Kinetic Formation of Tetraester Simulation from Secondary Data

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Abstract - **Transesterification is defined as a process that transforms an ester into a new ester through modification of the alkyl group. In this process of transesterification of the plant oils, it can produce a mixture of multiple FA alkyl esters by reacting the plant oils through many kinds of higher and lower chain length alcohol[1]. The objectives of this research were to study the effect of stirring rate on kinetic formation of tetra ester using the secondary data and to determine the effect of stirring rate on kinetic rate constant. Because of the unavailable of the literature on the study of pentaerythritol ester from transesterification of POME, the research will only use the secondary data as a basis of the research. The study will be using "Mat Lab" programmer to do the simulation of the process. The Matlab is used to study the effect of stirring. The parameter in this study is the speed of the stirrer. There are 3 readings that will be tested, 300 rpm, 600 rpm, and 900 rpm. The rate constant, k will be calculated based on the overall stoichiometric equation. As a result of the study, the kinetic constant is increasing as the stirring rate increased, and the rate of disappearance of PE is faster as the time increased. As a conclusion, the model equation developed can be used to determine the rate constant at the different stirring rate for the transesterification reaction at 160C.**

Keywords— **Pentaerythritol; POME; Kinetic constant; rate.**

INTRODUCTION

It is estimated that regarding 500% of all the oil used winds up within the surroundings.[2] Petroleum-based lubricants, that are the leading variety of base oil utilized in this business, are poorly degradable and represent an environmental hazard when discharged. This represents a powerful incentive to produce lubricants that are biodegradable. The bio-lubricant industry is growing based on these pressures, environmental issues, and sustainability. Bio-lubricants could also be defined usually as materials that are based on biodegradable and renewable base stocks[3].

There were many studies that had been made on producing the bio-lubricant. The good of the bio-lubricant had been proving in the previous study. For instance, vegetable oil-based lubricants (pure or artificially adjusted vegetable oils) are found to have ground-breaking lubricity than mineral-based oil particularly with respect to the boundary of the lubricant routine as announced in a few investigations [4]. This is for the most part since fatty acid (FA) particles inside the vegetable oils can respond with metal surfaces to create low shear quality metallic soap layer.

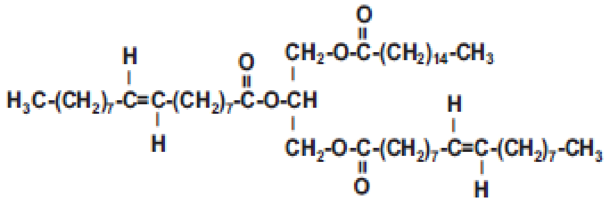

Figure 1: Molecule of a standard di-oleyl palmitoyl glycerol

Vegetable oils have chain length ranges from C12 to C22 that shown in figure 1. About 85% weight of its are made of the fatty acid[5]. There are three fatty acids that vary between feedstock. They play an important role in determining the properties of the oil. Double bonds in the cis conformation are displayed by these fatty acids and separated by one of the methylene group. The number of double bonds and the chain length are the main variables among the fatty acids. According to the previous research, the longer the length of chain the higher the melting point and the viscosity. But, the corresponding of the higher double bond resulting to lower the melting point, decreased the viscosity and decreased thermo-oxidative stability[5]. Other than that, monounsaturated fatty acids have been found to have a good balance of low melting point with good thermos-oxidative stability and viscosity[6]. Feedstock that has high monounsaturated fatty acids, such as oleic and palmitoleic acid contents are generally preferred and pursued.

There are several factors that can affect the transesterification process. One of the factors that can affect the transesterification process is the type of catalyst used in the process. In the previous study, based catalyzed is used for the experiment because by using the base-catalyzed in the process, the reaction on vegetable oils will take at a quicker rate of reaction as compared to acid-catalyzed reaction[7]. Other than that, the temperature of the reaction can affect the process. This study is using a constant temperature 160ºC. Other factors that can affect the transesterification process are reaction rate and the reactants (substrate molar ratio). The last factor that can affect this process is the intensity of mixing. So, this research is to study the kinetic formation of tetraester using simulation from secondary data through the effect of mixing.

