Comparative Study of the Chemical Kinetics of Two Catalysts Used for Esterification of Sludge Palm Oil

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*Abstract – Chemical kinetics study was carried out for batch esterification process. Reactant concentration (FFA) as function of time was plotted according to first and second order equations in order to study the catalytic activities of both toluene-4-sulfonic monohydrate acid (PTSA) and sulfuric acid. Pretreatment of Sludge Palm Oil (SPO) by esterification reaction was found to be a second order reaction. Sulfuric acid showed higher catalytic activity than PTSA. The rate constant K of using PTSA was 0.9 * 10^{-3} min^{-1} while K of using sulfuric acid was 2* 10^{-3} min^{-1}.*

I. INTRODUCTION

Biodiesel made from renewable biological sources such as vegetable oils and animal fats which are defined as substitute for or an additive to diesel fuel that are derived from the oils and fats of plants and animals. Chemically according to the American society for testing and materials (ASTM), it is defined as "monoalkyl esters of long chain fatty acids derived from a renewable lipid feedstock such as vegetable oil or animal fat" [1]. Biodiesel is a biomass-derived fuel that is considered to be one of the most promising petroleum diesel fuel substitutes [2].

Biodiesel has many merits as an alternative, renewable, non-toxic, biodegradable and environment friendly fuel [3]. Recently biodiesel has received increased attention because of increases in crude oil prices, limited resources of fossil oil and environmental concerns. There has been a renewed focus on vegetable oils and animal fats to make biodiesel fuels [4]. Biodiesel production from abundant bio-sources has drawn the attention of the academic as well as the industrial community in recent years [5].

Ones the raw material is available the opportunity of scaling up the process is very promising to produce beneficial products. The successful design of industrial reactors with the reliability of experimentally determined parameter is used in scale up calculations. Consequently, it is imperative to design equipment and experiments that will generate accurate and meaningful in terms of life time work of equipment and high selectivity of product [6]. However, choice of reactor type should be made in the early stage of process and catalyst development. It should consider the kinetic rates and their dependence on temperature and pressure, the transport effects on rates and selectivity, the flow pattern effect on yield and selectivity. First and second order reactions are the most common reaction types in the reaction chemistry and especially in biodiesel production [7]. Based on literature review, esterification reaction usually exists in first and second order reactions [8].

In this study, first and second order reactions were examined for production of biodiesel from SPO by esterification process. Esterification process using PTSA and sulfuric acid was applied in order to compare the catalytic activity in the reaction.

II. RESULTS AND DISCUSSION

A. The kinetic Analysis of Experimental data

A more precise meaning of the term rate of reaction, defined as how fast the reactant changes with time, can be illustrated on graphs of concentration versus time. The initial rate is a very important quantity in kinetics, especially for complex reactions involving many steps where secondary reactions and products of reaction may affect the rate [9]

B. Deverative of First Order Reaction for pretreatment of SPO

A first order reaction is a reaction whose rate depends on the reactant concentration raised to the first power [10]. In a first order reaction of the type

A $\longrightarrow$ product or FFA $\longrightarrow$ FAME
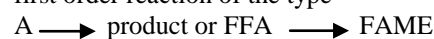
The rate is

$$\text{Rate} = -\frac{\Delta[FFA]}{\Delta t} \qquad (1)$$

From the rate law,

$$\text{Rate} = K[FFA] \tag{2}$$

In order to obtain the units of K for this rate law, then

$$K = \frac{rate}{[FFA]} = \frac{M/time}{M} = \frac{1}{time}$$

Combining Equation (1) & (2) for the rate of reaction

$$-\frac{\Delta[FFA]}{\Delta t} = K[FFA] \tag{3}$$

In differential form, Equation (3) becomes

$$-\frac{d[FFA]}{dt} = K[FFA] \tag{4}$$

Rearranging the Equation (4)

$$\frac{d[FFA]}{[FFA]} = -Kdt \tag{5}$$

In kinetics the change in concentration with time is followed from the start of the reaction, $[FFA]_0$ at t = 0 to $[FFA]_t$ at time t. These are the limits between the integral which is taken. However, Integrating Equation (5) between t = 0 and t = t gives

$$\int_{[FFA]_o}^{[FFA]_t} \frac{d[FFA]}{[FFA]} = -K\int_o^t dt \tag{6}$$

$$\ln[FFA]_t - \ln[FFA]_0 = -Kt \tag{7}$$

Mathematically Equation (7) can be written as follows:

$$\ln\frac{[FFA]_t}{[FFA]_0} = -Kt \tag{8}$$

Equation (7) can be rearranged as follows

$$\ln[FFA]_t = -Kt + \ln[FFA]_0 \tag{9}$$

Equation (9) has the form of the linear equation y = m x + b, in which m is the slope of the line that is the graph of the equation:

$$\ln[FFA]_t = (-K)(t) + \ln[FFA]_0 \tag{10}$$

$$y = m \quad x + b$$

For a first order reaction, a plot of ln $[FFA]_t$ versus t (y versus *x*), should have a straight line with a slope equal to ($-K$) and intercept equal to (ln $[FFA]_0$).

