



## Response Surface Optimization for Transesterification Reaction of Waste Cooking Oil Using Potassium-Chitosan Biocomposite Catalysts

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### Abstract

The sustainable production of biodiesel from waste cooking oil has gained significant attention due to reduce environmental pollution and dependency on fossil fuels. Therefore, this study aimed to optimize the production of biodiesel using the Response Surface Method (RSM) with potassium-chitosan biocomposite as a catalyst. The catalyst was prepared by wetness impregnation method, where potassium ions were incorporated into the chitosan polymer. The transesterification reaction was monitored by gas chromatography-flame ionization detector (GC-FID) and optimized based on reaction times, oil to methanol ratios and reaction temperatures. The highest biodiesel yield of 94.36% was achieved at 2 hours of reaction time, 1:18 oil to methanol ratio, and reaction temperature of 65°C. ANOVA analysis showed significant agreement between actual and predicted biodiesel yield with the  $R^2$  value of 0.9505,  $F$ -value of 10.68, and  $p$ -value of 0.0089. The optimal conditions suggested by the model were a reaction time of 1 hour, 1:19 oil to methanol ratio, and reaction temperature of 67°C, with a predicted biodiesel yield of 96.39%. However, only 29.77% of the biodiesel yield was achieved experimentally with a percent error of difference of 66.62% compared to the model prediction. The kinetic model for the transesterification reaction was determined using four different models, and the pseudo-first order model was found to be the best fit for the experimental data with the  $R^2$  value of 0.9433. The rate constant ( $k$ ) was determined to be 0.4267  $\text{hr}^{-1}$  and 0.9131  $\text{hr}^{-1}$  at 55°C and 65°C, respectively. The activation energy ( $E_a$ ) and Arrhenius factor were found to be 70.121 kJ/mol and  $6.27 \times 10^{10} \text{ hr}^{-1}$ , respectively. Thermodynamic studies showed that the reaction followed an endothermic non-spontaneous pathway with a reversible reaction. The enthalpy ( $\Delta H$ ), entropy ( $\Delta S$ ), and Gibbs' energy ( $\Delta G$ ) were calculated to be 67.35 kJ mol<sup>-1</sup>, -47.44J mol<sup>-1</sup>K<sup>-1</sup>, and 83.147 kJmol<sup>-1</sup>, respectively.

**Keywords:** Response Surface Methodology; waste cooking oil; potassium-chitosan biocomposite; Transesterification

### 1.0 Introduction

Biodiesel is a fuel made from various feedstocks such as vegetable oil, animal fat, and waste oil. Waste cooking oil is becoming a popular choice for biodiesel production due to its low cost and environmental benefits (Pugazhendhi, A. et al., 2020). In Malaysia, an estimated 540 000 tonnes of waste cooking oil from vegetable and animal fats are discarded each year without being treated as wastes (Haruhiro, F. et al., 2015). According to the data provided by the International Energy Agency in their Renewables 2022 report, there has been a doubling increase in global biodiesel production between 2010 and 2022. Furthermore, the Renewables 2018 forecast predicts a significant growth in Malaysia's annual biodiesel output, with an expected rise from 800 million liters in 2017 to 1.2 billion liters by 2023.

Transesterification is a chemical process that creates biodiesel using a catalyst (Endalew, A.K. et al., 2011). There are two types of catalysts commonly used in the process: homogeneous and heterogeneous. However, the latter is more popular since it does not require rigorous purification (Semwal, S. et al., 2011). Free fatty acids (FFAs) are undesirable compounds in feedstock as they react with base catalysts to form carboxylic acid salts (soap) that reduces biodiesel yields and make products harder to separate. Therefore, the use of heterogenous polymer catalyst could minimize the

soap formation by reducing catalyst leaching issue.

Chitosan beads act as a structuring agent, offering a larger surface area, which prevents metal leaching and diffusion issues. The study proposes impregnating chitosan with potassium ions to create a stable catalyst for biodiesel production. The Response Surface Method (RSM) is a standard statistical technique used to improve, optimize and model biodiesel production and it can determine the relationship between the response of interest and various parameters variables in optimization study (Calabrese, A. et al., 2021). Box–Behnken design (BBD) is a popular response surface designs that require fewer experimental runs (Panichikkal, A.F. et al., 2018).

The kinetic study of a reaction relates the rate of the reaction, temperature and that the rate constant ( $k$ ), the activation energy ( $E_a$ ) as well as frequency factor ( $k_0$ ). Several kinetic mechanism or models has been proposed and studies by different researchers in the past for transesterification, some of it include zero order (Roy, T. et al., 2020; Permsuwan, A. et al., 2011), first order (Ma, Y. et al., 2017), pseudo-first order (Yahya, S. et al., 2019), second order (Ahiekpor, J.C. et al., 2010) and pseudo-second order (Gholipour Zanjani, N. et al., 2020). Many published literatures have reported that pseudo-first order was the best model to describe the catalytic transesterification. The important thermodynamic parameters to assess the characteristics of a transesterification process include enthalpy ( $\Delta H$ ), entropy ( $\Delta S$ ), and Gibbs' free energy ( $\Delta G$ ) which are important to assess whether the transesterification conducted in this study proceeds in either endothermic or exothermic manner, spontaneous or non-spontaneous and endergonic or exergonic manner (Pugazhendhi, A. et al., 2020).

