred to separator funnel. After it was left for around 12 h, two layers were formed. The upper layer comprised impurities of methanol, hydrochloric acid, and a few of water, whereas the lower layer consisted of esterified oil. This oil was washed with a warm water of around 40 °C to remove the small of impurity. The esterified oil was separated from water before it was used for next process.

The second step of transesterification was conducted according to the design of experiment as shown in Table-1. Esterified oil was placed in a two neck round-bottom flask. Sodium hydroxide was dissolved in methanol and the solution of sodium methoxide was poured in the flask. Transesterification was performed by stirring the mixture in 500 rpm and at certain reaction temperature. After certain time, the reaction was terminated and the mixture was poured in separator funnel. The solution was left for around 12 h in order to be formed two layers. The lower layer comprised impurities of glycerol, methanol, and sodium hydroxide was separated from the upper layer consisted of methyl ester. The upper layer was washed with 40 °C of water. The methyl ester solution was separated from residual water and it was kept in a clean and dry bottle.

The oil and methyl ester acid values which express the free fatty acid contents were determined by titration with standard KOH solution and phenolphthalein as indicator. The ester, mono-, di-, and triglyceride content of the transesterification product also were determined by

gas chromatography. The methyl ester (biodiesel) yield (Y_{BD}) was calculated as follows,

$$Y_{BD}(\%) = \frac{W_{BD_{actual}}}{W_{BD_{theoretical}}} \times 100\% \quad (2)$$

$$W_{BD_{actual}} = W_{BD_{exp}} \times OC_{BD} \quad (3)$$

where $W_{BD_{actual}}$ is the actual biodiesel weight (g), $W_{BD_{theoretical}}$ is the theoretical biodiesel weight or *Calophyllum inophyllum* oil weight (g), $W_{BD_{exp}}$ is the experimental biodiesel weight, and OC_{BD} is oil conversion to biodiesel or the purity of biodiesel which was determined by gas chromatography (%).

RESULTS AND DISCUSSIONS

Calophyllum inophyllum oil used in this experiment had properties as presented in Table-2.

Table-2. Properties of Calophyllum inophyllum oil.

1. Fatty acid composition :	
Palmitic acid (C ₁₆ H ₃₂ O ₂)	11.03 %
Stearic acid (C ₁₈ H ₃₆ O ₂)	20.33 %
Oleic acid (C ₁₈ H ₃₄ O ₂)	41.51 %
Linoleic acid (C ₁₈ H ₃₂ O ₂)	24.57 %
arachidic acid (C ₂₀ H ₄₀ O ₂)	2.14 %
2. Density (g·mL ⁻¹) at 15°C	(0.931 ± 0.003)
3. Acid value (mg KOH·g ⁻¹)	(59.97 ± 2.71)
4. Kinematic viscosity (mm ² ·s ⁻¹) at 40°C	(58.79 ± 1.34)
5. Molecular weight (g·mol ⁻¹)	877.8

The density, kinematic viscosity, and acid value of Calophyllum inophyllum oil were higher than biodiesel properties. Hence, this oil must be esterified or transesterified to decrease its property values to be in the range of biodiesel properties. Since the acid value of oil was very high, alkaline-catalysed transesterification could not be applied to convert the oil to biodiesel. The acid value of oil must be reduced to around 4 mg KOH/g by esterifying with acid catalyst. Then, transesterification could be employed for further acid value reduction to be less than 1 mg KOH·g⁻¹. Moreover, these reactions could be lessened the density and kinematic viscosity.

In this experiment, esterification of Calophyllum inophyllum oil with hydrochloric acid as an acid catalyst could reduce the acid value of oil from (59.97 ± 2.71) mg KOH·g⁻¹ to (5.33 ± 0.71) mg KOH·g⁻¹ and the yield of esterified oil was (95.67 ± 2.85)%. This esterified oil was used as a feedstock in transesterification with sodium hydroxide catalyst.