C. Deverative of Second Order Reaction for pretreatment of SPO

A second order reaction is a reaction whose rate depends on the concentration of one reactant raised to the second power or on the concentration of two different reactants, each raised to the first power [10].

2FFA $\longrightarrow$ product
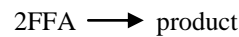
Where Equation …(1)

$$\text{Rate} = -\frac{\Delta[FFA]}{\Delta t} \tag{1}$$

From the rate law,

$$\text{Rate} = K[FFA]^2 \tag{11}$$

Units of K can be obtained by writing

$$K = \frac{rate}{[FFA]^2} = \frac{M/time}{M^2} = \frac{1}{M.time}$$

Combining Equations for the rate of reaction

$$-\frac{\Delta[FFA]}{\Delta t} = K[FFA]^2 \tag{12}$$

In differential form, Equation (12) becomes

$$-\frac{d[FFA]}{dt} = K[FFA]^2 \tag{13}$$

Rearranging the Equation (13)

$$\frac{d[FFA]}{[FFA]^2} = -Kdt \tag{14}$$

Integrating Equation (14) between the limits $[FFA]_0$ and $[FFA]_t$, and t = 0 and t, gives

$$\int_{[A]_o}^{[A]_t} \frac{d[FFA]}{[FFA]^2} = -K\int_o^t dt \tag{15}$$

Standard integrals:

$$\int_{X_o}^{X_t} \frac{dX}{X^2} = -\frac{1}{X_t} + \frac{1}{X_0}$$

Then this Equation can be solved as follows:

$$-\frac{1}{[FFA]_t} + \frac{1}{[FFA]_0} = -Kt \qquad (16)$$

Rearranging the Equation (16)

$$\frac{1}{[FFA]_t} = \frac{1}{[FFA]_0} + Kt \qquad (17)$$

Equation (17) has the form of the linear equation y = m x + b, in which m is the slope of the line that is the graph of the equation:

$$\frac{1}{[FFA]_t} = K(t) + \frac{1}{[FFA]_0} \qquad (18)$$

$$y \ = \ m \ \ x \ + \ b$$

For a second order reaction, a plot of $\frac{1}{[FFA]_t}$ versus t (y

versus *x*), should have a straight line with a slope equal to

(K) and intercept equal to $\frac{1}{[FFA]_0}$.

The results of kinetics study of both catalysts were compared in order to investigate and select the optimum acid catalyst for esterification process. Consequently, based on optimum conditions of selected acid catalyst the treated SPO was prepared for further optimization of transesterification process.

During esterification using sulfuric acid the FFA content sharply decreased from 27.6% to 17.1% in the first one minute. FFA content becomes saturated at 90 min up to 200 min. While, the results of using PTSA showed that the FFA content decreased sharply from 27.6% to 18.1% in one minute at the same time the concentration of the reactants decreases and it becomes saturated at 100 min until 200 min.

The finding elucidate clearly that reduction of FFA content as well as the conversion of FFA to FAME using sulfuric acid was higher than using PTSA. Data of FFA content using sulfuric acid at different reaction times was then used to determine the order of reaction. For a first order reaction, if a plot of ln $[FFA]_t$ versus t (y versus *x*) has a straight line with a slope equal to $(-K)$ and intercept equal to (ln $[FFA]_0$), then the reaction will be considered as first

order reaction. Figure 1 shows the plot of ln $[FFA]_t$ versus time using sulfuric acid and PTSA.

A

B
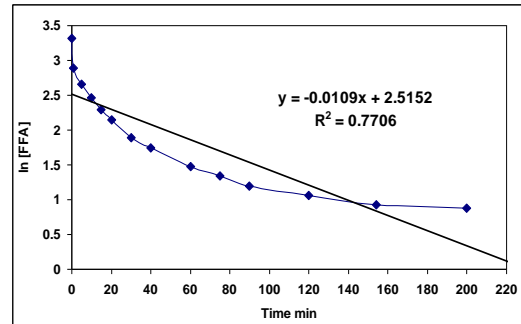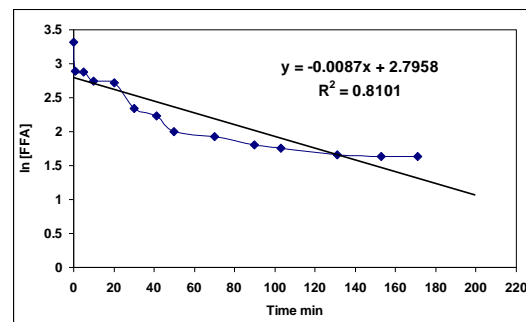
Figure 1: Plot of ln $[FFA]_t$ versus time using (A) sulfuric acid; and (B) and PTSA

