# Reversible Reaction Kinetic of Tetraester Formation Simulation from Secondary Data: Effect of Temperature

Fatin Nabila binti Mohd Aripin and Nor Faeqah Idrus

Faculty of Chemical Engineering, Universiti Teknologi Mara

Abstract — Renewable resources such as animal fats and plant oils can produced bio-lubricants that also known as oilbased lubricants whereas this product are environmentally friendly, biodegradable and non-toxic lubricants. A kinetic model that describe chemical transesterification of palm oilbased methyl esters (POMEs) with pentaerythritol (PE) has been developed. The kinetics of the transesterification reaction was modeled as four distinct elementary reversible seriesparallel reaction mechanisms is simplified to the overall equation. The model considers the transesterification reaction to take place in both forward and reverse directions. The resulting kinetics equations were solved using ode45 solver function in MATLAB, where the rate constants of the proposed kinetic model were determined by minimization of errors based on the optimum criteria of statistical analysis and by comparing the component concentrations at maximum and at equilibrium. The optimum temperature at 170°C. The validity of the model was tested by comparing the observed experimental values with the theoretical calculated data. A good correlation between simulated results and experimental data was observed, confirming that the model was able to predict the rate constants with plausible accuracy.

*Keywords:* Palm oil-based methyl esters (POMEs), pentaerythritol (PE), Transesterification, Bio-lubricant.

### I. INTRODUCTION

Renewable resources such as animal fats and plant oils can produced bio-lubricants that also known as oil-based lubricants whereas this product are environmentally friendly, biodegradable and non-toxic lubricants (Chan, et al., 2018). In lubricant production, plant-based oil is one of the potentials to replace the mineral oils since their structure is similar and comes along with the characteristics of being renewables, economic, environmental-friendly and nontoxic (Heikal, et al., 2017).

Regarding to European standards, bio-based carbon content and biodegradability that required for a certified bio-lubricants at least 25% and 60% respectively. There are factors affected the market demand which are government directives, global demand and consumer environmental awareness for lubricants. Bio-lubricant is an alternative way that researchers found to overcome the increasingly worse issue that provide hazardous that required high environmental cost and non-degradable lubricant entering the environment.

Process of transesterification is the main process in biolubricant production. The functions of bio-lubricant are to prevent heat loss and reduce wear resulting from contact of moving surfaces, to prevent corrosion and to reduce oxidation (Cerón, et al., 2018). Bio-lubricant can be described as liquid oils produced from renewable or biomass feed stock that can provide the oil easily biodegradable and harmless to human beings or aquatic habitat due to toxicity.

Other than transesterification process, hydrogenation and epoxidation process also can be applied for lubricant production. This process is the chemical modification due to the production of bio-lubricant have limitations of plant oil. This modification is to produce synthetic ester by enhance the bio-lubricant thermal stability (Resul, et al., 2012).

Reaction kinetics also known as chemical kinetics. Usually, the rate of a chemical reaction has unit of sec<sup>-1.</sup> Development of reaction kinetics was started from the law of mass action and formulated by Peter Waage and Cato Guldberg in 1864. Chemical reaction kinetics is related to the rates of chemical processes. Chemical kinetics is the study of chemical processes and rates of reactions including analysis of conditions that affect the time required of a chemical reaction. The law of mass action states the speed of a chemical reaction is proportional to the amounts of reactants. Factors that affected the reaction kinetics were concentration of reactant, temperature, presence of catalyst, physical state of reactants and pressure.

This study is to determine effect of temperature on the reaction rate constant, k, by using Matlab Software. The process for this research is specifically undergoes the reversible transesterification reaction under vacuum process of palm oil methyl ester, POME from vegetables oil with pentaerythritol, PE to produce pentaerythritol (PE) ester or also known as pentaerythritol (PE) tetraester. However, there are three intermediate products that produce for this

process which are monoester (ME), diester (DE) and triester (TE).