This research aims to (1) synthesise potassium-chitosan biocomposite catalyst for the transesterification reaction, (2) study the optimization of transesterification reaction using the response surface method (RSM) for potassium-chitosan biocomposite catalyst, (3) determine the kinetic model of transesterification reaction through kinetic studies using the potassium-chitosan biocomposite catalyst and (4) determine the thermodynamics behaviour of the transesterification reaction of waste cooking oil.

## 2.0 Methodology

### 2.1. Catalyst Preparation

The potassium-polymer catalyst was prepared by wetness impregnation of incorporate potassium ions into chitosan. Firstly, 10 g of chitosan was mixed with 2.5 mL of 0.5% acetic acid and stirred to homogenous solution (Jaafari, J. et al., 2020). The potassium nitrate was then added into the mixture and followed by continuous stirring on the stirrer for at least 3 hours until the potassium nitrate completely dissolved into the mixture. The solution was then left overnight to release the air bubbles in order to avoid it from floating on the surface of the sodium hydroxide solution later. Next, 1M of NaOH solution was prepared and stirred with magnetic stirrer at low speed. The polymerised solution was then dropwise into the NaOH solution using dropper to form beads. Let the beads to settle down overnight (Helmi, M. et al., 2021). Following that, the beads were then filtered and rinsed twice with distilled water and then dried in oven at 80°C for 48 hours until the beads appeared as brownish yellow in colour. After drying, the beads were calcined at 700°C for 2 hours.

### 2.2 Transesterification of Waste Cooking Oil to Biodiesel

The biodiesel transesterification was conducted via a refluxing process followed by separation process. 10 g of waste cooking oil with different oil to methanol ratios (1:12, 1:18, 1:24) and 0.6 g of potassium-chitosan catalyst were placed in a two-neck round bottle flask equipped with a magnetic stirrer, a water- cooled condenser and a thermometer. The mixture was then refluxed at different reaction temperatures (55°C, 65°C, 75°C) and times (1 hour, 2 hours, 3 hours). The mixture was then separated using separating funnel to obtain biodiesel at the top layer and to remove glycerol at the bottom layer. After done separation process, the biodiesel extracted was centrifuged at 5000 rpm for 20 minutes. The mass conversion can be calculated similar as Helmi and Hemmati (Helmi, M. and A. Hemmati, 2021).

### 2.3 Optimization Study by RSM

RSM via Box-Behnken Methods (BBD) was used as a tool to optimize parameters of the transesterification reaction. The transesterification reaction conditions were designed and optimised using Design-Expert Version 13. The numerical relationship between the response function (Y) and independent variables (A, B, C) are studied and the response surface was explained through empirical model of second order polynomial as shown in Equation (1).

$$Y = \beta_0 + \sum \beta_i X_i + \sum \beta_{ii} X_i^2 + \sum \beta_{ij} X_i X_j \quad (\text{Eq 1})$$

The three independent variables studied were reaction times (A), oil to methanol ratio (B) and reaction temperature (C). Meanwhile, the response was percentage yield of FAME that produced from the reaction. Table 1 lists the range and levels of the three independent variables based on experimental parameter. The independent variables were coded into two level known as low (-1) and high (+1). A box-Behnken Design (BBD) was employed to fit a second order response surface model with total of 15 experiments that performed randomly to minimize errors from the systematic trends in the variables. The design model was evaluated by analysis of variance (ANOVA). The proposed model was used to determine the interaction between the process parameter and the response. To predict the optimum response, a model must be significant with an appropriate *F-value* and a *p-value* less than 0.05 and have an insignificant lack of fit. The coefficient of determination ( $R^2$ ) correlation must close to 1.

**Table 1.** Independent variables for the Box-Behnken Design on the biodiesel production parameters

Coded	Transesterification	Units	-1 Level	0 Level	+1 Level
A	Reaction Time	hr	1	2	3
B	Oil to Methanol ratio	mol ratio	1:12	1:18	1:24
C	Reaction temperature	°C	55	65	75

### 2.4 Biodiesel Analysis using GC-FID

The product obtained was analysed by using gas chromatography-flame ionization detector (GC-FID) equipped with DB-Heavy Wax Column (30.0 m x 250  $\mu\text{m}$  x 0.25  $\mu\text{m}$ ) and helium as the carrier gas to identify the fatty acid methyl ester (FAME) present. The oven temperature was set at 240°C where the initial temperature for the column was station at 60°C for 2 minutes with ramp rate of 10°C/min and increased to 240°C for 7 minutes with ramp rate of 5°C/min. The inlets and detector temperature of GC-FID was both programmed at 250°C. The collected biodiesel was first diluted with 10000 ppm of methyl nanodecanoate (C19 internal standard) before injecting 1  $\mu\text{L}$  of the mixture manually into the GC system. The biodiesel purity and percentage of biodiesel yield calculated similar as reported by Sulaiman et al. (Sulaiman, N.F. et al., 2020).