In the transesterification process, there is a two-phase liquid system that is forming from the reactants. The reaction is called the diffusion-controlled. A slow rate on the phases resulted from poor diffusion. Methyl ester acted as a mutual solvent for the reactants. It eventually produces a single phase system. This reaction had been validated experimentally when the samples are settling by gravity in the slow rate area. A study by (Noureddini and Zhu 1997)[8] on transesterification of soybean. From the experiment, it summarizes that the delay or slow rate region is a function of mixing intensity at the constant reaction temperature.

Other than that, the study showed that the mixing effect is most important during slow rate area of the process. The mixing becomes insignificant when the single phase is established. The reaction rate is influenced by the temperature of the reaction. It revealed that the reduction of the reactants and formation of the products can make it more powerful in reversible reaction reverse reaction later. Equilibium can be reached when the final slow region is formed.

Research had been conducted in the vegetable oils. It shows that modified vegetable oils had good potential to implement adequately as lubricants through chemically and naturally[10]. There are many development and research that had been passed out to ameliorate the chemical characteristics of vegetable oil. This research was carried out so that the researcher will achieve the same with petroleum-based lubricants. There are many processes that can be used to produce biolubricant from vegetable oils. In this study, the transesterification process is used to produce the biolubricant from the vegetable oils.

This research is to study the kinetic formation of tetra ester. This research was being studied because there is no literature available on the study for pentaerythritol ester from transesterification of palm oil methyl ester (POME). The study is specific on one of the characteristic of the product, the kinetic formation. The kinetic reaction is very important in understanding the reaction because they also have practical implications. By understanding how a reaction takes place, many processes and product can be improved. The previous study on the formation of PE ester focused on optimization of reaction parameter and the application of the PE ester in industry. One of the parameters that affected the formation of PE tetra ester is the rate of stirring. Thus, the study on the effect of stirring rate on the kinetic formation of PE ester is required. This research will be the first study on this topic. The hypothesis for this research the will be proven is that as the stirring rate increase, the reaction rate also increasing. When the stirring rate is too high, the reaction rate constant will be decreased.

I. METHODOLOGY

A. *Kinetic Modelling*

Kinetic of transesterification of palm oil-based methyl ester and pentaerythritol (PE) are shown as three dissimilar basic series-parallel reaction mechanisms. This is caused due to the 3 hydroxyl group in PE to be replaced with an ester group that is cleaved from POME. In this study, the reaction yield methanol (M) which is a by-product is negligible since the reaction takes place in the vacuum condition. This study only focuses on the main product which is the tetra-ester only.

Palm oil methyl ester (POME) + Pentaerythritol (PE) $\xrightarrow{K1}$ Monoester (ME) + Methanol [1]

Palm oil methyl ester (POME) + Monoester (ME) $\xrightarrow{K2}$ Diester (DE) + Methanol [2]

Palm oil methyl ester (POME) + Diester (DE) $\xrightarrow{K3}$ Triester (TE) + Methanol [3]

Palm oil methyl ester (POME) + Triester (TE) $\xrightarrow{K4}$ Tetraester (TTE) + Methanol [4]

The overall reaction is given by:

4 POME + PE $\xrightarrow{K}$ TTE + 4 Methanol [5]

There is a K1 in the first reaction that refers to the forward reaction for palm oil methyl ester (POME) and pentaerythritol (PE) to form Pentaerythritol monoester (ME). Then, K2 is referred to as the forward reaction between POME and ME to form pentaerythritol diester (DE). Further reaction, K3 refers to the forward reaction between POME and DE to form the pentaerythritol triester (TE). Lastly, K4 referred to as the forward reaction between POME and TE to form the major product pentaerythritol tetraester (TTE). For this study, the assumption of the reaction is that the process is an irreversible reaction, and methanol in the process is negligible because it is a side product.

B. *Matlab*

In this study, the kinetic models were developed in terms of mass fraction because the composition of each component was measured in concentration during the experiment. The forward reaction between PE and POME to form ME will be expressed in relation between the rate of formation for PE and the significant rate constant in term of concentration. The parameter will be used in the previous study. The resulting kinetics equations in terms of concentration can be solved by using a numerical solution via MATLAB version 7.7[11].