The assumption has been made that the reaction is directly reversible from 4 mol of palm oil methyl ester react with 1 mol pentaerythritol to produce 4 tetraester and 4 mol methanol. Since the reaction is under vacuum condition, the side product that produce is methanol can be neglected. Since this study is about temperature parameter, thus the temperature varies at 140°C, 150°C, 160°C and 170°C.

This research is to study the kinetic formation of tetra ester via reversible transesterification process. Reaction kinetic also known as chemical kinetic. The importance of kinetic is to provide evidence for the chemical process mechanism. From kinetic reaction, the condition of the reaction can be controlled. Then, chemical kinetic is a measurement of how fast reaction occur. In the previous study on the formation of tetra ester, majority the researchers only focusing on optimization of reaction parameter and the application. However, there is no literature available for kinetic study of tetra ester from transesterification process of POME with PE in the previous study. Since temperature is one of the parameters that affected the kinetic formation of tetra ester, thus, specification on this study is focusing the effect of temperature are required. The initial hypothesis has been made for this study which is the higher the temperature resulted an increasing in reaction rate constant, k.

# II. METHODOLOGY

# A. Kinetic Mechanism and Assumption

The kinetic mechanism of the transesterification process to produce tetra ester is described as follows:

 $\begin{array}{l} \text{POME} + \text{PE} \leftrightarrow \text{ME} + \text{Methanol} \\ \text{POME} + \text{ME} \leftrightarrow \text{DE} + \text{Methanol} \\ \text{POME} + \text{DE} \leftrightarrow \text{TE} + \text{Methanol} \\ \text{POME} + \text{TE} \leftrightarrow \text{TTE} + \text{Methanol} \end{array}$ 

Assumptions:

1) Reversible series-parallel reaction mechanism that follows elementary rate law.

2) POME is in excess, thus, the PE becoming the limiting reactant resulted the order for the reaction was second order.3) The by-product of methanol can be neglected since the reaction is done under vacuum condition.

4) Rate law is based on elementary overall stoichiometric equation.

From the mechanisms and assumptions, the overall chemical reaction:

 $4 \text{ POME} + \text{PE} \leftrightarrow \text{TTE}$ 

First step: Postulate the rate law:

 $-r_{PE} = k1C_{PE}C_{POME} - k2C_{TTE}$  $-r_{POME} = k1C_{PE}C_{POME} - k2C_{TTE}$  $r_{TTE} = -k1C_{PE}CP_{OME} + k2C_{TTE}$ 

Based on the rate law, the conclusion that can be made is:

$$-rPE = -rPOME = rTTE$$

Combined the mole balance and rate law:

$$- dC_A/dt = r_A$$

$$dC_{PE}/dt = -k1C_{PE}C_{POME} + k2C_{TTE}$$

Molar concentration:

 $Ci = (ni \times \rho_T) / M_T$  -----(1)

Where:

Ci: molar concentration ni: mole of component  $\rho_T$ : total density  $M_T$ : total mass of mixture

Fraction:

$$Xi = (ni \times MW_i) / M_T$$

 $ni = (Xi \times M_T) / MW_i$ -----(2)

(2) into (1)

$$Ci = (Xi \times \rho_T) / MW_i$$

 $dC_{PE}/dt = -k1C_{PE}C_{POME} + k2C_{TTE}$ 

 $[d(X_{PE} \rho_T) / dt(MW_{PE})] = [(-k_1 X_{PE} \rho_T X_{POME} \rho_T MW_{PE}) / (MW_{PE})$ 

 $MW_{POME}$ ] + [(k2X<sub>TTE</sub>  $\rho_T$ )/MW<sub>TTE</sub>]

 $dX_{PE}/dt = \left[(-k1X_{PE}X_{POME}\rho_T)/(MW_{POME})\right] +$ 

 $[(k2X_{TTE}MW_{PE})/MW_{TTE}]$ 

Where:

X: mass fraction from secondary experimental data  $\rho_T$ : 926g/L MW<sub>PE</sub>: 136g/mol MW<sub>POME</sub>:847g/mol MW<sub>TTE</sub>: 1194g/mol

## B. Matlab Simulation

Determine the initial rate constants from experimental data

- 1) The data of concentration-time obtained from previous study that conducted an experiment.
- 2) Based on the data, graph is plotted by using Matlab.
- 3) Determine the gradient from the plotted curves.