### 2.5 Kinetic and Thermodynamic Studies of Biodiesel Production

In accordance with the previous study conducted by Yahya et al. (Yahya, S. et al., 2019) in determination of kinetic models, the experimental data was fitted to linear forms of first, second pseudo-first and pseudo-second order from each of their equation. This was then followed by determination of reaction rate constants, *k* from each of the linear graphs plotted and the models that gave the highest correlation coefficient,  $R^2$  was used to assign as the kinetic model for the transesterification reaction in this study. The linear graph of first, second, pseudo-first and pseudo-second can be expressed as similar in Huong et al. (Huong, L.T.T. et al., 2008), Yahya et al. (Yahya, S. et al., 2019), Vujicic et al. (Vujicic, D. et al., 2010), Gholipour et al. (Gholipour Zanjani, N. et al., 2020), respectively. Whereas the Arrhenius equation can be expressed as similar in Goa et al. (Gao, Y. et al., 2019). The thermodynamics behaviour including the enthalpy ( $\Delta H$ ), entropy ( $\Delta S$ ) and Gibb's free energy ( $\Delta G$ ) were investigated using Eyring-Polanyi model and the value of  $\Delta G$  in each temperature was calculated as similar in Helmi and Hemmati (Helmi, M. and A. Hemmati, 2021).

### 3.0 Results and discussion

#### 3.1. Optimization Parameters of Biodiesel Production by RSM

Box-Behnken Design of Response Surface Methodology (RSM-BBD) was used in the optimization study of potassium-polymer catalysts for biodiesel productions. The independents variables such as reaction temperature (A), oil to methanol ration (B) and reaction time (C) are significant parameters used for Box-Behnken Design. The levels coded with -1, 0 and 1 were listed as shown in Table 1 while coefficients of the quadratic polynomial model and the optimization were calculated by using Design Expert Software Version 13.

#### 3.2. Regression Model and Statistical Analysis

From the result obtained, quadratic equation was selected as it gave high *F-value* and low *p-value* which indicated the significance of model in representing the process and best fitted to the experimental data.

The influence of the independent variable on the yield was represented by a positive or negative sign. A positive value of variable B in Equation 2 indicated that a high level of the variable would cause an increase in biodiesel yield. Negative value of variable A and C demonstrated that higher biodiesel yields could be achieved when the variable was reduced to a lower level. Moreover, in terms of the interactions between two variables such as AB, AC, and BC, the positive value of variable BC showed an increase in biodiesel yields when both oil to methanol ratio and reaction time were shifted to the same level, regardless of whether they were high or low reaction temperature. In contrast, the negative value of variable AB and AC demonstrated the increase of response when two variables adjusted in opposite direction. It explained that one variable should change to a higher level while the other variable adjusted to a low level in order to achieve high biodiesel production (Macías-Sánchez, M. et al., 2018).

$$Y = 91.38 - 6.66*A + 12.36*B - 4.24*C - 4.80*AB - 18.60* AC + 0.6359*BC - 23.70 * A^2 - 18.19*B^2 - 2.26*C^2 \tag{Eq 2}$$

According to the design, a total of 15 runs were performed in a randomized order. The predicted values obtained from the model fitting technique to be sufficiently correlated to the experimental values as presented in Table 2. Meanwhile, there is an adequate correlation between the predicted and experimental values of the independent variable. The linear plot of the graph represented high regression coefficient, *R<sup>2</sup>* value which was found to be 0.9505 indicating that the 95.05% of the total variation in the biodiesel yield was attributed to the experimental variables studied. The closer the *R<sup>2</sup>* value to the one, the better the model as the predicted and actual yields (Wong, Y.C. et al., 2015).