For sulfuric acid, the regression coefficient (R^2) was 0.7706, and this value indicates that the theoretical FFA content calculated from corresponding regression equation does not fit with experimental values of FFA content. Hence, esterification reaction using sulfuric acid does not fit the first order model.

Similarly, first order reaction was studied for PTSA catalyst in esterification reaction of SPO. As shown in Figure 1 the R^2 for PTSA catalyst was 0.8101 indicating the esterification reaction of using PTSA does not fit first order model as well. The finding showed that esterification reaction for both acids (sulfuric acid and PTSA) in pretreatment of SPO were not first order reactions. The data were then tested using second order reaction model. For a second order reaction, a

plot of $\frac{1}{[FFA]_t}$ versus t (y versus *x*), should yield a straight
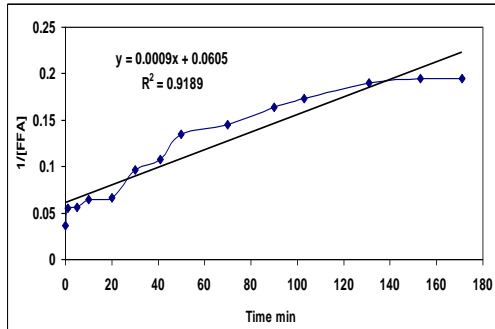
line with a slope equal to (K) and intercept equal

to $\frac{1}{[FFA]_0}$ as shown in Figure 2. Thus, the calculation of

the *K* can be obtained from the slope of this plot. Figure 2(a) shows the examination of R^2 using sulfuric acid in the esterification reaction of SPO.
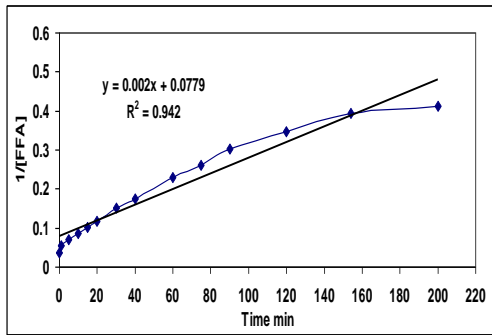
a

b

Figure 2: Plot of $1/[FFA]_t$ versus time using (a) sulfuric acid; (b) PTSA

As shown in Figure 2(a) the R^2 when sulfuric acid was used corresponds to 0.942. Value of R^2 indicates that the calculated FFA content obtained from corresponding regression equation fitted with experimental values of FFA content. K can be calculated based on the liner equation which was obtained from Figure 2(a):

$Y = 0.002X + 0.0779$

$R^2 = 0.942$

Where K using Equation (18):

K= 0.002 the unit of this value as below:

$$K = \frac{rate}{[FFA]^2} = \frac{m/m/time}{(m/m)^2} = \frac{1}{time}$$

Then, pretreatment of SPO by esterification reaction using

sulfuric acid has a rate constant $K = 2 * 10^{-3}$ min^{-1}

As shown in Figure 2(b) the R^2 when PTSA was used corresponds to 0.9189. The liner equation which was obtained from Figure 2(b) is below:

$Y = 0.0009X + 0.0605$

$R^2 = 0.9189$

Where K using second order equation

K= 0.0009 m.m^{-1}.min^{-1}

Then, pretreatment of SPO by esterification reaction via PTSA catalyst has rate constant $K = 0.9 * 10^{-3}$ min^{-1}. The

finding shows that the K of reaction using sulfuric acid was double K of using PTSA catalyst.

III. CONCLUSION

It can be concluded that using strong mineral acids such as sulfuric acid has higher catalytic activity in terms of reduction of FFA and conversion of FFA to FAME than strong organic acids such as PTSA catalyst. The pretreatment of SPO by esterification reaction using sulfuric acid and PTSA catalyst were found to be second order reaction. K of using sulfuric acid in esterification reaction of SPO was double than K of using PTSA catalyst. Kinetically, using sulfuric acid in pretreatment of SPO by esterification reaction is better than using PTSA catalyst.

IV. ACKNOWLEDGEMENTS

V. REFERNCES

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