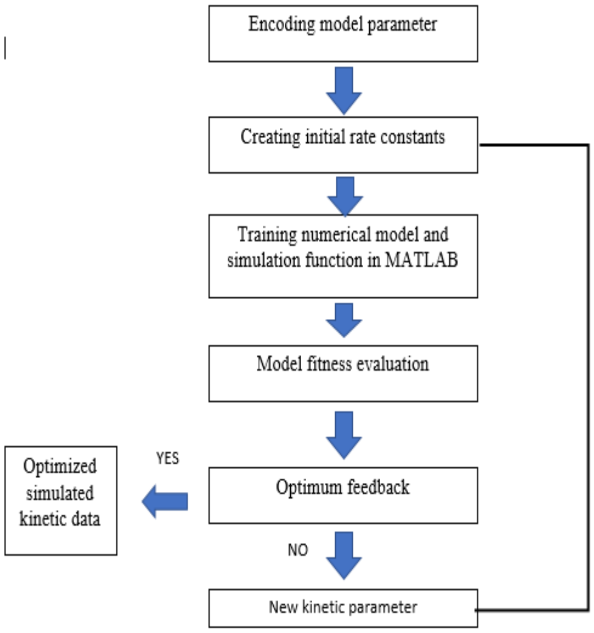

Figure 2: Step of MATLAB Simulation

C. *Determination of Rate Constant*

The intermediate products are the maxima points and the final product at final equilibrium will be determined the rate constants for this study. Data from the previous research will be used for this study to find the rate constant. Data are shown in table 1, table w and table 3 for each parameter of stirring rate.

From equation [4], the rate constant can be calculated using the rate law equation in this experiment. Before starting up the experiment, assumptions must be made. Assume that this experiment is irreversible process and methanol is negligible. The concentration of POME is equal to 1 because the value is too large.

The rate law of the reactions is shown in equation [6], [7] and [8].

$$-r_{PE} = k_1 C_{PE} C_{POME} \quad [6]$$

$$-r_{POME} = k_1 C_{PE} C_{POME} \quad [7]$$

$$-r_{TTE} = -k_1 C_{PE} C_{POME} \quad [8]$$

The limiting reactant of this experiment is the pentaerythritol (PE) and the equation for the limiting reactant is shown below:

$$-r_{PE} = \frac{-dC_{PE}}{t} \quad [9]$$

The equation for the concentration and mass fraction are shown in the equation [10], [11], and [12]

$$C_i = \frac{n_i \rho_T}{m_t} \qquad [10]$$

$$X_i = \frac{n_i mw_i}{m_t} \qquad [11]$$

$$n_i = \frac{x_i m_T}{mw_i} \qquad [12]$$

Combine equation [12] into [10] to calculate the concentration using a mass fraction.

$$C_i = \frac{X_i M_T \rho_T}{M_t MW_i} \qquad [13]$$

$$C_i = \frac{X_i \rho_T}{MW_i} \qquad [14]$$

Combine equation [9] into [6] and insert equation [14] into it to calculate the rate of the equation using a fraction.

$$\frac{-dC_{PE}}{dt} = k_1 C_{PE} C_{POME} \qquad [15]$$

$$\frac{-dX_{PE} \cdot \rho_T}{d_t} = k_1 \cdot \frac{X_{PE} \cdot \rho_T}{MW_{PE}} \frac{X_{POME} \cdot \rho_T}{MW_{POME}} \qquad [16]$$

$$\frac{-dX_{PE}}{d_t} = k_1 X_{PE} \frac{X_{POME} \cdot \rho_T}{MW_{POME}} \qquad [17]$$

Key in all the data for Xpome and Xpe that has been shown in table 1, table 2 and table 3 for the simulation to run. The value of the molecular weight of POME is 847.3 g/mole and the molecular weight of PE is 136.15 g/mol. The total density of the reaction is 0.926 g/mL. For this experiment, assume the value of the kinetic rate constant, k_1 to get the rate of the equation. The value of k_1 must be suitable for the value of the rate equation. The error percentage of the value k_1 must be the lowest one.

II. RESULTS AND DISCUSSION

A. The effect of stirring rate on kinetic formation constant

The result for the effect of stirring rate on kinetic constant is shown in figure 2, figure 3 and figure 4.