**Table 2.** Actual and predicted value of biodiesel production

No		Factor Variable			Biodiesel Production	
Std	Run	A:Reaction temperature (°C)	B:Methanol oil ratio (mol)	C:Reaction time (h)	Actual	Predicted
13	1	65	18	2	91.47	91.38
11	2	65	12	3	55.84	53.69
7	3	55	18	3	85.41	86.44
14	4	65	18	2	88.29	91.38
5	5	55	18	1	65.75	57.72
15	6	65	18	2	94.36	91.38
12	7	65	24	3	86.59	79.68
10	8	65	24	1	84.73	86.88
8	9	75	18	3	27.89	35.92
1	10	55	12	2	37.87	38.99
3	11	55	24	2	67.43	73.31
4	12	75	24	2	51.51	50.39

2	13	75	12	2	41.15	35.27
9	14	65	12	1	56.53	63.44
6	15	75	18	1	82.62	81.59

Based on Table 3, the model was significant with degree of freedom values (*F-value*) of 10.68 and *p-value* of 0.0089. Higher Fisher test value (*F-value*) with probability value (*p-value*) not greater than 0.05 confirmed the adequacy and significance of regression model as well as regression coefficient. Besides, lack of fit of 11.12 showed insignificant relative to pure error. The insignificant lack of fit had verified that the experimental data were satisfactorily fitted to the model. Thus, this implied that the model was statistically significance for biodiesel production at 95% confidence interval.

**Table 3.** ANOVA results of the response surface quadratic model for biodiesel production parameters using potassium-polymer catalyst for biodiesel production

Source	Sum of Squares	df	Mean Square	F-value	p-value	
<b>Model</b>	6268.09	9	696.45	10.68	0.0089	significant
A-Reaction temperature	354.93	1	354.93	5.44	0.0670	
B-Methanol oil ratio	1222.00	1	1222.00	18.74	0.0075	
C-Reaction time	143.53	1	143.53	2.20	0.1981	
AB	92.21	1	92.21	1.41	0.2878	
AC	1383.36	1	1383.36	21.21	0.0058	
BC	1.62	1	1.62	0.0248	0.8810	
A <sup>2</sup>	2073.50	1	2073.50	31.79	0.0024	
B <sup>2</sup>	1221.65	1	1221.65	18.73	0.0075	
C <sup>2</sup>	18.88	1	18.88	0.2895	0.6136	
Residual	326.09	5	65.22			
Lack of Fit	307.65	3	102.55	11.12	0.0836	not significant
Pure Error	18.44	2	9.22			
Total	6594.18	14				
Standard deviation	8.08	R <sup>2</sup>				0.9505
Mean	67.83	Adjusted R <sup>2</sup>				0.8615
C.V %	11.91	Adequate Precision				8.5088

### 3.3 One Factor Effect towards Biodiesel Production

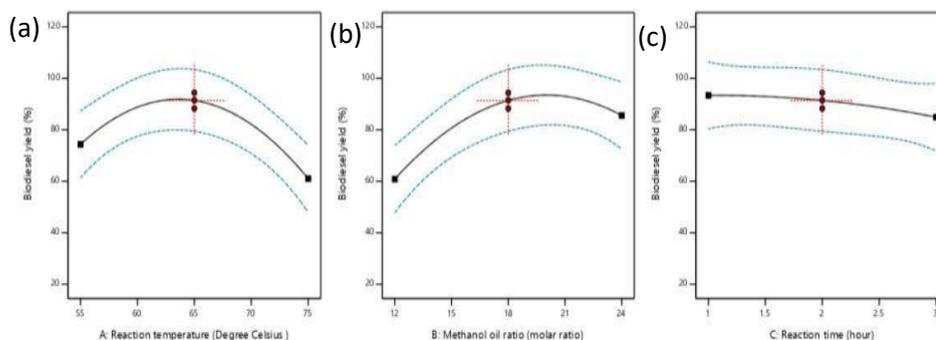
The biodiesel productions from waste cooking oil were evaluated through various parameters such as reaction temperature, oil to methanol ratios and reaction time. Figure 1(a) demonstrated the one factor effect of reaction temperature on biodiesel yields. Transesterification reaction temperatures were studied over 55°C, 65°C and 75°C. The biodiesel yields increased from 74.34 % to 94.36 % when reaction temperature changed from 55°C to 65°C. This is because when the temperature increase, the rate of reaction increases due to increase in a collision among the reacting molecules, which accelerates the chemical reaction (transesterification) and hence increases biodiesel yield (Elkelawy, M. et al., 2020). However, the biodiesel yield decreased when the reaction temperature increases to 75°C at which the biodiesel yields declined from 94.36% to 61.02%. The decrease of biodiesel yields was due to excessive increase in temperature above the evaporating temperature of methanol will reduce yield due to methanol evaporation over time (Wang, Z.-P. et al., 2017). Thus, it could be suggested that the optimum reaction temperature use for catalyst preparation was around 65 °C.

Next, Figure 1(b) showed the one factor effect of methanol oil ratio. The change of methanol oil ratio from 1:12 to 1:18 had increase the biodiesel yields from 60.83 % to 94.36%. Lower biodiesel

yields was obtained at oil to methanol ratio of 1:12 because the reduced amount of methanol reduced the methoxy species formation at the catalyst surface and the solid catalyst interaction (Agu, C.M. et al., 2022). However, the biodiesel yield was slightly decreased to 85.55% when the ratio of oil to methanol increased to 1:24.

