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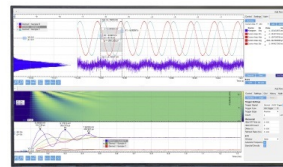View Online   Export Citation

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The S-Curve Model of Biodiesel Transesterification by Numerical Methods Based on Brief Experimental Data

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Abstract. An experiment related to biodiesel transesterification was successfully done. The chemical reaction of transesterification was conducted at 65 °C during 14 h of reaction time involving the ratio of methanol and used cooking oil was 70 : 1. An additional catalyst is required upon 10 % of HPA (Heteropoly Acid) as an organic catalyst. The maximum conversion (yield) was achieved by 88.68 % with activation energy (Ea) was 53.99 kJ/mole with Pre-Exponential Factor (A) was obtained 2.9 x 107. Based on those experiments, s-curve modeling was designed. The s-curve was generated through three different selected temperature reactions as follows: 60, 65, and 70 °C (333, 338, and 343 K) with various reaction times 0.5, 1.0, and 2 h respectively. The mechanism to build the s-curve model through three stages starting by determination of reaction rate constant (k') through linear regression equation continued with the curve formation between ln k' with 1/T to produce a value of Ea and A. To produce the s-curve model was observed through numerical processes, interpreted and analyzed by applying the Avrami equation to determine reaction and temperature time is required by trans esterification reaction between methanol and used cooking oil. Referring to the curve was obtained several results which are the optimum temperature to obtain the best yield, time to obtain a 100 % yield, and time to obtain a determining yield. According to the s-curve model was formed, the time reaction 46.95 h and 22.79 h is able to achieve 100 % and 96.5 % of yield product by plotting reaction of temperature and time. This simulation can be applied to other biodiesel reaction which has different raw materials and types of a catalyst by keeping the same method to be applied through the transesterification method.
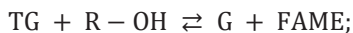
Keywords : Transesterification, s-curve model, avrami equation, arrhenius equation, reaction rate constant (k')

INTRODUCTION

Researches related to renewable energy especially renewable fuels such as biodiesel have received a lot of attention all over the world. This makes researchers compete to research in the field. Biodiesel is another name for alkyl or methyl esters obtained from the transesterification process of natural polymers namely triglycerides, in which the source is obtained from animal or vegetable oils. The reaction between triglycerides and alcohol (methanol) with the help of the catalyst produces alkyl esters and glycerol. Interestingly, the product conversion or yield produced varies greatly depending on the determination of the reaction parameters by researchers. Some of these parameters are the molar ratio of alcohol: oil, catalyst selection, catalyst concentration, heating temperature, and reaction time [1].

Research results are generally based on experiments conducted in quite a long time and costly enough to obtain an optimal result. This obstacle usually occurs when determining the use of a catalyst and determining its concentration. Theoretically, the catalyst is used to reduce the amount of activation energy required by a reaction to

increase the speed of the reaction in forming the desired product. If the levels of FFA or free fatty acids in the biodiesel feedstock are high at > 2.5 % or > 5 mg KOH/g, then an acid catalyst is used in the initial stage. The reaction is called esterification. Then, the base catalyst is used for the final product, the reaction is called transesterification. In general, we describe the transesterification [2] as follows:

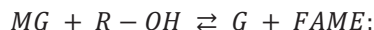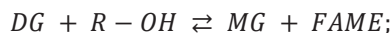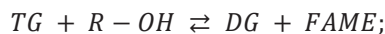$$TG \ + \ R-OH \ \rightleftarrows \ G \ + \ FAME;$$

whereas TG means triglycerides and R-OH means alkyl esters, both are reactant. Then, G means glycerol and FAME (Fatty Acid Methyl Ester), both are the products of the reaction. The kinetics are needed to determine the effect and magnitude of each parameter involved in the reaction to a given variable. That is called kinetics because it explains the phenomena that occur in the reaction as a function of time [3, 4]. By studying the kinetics, a model or simulation can be made as a guide for further experiments, making it easier for researchers not to carry out prolonged trials thereby reducing time efficiency.