Transesterification

ANOVA and regression analysis

The experiments were performed according to Table-1. The observed responses of biodiesel yield and acid value are also presented in Table-1. The observed biodiesel yield and acid value were fitted by empirical second-order polynomial equation to predict biodiesel yield (Y_{BD}), as shown in Equation. (4),

$$Y_{BD} = -228.39 + 9.24M_{M/O} + 82.31C_{NaOH} + 4.31 \cdot T + 136.93 \cdot t - 0.27M_{M/O}^2 - 0.47M_{M/O} \cdot C_{NaOH} - 0.02M_{M/O} \cdot T - 0.68M_{M/O} \cdot t - 27.37C_{NaOH}^2 + 0.12C_{NaOH} \cdot T - 9.58C_{NaOH} \cdot t - 0.02T^2 - 1.14 \cdot T \cdot t - 20.66 \cdot t^2 \quad (4)$$

and to predict the acid value (AV), as shown in Equation. (5). Positive sign in front of the terms indicates synergistic effect and negative sign indicates antagonistic effect.

$$AV = -9.25 + 0.49M_{M/O} + 2.17C_{NaOH} + 0.133 \cdot T + 2.31 \cdot t - 0.016M_{M/O}^2 - 0.019M_{M/O} \cdot C_{NaOH} - 0.002M_{M/O} \cdot T - 0.012M_{M/O} \cdot t - 1.43C_{NaOH}^2 + 0.028C_{NaOH} \cdot T - 0.029C_{NaOH} \cdot t - 0.001T^2 - 0.012T \cdot t - 0.67t^2 \quad (5)$$

where $M_{M/O}$ is molar ratio of methanol to oil, C_{NaOH} is sodium hydroxide concentration (wt.%), T is reaction temperature ($^{\circ}C$), and t is reaction time (h).

According to a 95% confidence level, the significance of terms was determined by comparing the computed F-value to the theoretical F-value and from the P-value. Table-3 and Table-4 describe the analysis of variance (ANOVA) for the predicted biodiesel yield equation and for the predicted acid value, respectively.

Table-3. ANOVA for predicted biodiesel yield of equation. (4).

Source	Sum of Squares	Df	Mean Square	F-value	P-value
Model	3419.76	14	244.27	53.06	<0.0001
A: $M_{NaOH}:M_{oil}$	53.16	1	53.16	13.06	0.0031
B:[NaOH]	1093.72	1	1093.72	268.76	<0.0001
C:T	10.13	1	10.13	2.49	0.1386
D:time	80.42	1	80.42	19.76	0.0007
AA	457.52	1	457.52	112.43	<0.0001
AB	13.99	1	13.99	3.44	0.0865
AC	13.43	1	13.43	3.30	0.0924
AD	29.39	1	29.39	7.22	0.0186
BB	1123.73	1	1123.73	276.14	<0.0001
BC	5.39	1	5.39	1.33	0.2702
BD	91.69	1	91.69	22.53	0.0004
CC	145.38	1	145.38	35.72	<0.0001
CD	515.93	1	515.93	126.78	<0.0001
DD	640.42	1	640.42	157.37	<0.0001
Residual	59.85	13	4.60		
Lack of fit	56.43	10	5.64	4.95	0.1074
Pure error	3.42	3	1.14		
Corr. total	3479.61	27			

Table-4. ANOVA for predicted acid value of equation. (5).

Source	Sum of Squares	Df	Mean Square	F-value	P-value
Model	7.78	14	0.560	35.69	<0.0001
A: $M_{NaOH}:M_{oil}$	1.572	1	1.572	334.56	<0.0001
B:[NaOH]	1.671	1	1.671	355.57	<0.0001
C:T	0.301	1	0.301	64.01	<0.0001
D:time	0.213	1	0.213	45.32	<0.0001
AA	1.626	1	1.626	345.95	<0.0001
AB	0.025	1	0.025	5.33	0.0381
AC	0.130	1	0.130	27.69	0.0002
AD	0.009	1	0.009	1.87	0.1946
BB	3.055	1	3.055	650.03	<0.0001
BC	0.316	1	0.316	67.26	<0.0001
BD	0.001	1	0.001	0.18	0.6766
CC	0.504	1	0.504	107.23	<0.0001
CD	0.054	1	0.054	11.38	0.0050
DD	0.673	1	0.673	143.11	<0.0001
Residual	0.200	13	0.0160		
Lack of fit	0.190	10	0.0190	6.38	0.0771
Pure error	$9.10 \cdot 10^{-3}$	3	$3.03 \cdot 10^{-3}$		
Corr. total	7.990	27			

The fitted second-order polynomial equations and regression coefficients have significant effects on the responses if the computed F-values were higher than the theoretical F-value and the P-value less than 0.05.