4) Replace the values of obtained from the graph into the mole balance equation to get the rate constant of the reaction k1 and k2.



# III. RESULTS AND DISCUSSION

#### A. Effect of temperature on transesterification process

The reaction temperature of transesterification process between POME and PE to produce TTE was carried out at various temperatures which were 140°C, 150°C, 160°C, 170°C and 180°C. The final composition of TTE product was shown in figure 1. The chart shows that the production of mass fraction of TTE at various temperature with 10°C of temperature interval. Based on the chart, the highest mass fraction of TTE production is indicated at temperature of 170°C which was 0.133178. However, the lowest mass fraction of TTE production is 0.09781 at temperature 140°C. This is because the low temperature tends to reverse the reaction easily. This statement was approved by using another vegetable oil as bio-lubricant feedstock. On the other hand, higher temperature reflected on colour of TTE products due to oil oxidation which turned TTE into dark oil and coke formation will be formed due to catalyst reduction. Increasing the temperature above the optimum temperature also cause reactant volatile substance to vaporize.

Figure 1: Bar Chart of Mass Fraction of TTE vs Temperature



## B. Effect of reaction time at various temperature

gives Reaction time the significant impact in transesterification process. This phenomenon can be shown at the curve figure 2. Regarding to the figure 2, the curve that shows the slowest reaction is at lowest temperature which was 140°C. The optimum curve that found in the figure 3 is at temperature of 170°C that shows the highest mass fraction of TTE at 240 min. However, the highest temperature at 180°C shows that at time 0-30min, it increased rapidly, but at the final time reaction, it did not reach maximum yield compared to the temperature of 170°C. This is may be because the usage of catalyst depends on type, amount and its properties. In order to maximize the reaction rate, there are a few assumptions that are preferred for kinetic model such as used sufficient catalyst to shift the reaction into equilibrium state, thus the catalyst can be ignored and the concentration of catalyst is constant so it can be assumed insignificant.

The occurrence of the reverse reaction of TTE was significant at higher temperatures, hence reducing the overall yield of TTE. This is because, after a certain period of times, the rate of the reverse reaction gradually increased until it attained an equilibrium condition, where the rate of the forward reaction and the rate of the reverse reaction equaled. Consequently, the results indicate that the assumption of irreversible reaction is only applicable for short reaction times and moderate temperatures.



#### C. Effect of rate constant at various temperature

Rate constant k1 and k2 were obtained from simulation of Matlab. Theoretically, k1 is larger than k2 since k2 is rate constant of reversible process. K2 will not be zero because the assumption has been made that methanol was remove via vacuum continuously. K1 and k2 is obtained by performing fit curve that give the smooth curve to the secondary experimental data. Based on the table 1, as temperature increased, the value of k also increased. This is also followed the Arrhenius equation. The optimum of k1 and k2 is 0.160 and 0.180 respectively at temperature of 170°C. However, at the highest temperature which was 180°C, the value of k is decreased from 0.160 to 0.140. This is because, the transesterification process has already achieved the limit, so it deviates the reaction.

Rate constant has relationship between the Arrhenius equation since the factor that affect the Arrhenius equation is temperature. The formula of Arrhenius equation shown as follow:

k=Ae^[-Ea/RT] Where: k: rate constant T: absolute temperature (in kelvin) A: pre-exponential factor Ea: activation energy R: universal gas constant

According to Darnoko and Cheryan, the activation energy that involved in the transesterification process between reaction of palm oil and methanol in the range of 6.4 - 14.7 kcal/mol under atmospheric pressure and at temperature of  $50-65^{\circ}$ C. Since the experiment is carried out under vacuum, the reactions were more sensitive to temperature variation and resulted in higher activation energies.