There was some experience related to kinetics modeling where data showed that the reaction order of biodiesel experiment especially for oil feedstock, was occurred in pseudo-first order. Jamal et al. reacted soybean oil with organic catalyst, Kaur and Ali in making Jatropha curcas L. Oil with Zr/CaO catalyst, Li E et al. reacted canola oil with Mg-Co-Al-La HDL catalyst, then Stamenković et.al. was successfully produced biodiesel by using sunflower oil with Ca(OH)$_2$ catalyst, and by using HPA catalyst, Kiakalaieh-Talabian, Amin et al. showed that waste cooking or used cooking oil was also eligible to be produced as a biodiesel feedstock. All these reports was been taken, according to the literature of biodiesel kinetics [5].

There are several explanations why it occurs in that law: (1) the rate of reactions depends only on the isolated reactant (independent of excess of reactant concentration); (2) the difference in gibbs free energy (ΔG) = zero; (3) the gradient or slope of the -ln (1–x) vs time curve produced shows the reaction rate constant.

Some researchers in the biodiesel field performed a numerical process for that order by using response surface methodology (RSM) method, whilst another did it by using computational fluid dynamic (CFD) method. The same thing between them is the iteration for all transesterification variable and its parameter as a three-step reaction [4, 6, 7] as follows:

$$TG \ + \ R-OH \ \rightleftarrows \ DG \ + \ FAME;$$

$$DG \ + \ R-OH \ \rightleftarrows \ MG \ + \ FAME;$$

$$MG \ + \ R-OH \ \rightleftarrows \ G \ + \ FAME;$$

In some scale biodiesel research, both methods are suitable. However, in another scale of research, a simple model or method is more needed without removing the substance of the kinetics.

Based on this background, we simply made a novel model to find the optimal parameters for biodiesel transesterification from oil feedstock by determining the best conversion or yield gained at various temperatures. The s-curve will eliminate redundancy of trial-error time when finding out an optimum reaction temperature. All of these were done based on two-hour experimental data which was obtained from our trustworthy source [6] with a numerical method whereas the study determined an optimum percentage of catalyst and the ratio of used cooking oil with methanol was 10 % wt and 1 : 70, respectively.

RESEARCH METHODOLOGY

We made biodiesel conversion kinetics (s-curve) by using MATLAB application. Our two-hour experimental data was obtained by a formula from previous experimental data so it was divided into three-time data which are 0.5, 1, and 2 h reaction time. Then, it was processed numerically. We also presented curves that are required before making s-curve. The numerical methods we used are as follows: (1) Linear regression (curve fitting); and (2) The ordinary differential equation.

The independent parameters at the model are mixer rpm, % catalyst mass, and molar ratio methanol to oil. Meanwhile, the dependent parameter is temperature. The variables determined in this simulation is reaction time.

With the determination of time, an optimum yield (biodiesel conversion) is also determined. It was done according to the following formula [3, 8]:

$$Y = 1 - e^{-k't^n} \tag{1}$$

where, Y = yield or the volume fraction of biodiesel conversion at a defined temperature;

t = time (hour);

k' = reaction rate constant;

n = reaction order.

The ordinary differential equation with a numerical method was used as a solution to Equation 1, based on the formula:

$$\frac{dY}{dt} = f(t, Y) \tag{2}$$

Therefore:

$$\frac{dY}{dt} = f(t, Y) = k' \, e^{-k't}$$

Reaction rate constant was determined as a slope of the linear equation according to Equation 1 with pseudo-first order, therefore :

$$Ln\,(\,1{-}Y\,) \quad = -k'\,t$$
$$-\,Ln\,(\,1{-}Y\,) = k'\,t$$

Relationship or influence of variables x-axis and y-axis on trendline is known as the correlation coefficient or R2 which show the accuracy of data, hence [9] :

$$R^2 = \frac{\sum_{1=1}^{n}(y_i - a_0 - a_1\,x_i)^2}{\sum(y_i - \bar{y})^2} \tag{3}$$

whereas the numerator shows a sum of squares between the data and the model; and the denominator shows a sum of the squares of the y component between data and model.