In Table-3 and Table-4, as the F-values of fitted biodiesel yield and acid value models were 53.06 and 35.69, respectively, higher than their theoretical F-values as well as their P-values were less than 0.0001, the fitted models demonstrated significant and sufficient to predict the biodiesel yield and acid value.

In Table-3, the model terms of C, AB, AC, and BC had insignificant effects on the biodiesel yield since the computed F values for the respective terms were lower than the theoretical F-value and P-values were higher than 0.05 (5%). The rest terms had significant effects on the biodiesel yield. In Table-4, insignificant effects on acid value were shown for the fitted equation terms of AD and BD, while other terms had important in effects on acid value.

The comparisons of predicted to observed value for biodiesel yield and acid value with their determination coefficients are displayed in Figure-1 and Figure-2, respectively.

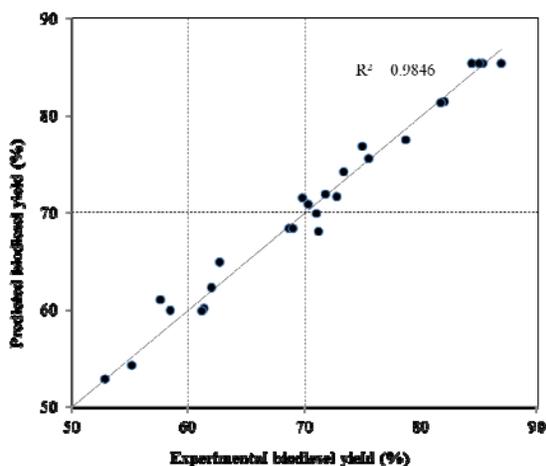


Figure-1. Comparison of experimental to predicted biodiesel yield (%).

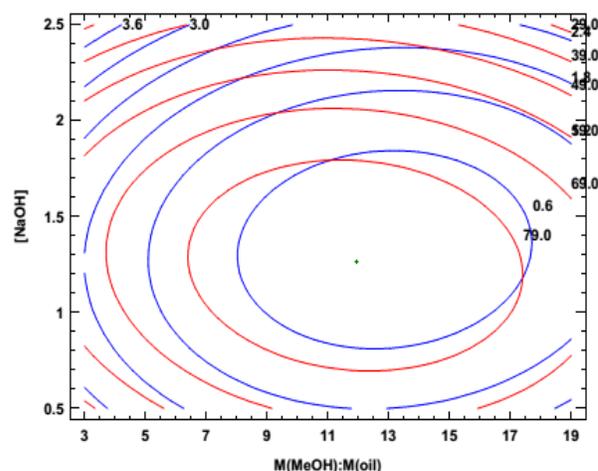


Figure-3. Contour of the biodiesel yield (red line) and acid value (blue line) for 1.5 h reaction time at 50 °C.

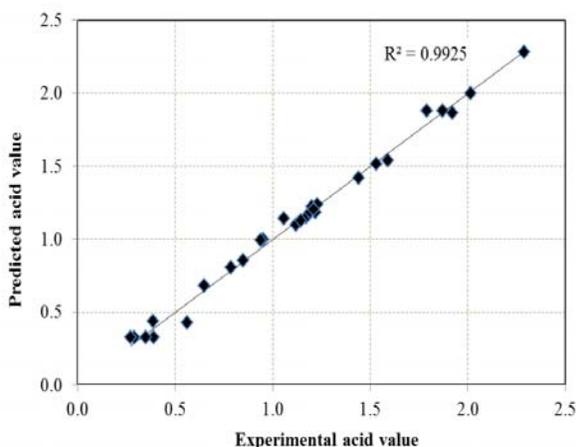


Figure-2. Comparison of experimental to predicted acid value (mg KOH•g⁻¹).

Determination coefficient of biodiesel yield was 0.9846. It meant that the second-order biodiesel yield equation described 98.46% of the variability in biodiesel yield and only 1.54% of the total variations could not be explained by this second-order equation. The value of adjusted determination coefficient (adjusted R²), which was more suitable for comparing model with different numbers of independent variables, was also very high, namely 0.9686. Meanwhile, for acid value, the determination coefficient was 0.9925 as demonstrated in Figure-2, and adjusted determination coefficient (adjusted R²) was 0.9846.