Table 4: Kinetic rate constant and error percentage

Stirring Rate (RPM)	Kinetic Rate Constant, k ($M^{-1}min^{-1}$)	Error Percentage (%)
300	11.5	0.72
600	11.6	0.83
900	13.4	0.25

In this work, the experiment was performed at 300, 600 and 900 rpm. Based on the simulation in MATLAB, the kinetic constant for the data of 300 rpm is 11.5 M^{-1} min^{-1}. The error percentage for this kinetic constant value is 0.72%. For the data of 600 rpm, the kinetic constant value is 11.6 M^{-1} min^{-1} and the error percentage is only 0.83%. The kinetic rate constant for the data 900 rpm is 13.4 M^{-1} min^{-1}. It is the highest value compared to another kinetic rate constant value. The error percentage for this value is only 0.25%.

Figure 2, Figure 3 and Figure 4 show the mass fraction profile of disappearance of pentaerythritol (PE). The value of the mass fraction is decreasing along with time. It means that the pentaerythritol is disappearing because of the reaction.

Furthermore, it shows that the kinetic formation constant value is increasing as the stirring rate increased. The rate constant, k, measures how fast a chemical reaction reaches equilibrium assuming the reactants were supplied with enough activation energy to enable the reaction to proceed in the forward direction—reactants to products[12]. The reaction must have some sort of energy input before it can proceed; otherwise, the reactants cannot cross the activation energy threshold and convert to products. The reaction is activated by energy supplied to the reactants by different energy sources. The rate of reaction, the rate constant, and the kinetic energy required for activation of reaction indicate how fast the reaction reaches equilibrium[13].

Other than that, it shows that the kinetic energy increased as the stirring rate increased. From the view of molecular motion, as the stirring rate increase, the molecule move even faster. This resulting from the high activation energy, Ea. the higher the activation energy, the higher the value of the rate constant. According to the Arrhenius equation, the kinetic energy of a molecule is proportional to the velocity of the molecules.

Molecular motion can be defined as the movement of constituent particles or molecules in a certain direction[14]. The molecular motions are affected by heat and temperature. Also, the kinetic rate constant can affect molecular motion. This is because; temperature and kinetic rate constant is the measurement of the average kinetic energy of the molecules and represents the motion of molecules.

Similarly, heat transfers energy among constituent molecules that increase the kinetic energy of molecules. The mathematical relation between kinetic energy and temperature can be shown as below;

$$E = kT \qquad [18]$$

Therefore, when rate constant increases, the kinetic energy also increases; as rate constant increases, more molecules have higher kinetic energy, and thus the fraction of molecules that have high enough kinetic energy to overcome the energy barrier also increases. So, the higher the activation energy, the faster a chemical reaction reaches equilibrium. As the activation increases, the movement of the molecular become more rapidly and the chemical reaction reaches equilibrium will be faster. The value of the rate constant will increase.