We determined three reaction temperatures in making this biodiesel reaction model. The reaction rate constant that have been obtained for each temperature was brought to further step, that was linear regression curve to determine Activation Energy (Ea) needed for making a two-hour conversion for each reaction temperature, based on Arrhenius equation [10] below:

$$k' = A \; e^{-\frac{Ea}{R\,T}} \tag{4}$$

where, k' = as Equation 1;

Ea = activation energy (J/mol);

R = ideal gas (8,314 J/mol K);

T = reaction temperature (K);

A = collision Factor or Pre-Exponential Factor (constant);

It was be processed whilst making of s-curve model and its analysis be processed simultaneously.

RESULTS AND DISCUSSION

Biodiesel Yield/Conversion Data

We obtained the two-hour yield data of biodiesel transesterification using used cooking oil with HPA catalyst by following defined parameters: 10 percent of solution weight for catalyst dosage, the ratio of used cooking oil with methanol 1:70 and 300 rpm stirring speed, as shown in Table 1. From Table 1, it shows that the trend of yield or biodiesel conversion was gradually growing based on a two-hour reaction at each temperature.

Numerical Method Steps

We processed the data at each temperature with a numerical method to produce a linearization curve to obtain k' value as show in Fig. 1. From numerical data processing that represented in Fig. 1, we obtained the slope value or reaction rate constant (k') as follows: for T1 the value of k'1 = 0.0943 with accuracy R2 = 0.99, for T2 the value of k'2 = 0.1471 with accuracy R2 = 0.99 and for T3 the value of k'3 = 0.1057, with accuracy R2 = 0.99. The trend was fit with a first-order reaction which said that reactant concentration was directly proportional to reaction rate [11] as shown in the formula :

$$r = k'[C_a]^m[C_b]^n$$

where r means reaction rate (mol dm^{-3} s^{-1}), [C] means the concentration of the reactant (mol dm^{-3}), k' and m (or n) means reaction rate constant and reaction order, respectively. In this transesterification, as we stated above that reaction occurred in first-order, so the concentration of methanol (expressed in $[C_b]$) be considered constant during reaction whilst $[C_a]$ as the concentration of used cooking oil acted the other way around.

After we made a linearization that produces reaction rate constant, the next step was formation making between ln k' with 1/T within a curve to determine activation energy (Ea) and collision factor (A) based on Equation 4, therefore :

$$\text{Ln } k' = \ln A - \frac{Ea}{R\,T}$$

Figure 2 shows that slope in the graph means Ea/R so we determined the value of Ea and A, which are 1.126 kJ/mol and 1.676, respectively. This value was definitely different from our source before because we measured within two-hour experimental data, while previously, it was measured within 14 h of experimental data. The less value showed that a collision between reactant particles started to increase over time, so do the value of energy for changing into a product expressed by Ea.

TABLE 1. Transesterification of used cooking oil with HPA catalyst - yield data.

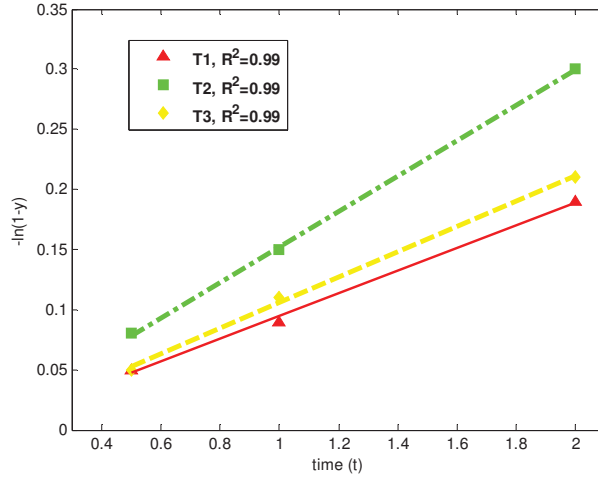| T (Kelvin)	t (hr)	Y
333	0.5	0.0461
	1	0.09
	2	0.1719
338	0.5	0.073
	1	0.1407
	2	0.2615
343	0.5	0.0521
	1	0.1016
	2	0.1928