This was due to the fact that increasing the methanol amount decreases the glycerol content as equilibrium is in the forward direction towards biodiesel formation [23]. Hence, an excessive amount of methanol also increases the solubility of glycerol and complicates the separation process at which reduces biodiesel production.

Figure 1(c) illustrated quadratic effect of reaction time on the biodiesel production. The results showed the biodiesel yield declined slightly from 1 hr to 2 hrs from 93.35% to 94.36%. However, the biodiesel yields gradually decrease to 84.88% when prolong the reaction time to 3 hrs. The excessive reaction time reduces biodiesel yield due to the backward reaction of transesterification, leading to the loss of esters and the formation of additional fatty acids as soaps.



**Figure 1.** One factor effect of the biodiesel production of each independent variables (a) Reaction temperature (b) Methanol Oil ratio (c) Reaction time

### 3.4 Optimization Response and Verification of Model

Table 4 shows the lower and upper limit of each variable adjusted to obtain optimum conditions for maximum biodiesel production. Based on the criteria selected, the factor range of catalyst parameters were restricted to factorial levels while the desirability for biodiesel yields was set in target of 100 as limit for maximization goals. The results revealed that the optimum conditions achieved from this model were 67°C, 1:19 methanol to oil ratio and reaction temperature of 1 hour with prediction 96.39% of biodiesel production. The optimum conditions were applied to validate experimentally and estimate the values of the response using the model equation.

**Table 4.** Optimum condition and method validation using potassium-chitosan biocomposite catalyst for biodiesel production

Name	Goal	Lower Limit	Upper Limit	Optimal condition
A:Reaction temperature	in range	55	75	67
B:Methanol oil ratio	in range	12	24	19
C:Reaction time	in range	1	3	1
Biodiesel yield	maximize	27.8907	100	96.39

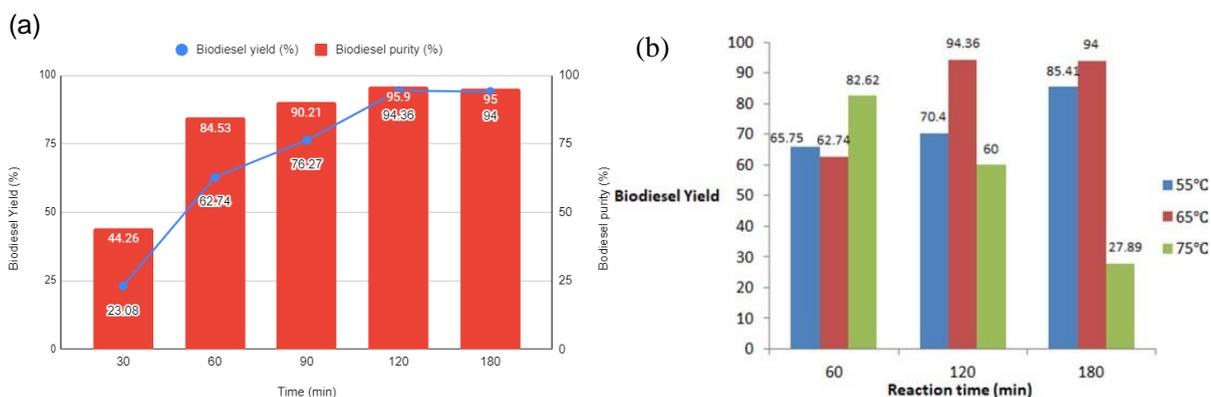
Based on the experimental data obtained, it has been found that biodiesel yield at the suggested optimum conditions was 29.77%. There is a significant deviation from the predicted biodiesel yield 96.39% which can be proved in Figure 2 later. The reason for this discrepancy can be attributed to the fact that the suggested reaction time of 1 hour is not sufficient for the complete transesterification reaction to take place. Additionally, the suggested reaction temperature of 67°C is higher than the boiling point of methanol, which may have led to some methanol loss through evaporation. To improve the yield of biodiesel, the experimental results suggest that the optimized reaction conditions should include an extended reaction time of 2 hours, a ratio of 1:18 oil to methanol, and a slightly lower

reaction temperature of 65°C. Under these conditions, the actual biodiesel production from the reaction was found to be 94.36%, which is a significant improvement over the suggested optimum conditions.

### 3.5 Effect of Reaction Time and Reaction Temperature on Transesterification of WCO

The reaction time was studied to evaluate the optimal time for transesterification when using potassium-chitosan biocomposite catalyst. To study this parameter, the reaction temperature was kept constant at 65°C along with 1:18 oil to methanol molar ratio. Figure 2(a) shows the plot of effects of reaction time towards the biodiesel yield and purity. Overall, the biodiesel yield increased with the reaction time until the reaction achieved its equilibrium. Significant increase was observed during 120 minutes reaction time as the biodiesel yield was 94.36 % with biodiesel purity of 95.9 %. The purity above 90% shows a good quality of biodiesel production from the reaction. According to (Gholipour Zanjani, N. et al., 2020), they concluded that longer reaction time has becomes one of the integral factors to drive the reaction process towards its completion instead of other parameters. The reaction rate was very slow during the first minute due to low miscibility of methanol in the oil. They also agreed that for the transesterification process, the general rule is that the conversion rate of FAME increases with the reaction time.