Parameter effects

Figure-3 depicts effect of the interaction between molar ratio of methanol to oil and sodium hydroxide concentration on biodiesel yield and acid value during 1.5 h reaction time at 50 °C reaction temperature.

Increasing molar ratio of methanol to oil from 3:1 to 11.95:1 and sodium hydroxide concentration from 0.5 to 1.26 wt.% enhanced the oil conversion to biodiesel and decreased the acid value or free fatty acid content. Nevertheless, further increasing molar ratio of methanol to oil and rising sodium hydroxide concentration diminished the biodiesel yield, as a result of negative interaction term of $M_{M/O}$ and C_{NaOH} in Equation. (4). At this condition, raising the molar ratio of methanol to oil could dilute the catalyst and oil concentrations in the reaction system. The interactions between them decreased and it can be reduced the oil conversion to the biodiesel. In addition, higher catalyst concentration added during the reaction led the side reaction of saponification which disrupted the separation process and gained the acid value of biodiesel.

Figure-4 shows the interactive effect of reaction temperature and reaction time. Increasing reaction temperature from 30 °C to 50 °C along with raising reaction time from 0.5 h to 1.52 h augmented biodiesel yield and reduced the acid value. However, next increment of reaction temperature in line with rising reaction time diminished the oil conversion to biodiesel though enhanced the acid value. Higher reaction temperature and longer reaction time tended to incline soap formation from saponification. Soap formation interfered biodiesel separation from the impurities.

Hence, it could reduce the yield of biodiesel. Since the computed F-value of CD term of predicted biodiesel yield equation (126.78) was higher than one of predicted acid value equation (11.38), effect of interaction between reaction temperature and time on biodiesel yield was more significant than that on acid value of biodiesel.

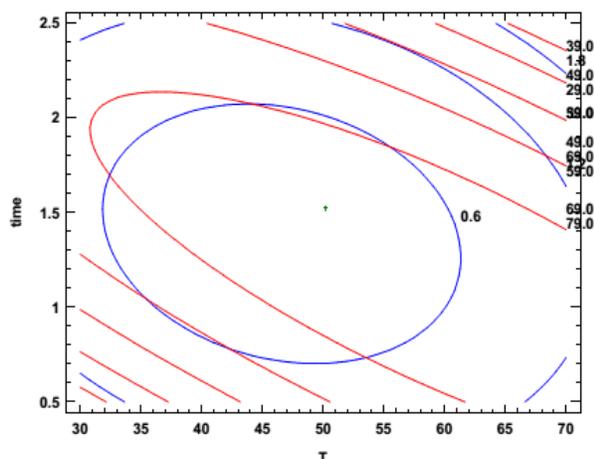


Figure-4. Contour of the biodiesel yield (red line) and acid value (blue line) for molar ratio of methanol to oil of 11:1 and sodium hydroxide concentration of 1.5 wt.%.

Optimization analysis

Table-5 describes low and high factor value as well as optimum conditions. The prediction of biodiesel yield and acid value obtained from optimization of the experimental design were 87.16% and 0.23 mg KOH·g⁻¹, respectively. These predicted values should be verified by conducting experiments at the reaction optimum conditions three times.

Table-5. Optimum condition.

Factor	Low	High	Optimum
M(MeOH):M(oil)	3.0	19.0	11.95
[NaOH] (wt.%)	0.5	2.5	1.26
T (°C)	30.0	70.0	50.21
t (h)	0.5	2.5	1.52
AV (mg KOH/g)			0.23
Y (%)			87.16

The experimental biodiesel yield was (84.90 ± 0.31)% and the experimental acid value of biodiesel was (0.303 ± 0.015) mg KOH·g⁻¹. Both experimental results were closer to the predicted results.

Reaction kinetics

Figure-5 shows the effect of reaction temperature along with reaction time on the biodiesel yield. During the early stage of the reaction, the oil conversion rate was very high at all reaction temperatures. Further reaction time, the oil conversion rate decreased significantly. It revealed that the reaction changed from irreversible reaction to reversible reaction or equilibrium state condition and in this condition, the biodiesel yield slightly increased.