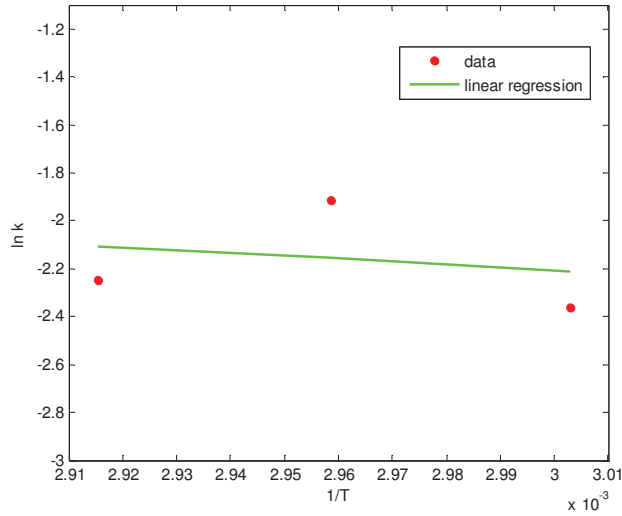**FIGURE 1.** Linear relationship to determine k'.

FIGURE 2. Linear relationship to determine Ea and A.

Further discussion was the s-curve diagram, where the solution was referred to Equation 1 and Equation 2. We determined the time interval from zero until 100 (hours) and put a starting value y = zero (0), so we got a graph of Y vs log (t) as shown in Fig. 3.

In the modeling (as seen in Fig. 3), it was reported that at T2 = 338 K (65 °C) conversion of biodiesel products or yield of the transformation results is the most optimal among the other curves because for the minimum reaction time it can produce the highest yield. Based on these experimental datas and the s-curve model, an experimental within T2 temperature was deserved to be continued until finish. Compared to the previous numerical model at the same T2 which got maximum conversion within 14 h by RSM [5], hence we broke down our numerical iteration within T2, as given in Table 2.

The Table 2 shows that the value within 14 h (87.24 %) was close to the RSM method which obtained 87.98 %. The curve in Fig. 3 also shows that in the process to achieve the conversion of biodiesel product or the yield that is determined, i.e. 96.5 % and 100 %, this simulation calculated that the reaction time required is 22.79 h and 46.95 h numerically. Since the product came from an immiscible solution and according to various experimental reports [5, 11, 12], a 100 % yield was rarely happened. However, it is still important to be considered within this model.
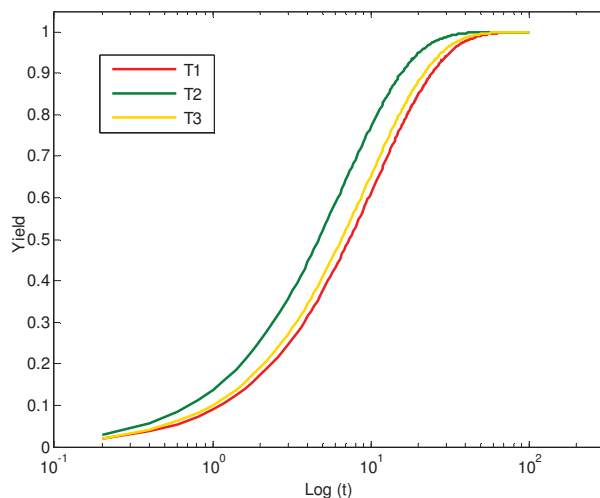
FIGURE 3. The s-curve model

TABLE 2. Iteration data within T2

Time (hr)	Yield (% vol.)
0	0
1	0.1368
2	0.2549
3	0.3568
4	0.4448
5	0.5207
6	0.5863
7	0.643
8	0.6919
9	0.734
10	0.7704
11	0.8017
12	0.8288
13	0.8522
14	0.8724

CONCLUSION

From the s-curve model it was proven that a brief experimental data with an ordinary numerical method or small computation analysis can be used as a novel biodiesel transesterification model to obtain the optimum temperature for the best yield, reaction time to obtain 100 % yield, and reaction time to obtain a determined yield. The s-curve model can predict which temperature parameter is the most optimum to be carried out as a further step or a stage production.