To determine the optimum reaction temperature which can achieve maximum biodiesel yield, the study was performed at three different temperatures of 55°C, 65°C and 75°C for 60, 120 and 180 minutes. As shown in Figure 2(b), the biodiesel yield at 55°C and 65°C showed an increase trend in biodiesel yield from reaction time of 60 minutes to 120 minutes. Particularly, reaction temperature of 65°C at 120 minutes, the highest biodiesel yield of 94.36% was observed. In contrast, the reaction temperature of 75°C showed an inverse trend as compared to 55°C and 65°C. During the reaction time of 60 minutes, the highest biodiesel yield of 82.62% was observed. However, the biodiesel yield decreased to 60% at 120 minutes and achieved the lowest biodiesel yield of 27.89% at 180 minutes.



**Figure 2.** (a) The performance of potassium-chitosan biocomposite catalyst at reaction time (b) Reaction temperatures on biodiesel yield using potassium chitosan catalyst

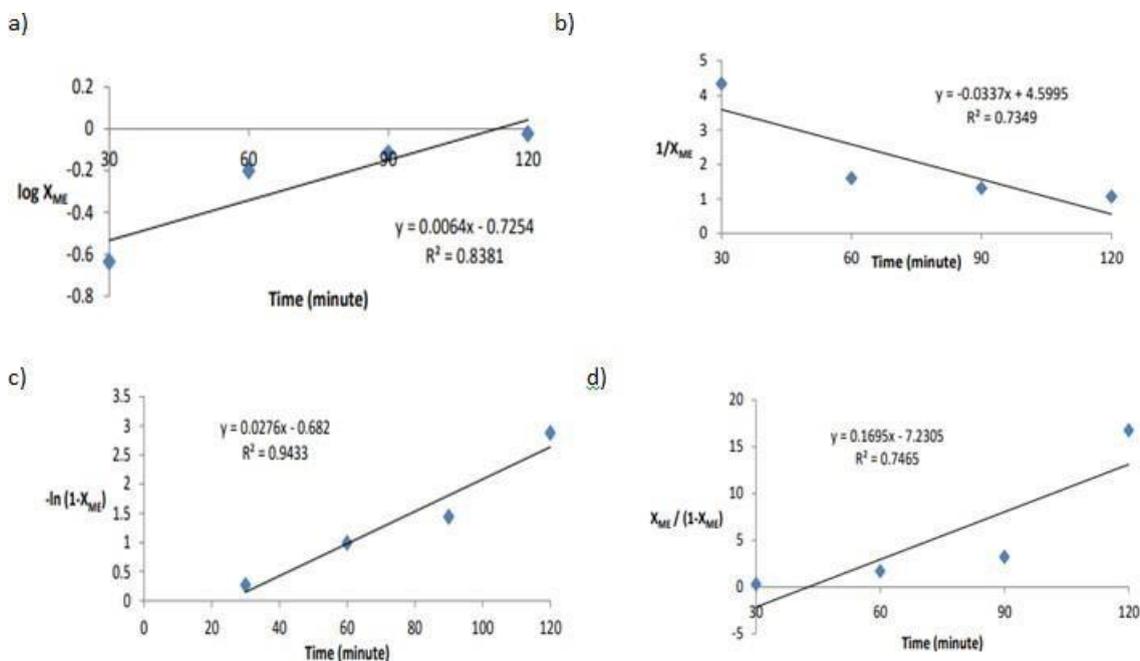
### 3.6 Determination of Reaction Kinetics

The kinetic study for determination of reaction order in transesterification of waste cooking oil utilizing potassium-chitosan biocomposite catalyst was executed at the reaction temperature of 65°C, 1:18 methanol to oil molar ratio and reaction time of 2 hours. The data was fitted to four kinetic models of first order, second order, pseudo-first order and pseudo-second order and comparisons were made to determine which model the data fits best.