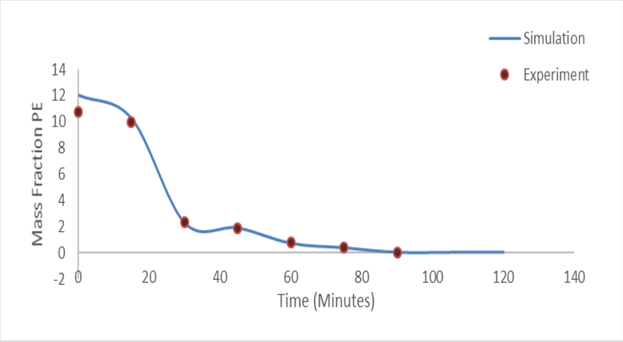

Figure 2: Mass Fraction PE vs Time for 300 rpm

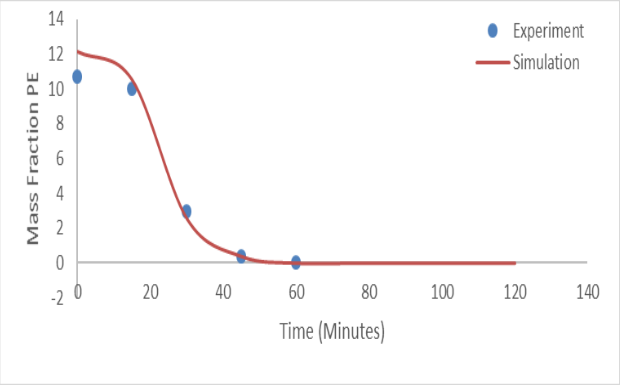

Figure 3: Mass Fraction PE vs Time for 600 rpm

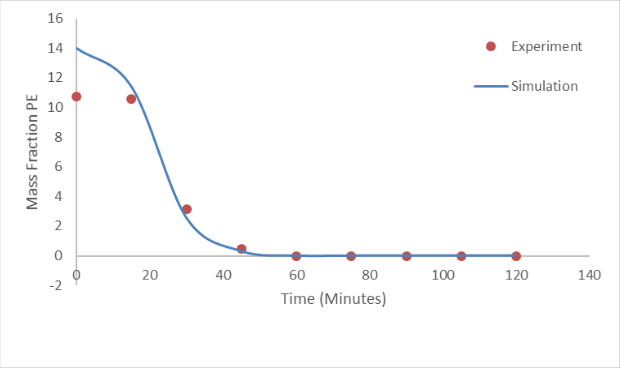

Figure 4: Mass Fraction PE vs Time for 900 rpm

B. *The effect of stirring rate on formation of pentaerythritol tetra ester*

The result of the experiment is shown in figure 4 below. The value of the parameter is 300 rpm, 600 rpm, and 900 rpm.

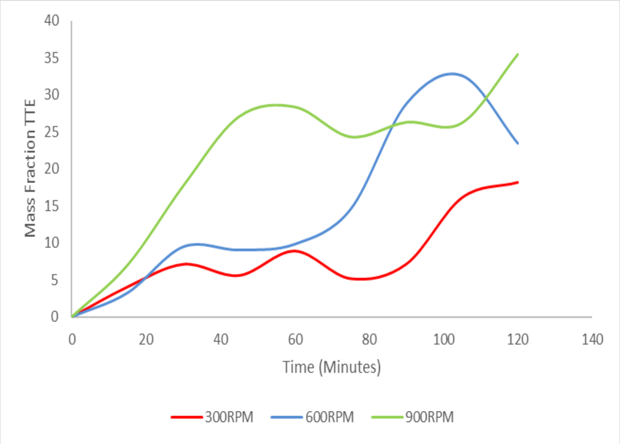

Figure 5: Mass fraction profile for TTE formation

Figure 5 shows that the rate of formation of pentaerythritol tetraester of 900 rpm has the highest mass fraction at the end of the experiment. While the rate on the formation of pentaerythritol tetraester for 300 rpm and 600 rpm almost the same. But, the rate of formation for 300 rpm is the slowest. Mass fraction for the 900 rpm is the highest because the higher the stirring rate of the reaction, the more the molecular movement around the reaction. As the molecules move more rapidly, the kinetic energy will be increased along with the rate of formation increased. In the early of the experiment, there is some error that made the rate of formation for 600 rpm slightly slower than 300rpm. At the time of 105 minutes, it is shown that the mass fraction for 600 rpm suddenly increases drastically. This error may be caused by human error or the condition of the surrounding area. But at the end of the experiment, the result is expected.

III. CONCLUSION

The transesterification reaction kinetics formation of tetra ester (TTE) with pentaerythritol was investigated at three different stirring rates at the same time interval. The fraction data for the transesterification reaction are from the previous study. The kinetic formation constant were analyzed using computer programming called MATLAB. The value of kinetic formation constant was calculated and it seems that the value of each stirring rate of 300 rpm, 600 rpm, and 900 rpm are 11.5$M^{-1}S^{-1}$, 11.6$M^{-1}S^{-1}$, and 13$M^{-1}S^{-1}$. This model fitted very well and showed the least possible error in the experimental data. From the simulation data, it shows that the kinetic formation constant were increasing as the stirring rate increased. The yield for TTE also increased when the rate constant increased. The results were expected as the increased in stirring rate can cause the increased of the kinetic energy that will make the reaction goes faster.

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