ACKNOWLEDGMENTS

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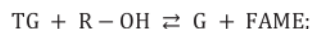
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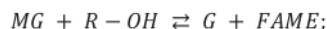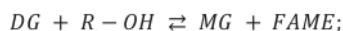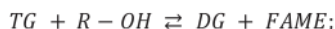
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With the determination of time, an optimum yield (biodiesel conversion) is also determined. It was done according to the following formula [3, 8]:

$$Y = 1 - e^{-k't^n} \tag{1}$$

where,   Y   = yield or the volume fraction of biodiesel conversion at a defined temperature;
       t   = time (hour);
       k'   = reaction rate constant;
       n   = reaction order.

The ordinary differential equation with a numerical method was used as a solution to Equation 1, based on the formula:

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Therefore:

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Reaction rate constant was determined as a slope of the linear equation according to Equation 1 with pseudo-first order, therefore :

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$$k' = A \, e^{-\frac{Ea}{RT}} \tag{4}$$

where,   k'   = as Equation 1;
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It was be processed whilst making of s-curve model and its analysis be processed simultaneously.

RESULTS AND DISCUSSION

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We processed the data at each temperature with a numerical method to produce a linearization curve to obtain k' value as show in Fig. 1. From numerical data processing that represented in Fig. 1, we obtained the slope value or reaction rate constant (k') as follows: for T1 the value of k'1 = 0.0943 with accuracy R2 = 0.99, for T2 the value of k'2 = 0.1471 with accuracy R2 = 0.99 and for T3 the value of k'3 = 0.1057, with accuracy R2 = 0.99. The trend was fit with a first-order reaction which said that reactant concentration was directly proportional to reaction rate [11] as shown in the formula :

$$r = k'[C_a]^m[C_b]^n$$

where r means reaction rate (mol dm^{-3} s^{-1}), [C] means the concentration of the reactant (mol dm^{-3}), k' and m (or n) means reaction rate constant and reaction order, respectively. In this transesterification, as we stated above that reaction occurred in first-order, so the concentration of methanol (expressed in $[C_b]$) be considered constant during reaction whilst $[C_a]$ as the concentration of used cooking oil acted the other way around.

After we made a linearization that produces reaction rate constant, the next step was formation making between ln k' with 1/T within a curve to determine activation energy (Ea) and collision factor (A) based on Equation 4, therefore :

$$\text{Ln } k' = \ln A - \frac{Ea}{RT}$$

Figure 2 shows that slope in the graph means Ea/R so we determined the value of Ea and A, which are 1.126 kJ/mol and 1.676, respectively. This value was definitely different from our source before because we measured within two-hour experimental data, while previously, it was measured within 14 h of experimental data. The less value showed that a collision between reactant particles started to increase over time, so do the value of energy for changing into a product expressed by Ea.

TABLE 1. Transesterification of used cooking oil with HPA catalyst - yield data.

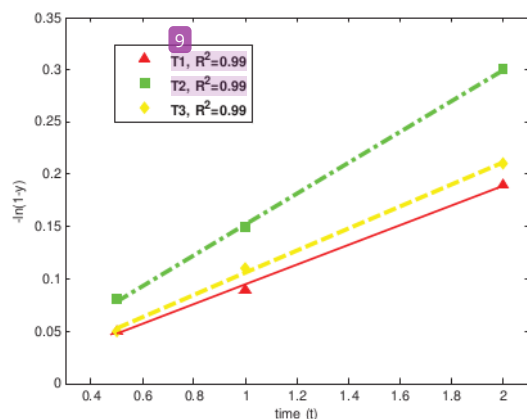| T (Kelvin)	t (hr)	Y
333	0.5	0.0461
	1	0.09
	2	0.1719
338	0.5	0.073
	1	0.1407
	2	0.2615
343	0.5	0.0521
	1	0.1016
	2	0.1928