### 3.7 Kinetics of Biodiesel Production

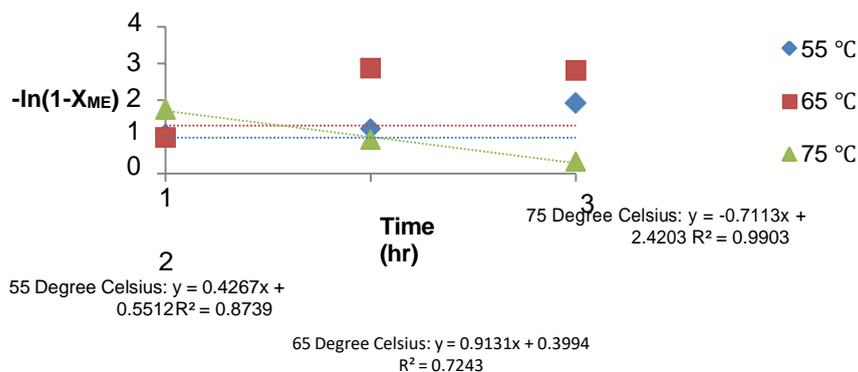
The data obtained from experiment for transesterification utilizing potassium-chitosan biocomposite catalyst was fitted into four models and the slope was representing the rate constant for each model. For first order, it gives out  $R^2$  value of 0.8381 with a positive slope of 0.0064 and the graph can be seen in Figure 3(a). Fitting the data into second order linear equation gives a graph with negative slope as shown in Figure 3(b) and an  $R^2$  value of 0.7349. The negative slope given by the second order indicated that the model is not suitable to describe the reaction (Yahya, S. et al., 2019). A positive slope was observed with a value of 0.0276 and a regression value 0.9433 as shown in Figure 3(c) for the pseudo-first order plot. In Figure 3(d), a linear pseudo-second order was plotted which

gives out  $R^2$  of 0.7465 and a positive slope of 0.1695. Among the four models, the pseudo-first order gives out the highest  $R^2$  value. Thus, the best model to describe the kinetic of transesterification utilizing potassium- chitosan biocomposite catalyst in this study were determined to be the pseudo-first order kinetic which agreed with previous studies (25. Yahya, N.Y. et al., 2018; Sharma, A. et al., 2019; Zhang, L. et al., 2010).



**Figure 3.** Linear plot of a) first order b) second order c) pseudo-first order d) pseudo-second order

After agreeing that pseudo-first order was the best model to describe the transesterification reaction in this study, another plot was made to assess the reaction rate constant at three different temperatures. Figure 4 shows a plot of  $-\ln(1-X_{ME})$  at different time interval and reaction temperature which were 55°C, 65°C and 75°C. The comparison of the three reaction temperatures in Table 5 indicated the rate constant value increase from 0.4267  $\text{hr}^{-1}$  to 0.9131  $\text{hr}^{-1}$  from temperature 55°C to 65°C and decrease to negative value with increment in temperature. The trend indicated that the rate of reaction increases until optimum temperature was achieved and declined when it exceeds the boiling point of methanol, therefore negative rate constant for 75°C reaction temperature was excluded in the kinetic study.

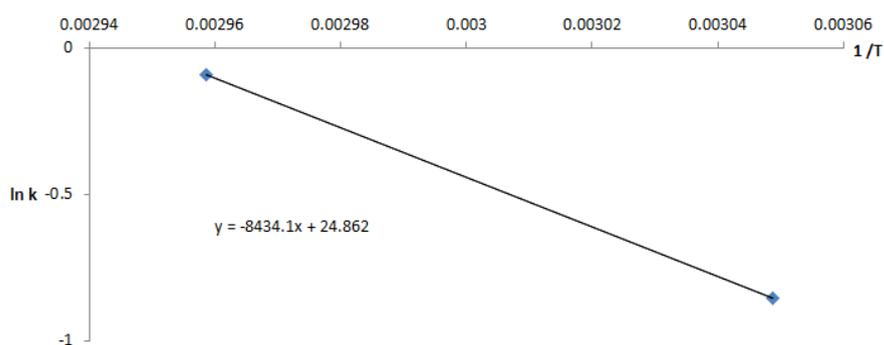


**Figure 4.** Linear pseudo-first order plot at various temperature

The activation energy,  $E_a$  was determined by correlating the pseudo-first order rate constants of 55°C and 65°C by using the Arrhenius equation. Plot of  $\ln k$  against  $1/T$  in Figure 5 gives a straight line which indicates the pseudo-first order kinetic was well fitted to the transesterification process. The  $E_a$  was calculated from the slope multiplied by the value of gas constant and the value obtained to be 70.121 kJ/mol. The pre-exponential factor or Arrhenius factor ( $k_0$ ), which was used to calculate the frequency of reaction occurrences was calculated from the intercept of the Arrhenius plot in Figure 5 and was found to be  $6.27 \times 10^{10} \text{ hr}^{-1}$ .