Increase in reaction temperature from 30°C to 50 °C enhanced biodiesel yields. Transesterification rate could be accelerated by inclining reaction temperature to

obtain higher yields of biodiesel. According to Arrhenius equation, higher reaction temperature could augment reaction rate constant which is proportional to reaction rate. At 45 and 50 °C, equilibrium conditions could be reached in shorter reaction time, which was 60 min, than at 30 and 40 °C.

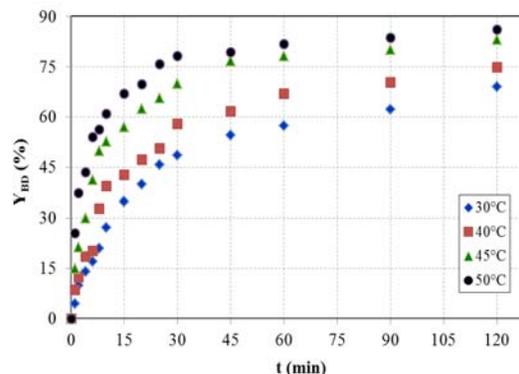


Figure-5. Biodiesel yield at various reaction temperatures and time.

Kinetic study is used to determine the reaction order and reaction rate constant of transesterification. In this study, the rate law derived according to the design equation of constant volume batch reactor and the analysis data was carried out using integral method to determine the reaction order and reaction rate constant. It was assumed that the reverse reaction could be ignored because it was very slower than the forward reaction. In order to determine the reaction kinetics, experimental data obtained in irreversible condition was used.

If the reaction was assumed as a first-order and reverse reaction was ignored, the rate law was,

$$-\frac{dC_{TG}}{dt} = k \cdot C_{TG} \quad \text{or} \quad -\ln(1-X) = k \cdot t \quad (6)$$

where C_{TG} is triglyceride concentration (mol·L⁻¹), k is reaction rate constant (s⁻¹), X is oil conversion to biodiesel.

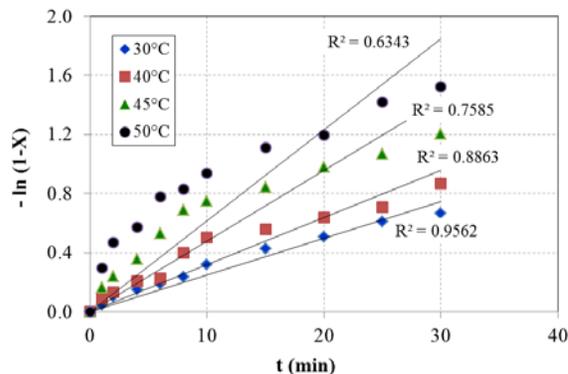


Figure-6. The relation between $-\ln(1-X)$ and reaction time.



If the assumption is correct, by plotting of $-\ln(1-X)$ versus t , a straight line was obtained with high correlation coefficient. However, Figure-6 depicts that the plotting line of the experimental data did not give a straight line. The straight line was only achieved for transesterification at 30 °C with correlation coefficient of 0.9562, while at other reaction temperature; experimental data was not fitted as straight lines due to lower correlation coefficients than 0.90. Therefore, transesterification of *Calophyllum inophyllum* oil was not the first-order reaction.

If the reaction order was assumed as a second-order and reverse reaction was neglected, the rate law was,

$$-\frac{dC_{TG}}{dt} = kC_{TG}^2 \quad \text{or} \quad \frac{1}{C_{TG}} - \frac{1}{C_{TG_0}} = \frac{1}{C_{TG_0}} \frac{X}{(1-X)} = k \cdot t \quad (7)$$

Plotting $\frac{X}{1-X}$ versus t must be linear with the slope of $C_{TG_0}k$. Figure-7 describes that the experimental data was fitted satisfactorily as a second-order reaction due to high correlation coefficients.