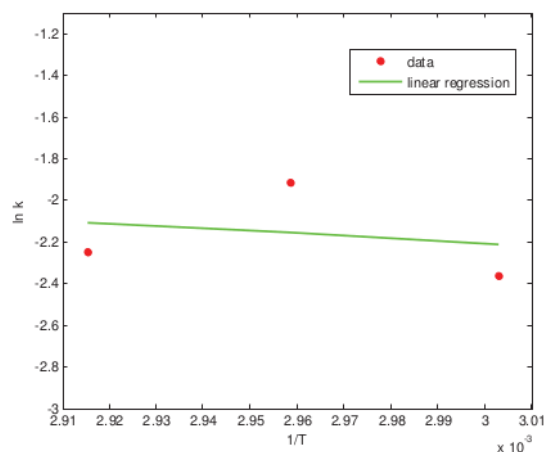**FIGURE 1.** Linear relationship to determine k'.

FIGURE 2. Linear relationship to determine Ea and A.

Further discussion was the s-curve diagram, where the solution was referred to Equation 1 and Equation 2. We determined the time interval from zero until 100 (hours) and put a starting value y = zero (0), so we got a graph of Y vs log (t) as shown in Fig. 3.

In the modeling (as seen in Fig. 3), it was reported that at T2 = 338 K (65 °C) conversion of biodiesel products or yield of the transformation results is the most optimal among the other curves because for the minimum reaction time it can produce the highest yield. Based on these experimental datas and the s-curve model, an experimental within T2 temperature was deserved to be continued until finish. Compared to the previous numerical model at the same T2 which got maximum conversion within 14 h by RSM [5], hence we broke down our numerical iteration within T2, as given in Table 2.

The Table 2 shows that the value within 14 h (87.24 %) was close to the RSM method which obtained 87.98 %. The curve in Fig. 3 also shows that in the process to achieve the conversion of biodiesel product or the yield that is determined, i.e. 96.5 % and 100 %, this simulation calculated that the reaction time required is 22.79 h and 46.95 h numerically. Since the product came from an immiscible solution and according to various experimental reports [5, 11, 12], a 100 % yield was rarely happened. However, it is still important to be considered within this model.
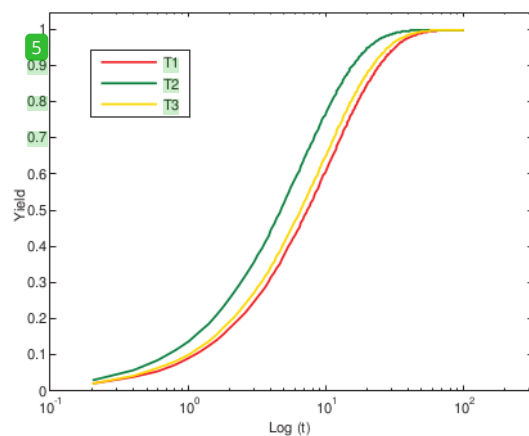
FIGURE 3. The s-curve model

TABLE 2. Iteration data within T2

Time (hr)	Yield (% vol.)
0	0
1	0.1368
2	0.2549
3	0.3568
4	0.4448
5	0.5207
6	0.5863
7	0.643
8	0.6919
9	0.734
10	0.7704
11	0.8017
12	0.8288
13	0.8522
14	0.8724

CONCLUSION

From the s-curve model it was proven that a brief experimental data with an ordinary numerical method or small computation analysis can be used as a novel biodiesel transesterification model to obtain the optimum temperature for the best yield, reaction time to obtain 100 % yield, and reaction time to obtain a determined yield. The s-curve model can predict which temperature parameter is the most optimum to be carried out as a further step or a stage production.

ACKNOWLEDGMENTS

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