**Table 5.** Determination of activation energy and Arrhenius factor for transesterification of waste cooking oil by the mean of Arrhenius plot

Temperature (°C)	Rate constant (hr <sup>-1</sup> )	R <sup>2</sup>	E <sub>a</sub> (kJ/mol)	Arrhenius factor (hr <sup>-1</sup> )
55	0.4267	0.8739		
65	0.9131	0.7243	70.121	6.27 × 10 <sup>10</sup>
75	-0.7113 (ignore)	0.9903		



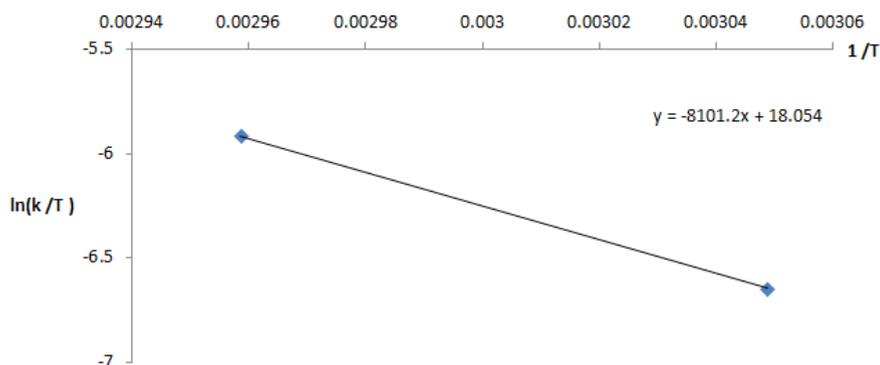
**Figure 5.** Arrhenius plot of  $\ln k$  vs  $1/T$  of fatty acid methyl ester formation from waste cooking oil

### 3.8 Thermodynamic Studies of Biodiesel Production

Figure 6 shows the corresponding Eyring-Polanyi plot of  $\ln(k/T)$  versus  $1/T$ . The slope, intercept, and calculated value of thermodynamics parameters for methyl esterification of waste cooking oil in this study were tabulated in Table 6. The slope of the plot helped to evaluate the enthalpy ( $\Delta H$ ) in this study which were found to be 67.35 kJ/mol indicating external heat energy were required for the whole process. The positive value of  $\Delta H$  and  $\Delta G$  in this study are similar to the values obtained by (Roy, T. et al., 2020) when they used potassium catalyst for synthesizing biodiesel from castor oil. The entropy ( $\Delta S$ ) was calculated to be  $-47.44 \text{ J mol}^{-1}\text{K}^{-1}$  by the help of the same plot and the average Gibbs' free energy ( $\Delta G$ ) of the whole reaction was 83.147 kJ/mol. The positive sign of the  $\Delta H$  and  $\Delta G$  imply that the above transesterification was following the non-spontaneous endothermic reaction pathway, meanwhile the negative sign for the  $\Delta S$  value indicated that during the process, randomness of the system was reduced. According to Bello and Yacob (Bello, A.M. and A.R. Yacob, 2021), the negative value of  $\Delta S$  demonstrated that the reactant species join together to form a more ordered transition state along the reaction pathway and signifies a reversible reaction.

**Table 6.** Calculated values of thermodynamic parameters

Temperature (°C)	$\Delta H$ (kJ mol <sup>-1</sup> )	$\Delta G$ (kJ mol <sup>-1</sup> )	$\Delta S$ (J mol <sup>-1</sup> K <sup>-1</sup> )
55		82.910	
65	67.35	83.384	-47.44



**Figure 6.** Eyring-Polanyi of  $\ln(k/T)$  against  $1/T$  of fatty acid methyl ester formation from waste cooking oil

#### 4.0 Conclusion

In this research, potassium-chitosan biocomposite catalyst was used to produce biodiesel from waste cooking oil through the transesterification process. The optimization of biodiesel production process conditions was successfully done and validated by the Box-Behnken Design of Response Surface Methodology (RSM-BBD). The ANOVA analysis showed the good agreement between actual and predicted biodiesel yield with  $R^2$  value of 0.9505, 10.68 of  $F$ -value and 0.0089 for the  $p$ -value. The optimum condition was suggested from this model at 1 hour of reaction time with 1:19 oil to methanol ratio and reaction temperature of 67°C with prediction 96.39% of biodiesel yield. However, only 29.77% of biodiesel yield was achieved when conducted experimentally with percent error of difference 66.62% compared with model prediction. From the experimental results, the optimum condition by experimental data was at 2 hour of reaction time, 65°C with 1:18 oil to methanol which achieved 94.36% of biodiesel yield. In terms of kinetic and thermodynamics, the best kinetic model to describe the transesterification was the pseudo-first order kinetics. The rate constant at 65°C was determined to be 0.9131  $\text{hr}^{-1}$ . The activation energy of the reaction was 70.121 kJ/mol with increasing rate constant as the temperature increases and decrease when exceed the boiling point of methanol. The thermodynamic parameter such as  $\Delta H$ ,  $\Delta S$ ,  $\Delta G$  found to be 67.35 kJ/mol, -47.44  $\text{kJ mol}^{-1} \text{K}^{-1}$  and 83.147 kJ/mol respectively.

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