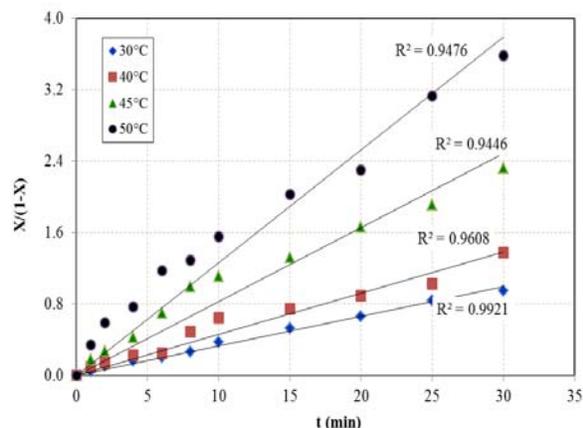


Figure-7. The relation of $\frac{X}{1-X}$ versus t .

The reaction rate constant k could be calculated from the slope values, which were in the range of 0.047 to 0.180 ($M^{-1} \cdot \text{min}^{-1}$). The activation energy for transesterification of *Calophyllum inophyllum* oil could be determined using the Arrhenius equation. Figure-8 shows a good linearity between $\ln k$ and $1/T$. Using the slope, the activation energy (E_a) obtained was 54.53 $\text{kJ} \cdot \text{mol}^{-1}$ and the pre-exponential factor (k_0) could be calculated from the intercept, which was 9.93×10^7 ($M \cdot \text{min}^{-1}$).

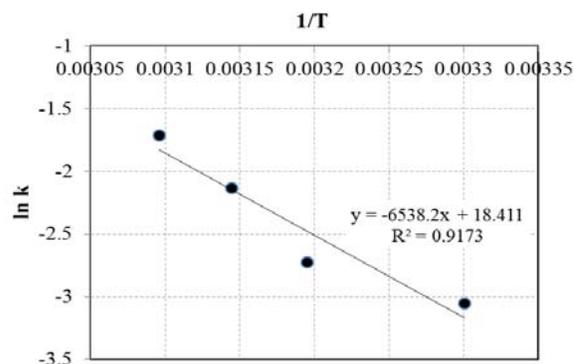


Figure-8. Arrhenius plot reaction rate constant versus reaction temperature.

Biodiesel properties

The properties of biodiesel produced at optimum conditions included molar ratio of methanol to oil of 11.95, sodium hydroxide concentration of 1.26 wt.%, 500 rpm stirring speed for 1.52 h reaction time at 50 °C are presented in Table-6. The properties were in agreement with standard requirements of EN 14214 and ASTM D6751.

Table-6. Biodiesel properties.

Parameter	Unit	Value	Method	Limits
Density at 15°C	$\text{kg} \cdot \text{m}^{-3}$	812	ASTM D-4052	860-900
Kinematic viscosity at 40°C	$\text{mm}^2 \cdot \text{s}^{-1}$	3.27	ASTM D-445	1.9-6.0
Acid value	$\text{mg KOH} \cdot \text{g}^{-1}$	0.303	ASTM D-664	0.8 max
Ester content	% mass	> 99	EN 14103	96.5 min
Total glycerin	% mass	< 0.10	ASTM D-6584	0.240 max
Free glycerin	% mass	< 0.001	ASTM D-6584	0.020 max
Flash point (closed cup)	°C	157	ASTM D-93	130 min

CONCLUSIONS

Optimization and reaction kinetics determination of two step transesterification of high free fatty acid *Calophyllum inophyllum* oil has been undertaken. The first step of esterification was carried out with hydrochloric acid as acid catalyst in constant reaction conditions which resulted acid value reduction from (59.97 ± 2.71) to (5.33 ± 0.71) $\text{mg KOH} \cdot \text{g}^{-1}$. In second step, response surface methodology, central composite design, were utilized to determine the optimum conditions of transesterification included molar ratio of methanol to oil of 11.95, sodium hydroxide concentration of 1.26 wt.% for 1.52 h reaction time at 50 °C. At these optimum conditions, the maximum biodiesel yield of (84.90 ± 0.31) % and minimum acid value of (0.303 ± 0.015) $\text{mg KOH} \cdot \text{g}^{-1}$ were achieved which were comparable with predicted values. Transesterification was the second-order reaction with



reaction rate constant of 0.047 to 0.180 ($M^{-1}\cdot\text{min}^{-1}$) at 30 to 50°C. The activation energy of 54.53 $\text{kJ}\cdot\text{mol}^{-1}$ was acquired.

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