Temperature, °C	k1	k2
140	0.057	0.048
150	0.070	0.059
160	0.120	0.096
170	0.160	0.180
180	0.140	0.178

Table 1: Table of Value K1 and K2 at different Temperature

# IV. CONCLUSION

A kinetic model describing the process of transesterification between POME and PE to produce TTE via series reaction. The kinetic of the transesterification process was modeled as four distinct elementary reversible series-parallel reaction mechanism. However, the data that were key in in the Matlab is based on overall reversible transesterification reaction. The validity of the model was comparing the observed experimental values with the theoretical calculated data. A good correlation between simulated results and experimental data was observed, confirming that the model is able to predict the rate constants with plausible accuracy.

#### ACKNOWLEDGMENT

Thank you to my supervisor and Universiti Teknologi Mara.

#### References

- [1] Chan, C., Tang, S. W., Mohd, N. K., Lim, W. H., Yeong, S. K., & Idris, Z. (2018). Tribological behavior of biolubricant base stocks and additives. Renewable and Sustainable Energy Reviews, 93, 145-157. doi:10.1016/j.rser.2018.05.024
- [2] Heikal, E. K., Elmelawy, M., Khalil, S. A., & Elbasuny, N. (2017). Manufacturing of environment friendly biolubricants from vegetable oils. Egyptian Journal of Petroleum, 26(1), 53-59. doi:10.1016/j.ejpe.2016.03.003
- [3] Ma, F., & Hanna, M. A. (1999). Biodiesel production: A review1Journal Series #12109, Agricultural Research Division, Institute of Agriculture and Natural Resources, University of Nebraska–Lincoln.1. Bioresource Technology, 70(1), 1-15. doi:10.1016/s0960-8524(99)00025-5
- [4] Archer, S. A., Murphy, R. J., & Steinberger-Wilckens, R. (2018). Methodological analysis of palm oil biodiesel life cycle studies. Renewable and Sustainable Energy Reviews, 94, 694-704. doi:10.1016/j.rser.2018.05.066
- [5] Ghadge, S. V., & Raheman, H. (2006). Process optimization for biodiesel production from mahua (Madhuca indica) oil using response surface methodology. Bioresource Technology, 97(3), 379-384. doi:10.1016/j.biortech.2005.03.014
- [6] Cordero-Ravelo, V., & Schallenberg-Rodriguez, J. (2018). Biodiesel production as a solution to waste cooking oil (WCO) disposal. Will any type of WCO do for a transesterification process? A quality assessment. Journal of Environmental Management, 228, 117-129. doi:10.1016/j.jenvman.2018.08.106
- [7] Zhang, Y. (2003). Biodiesel production from waste cooking oil: 1. Process design and technological assessment. Bioresource Technology, 89(1), 1-16. doi:10.1016/s0960-8524(03)00040-3
- [8] Cerón, A. A., Boas, R. N., Biaggio, F. C., & Castro, H. F. (2018). Synthesis of biolubricant by transesterification of palm kernel oil with simulated fusel oil: Batch and continuous processes. Biomass and Bioenergy, 119, 166-172. doi:10.1016/j.biombioe.2018.09.013
- [9] Resul, M. F., Ghazi, T. I., & Idris, A. (2012). Kinetic study of jatropha biolubricant from transesterification of jatropha curcas oil with trimethylolpropane: Effects of temperature. Industrial Crops and Products, 38, 87-92. doi:10.1016/j.indcrop.2012.01.012
- [10] Ocholi, O., Menkiti, M., Auta, M., & Ezemagu, I. (2018). Optimization of the operating parameters for the extractive synthesis of biolubricant from sesame seed oil via response surface methodology. Egyptian Journal of Petroleum, 27(3), 265-275. doi:10.1016/j.ejpe.2017.04.001
- [11] Ocholi, O., Menkiti, M., Auta, M., & Ezemagu, I. (2018). Optimization of the operating parameters for the extractive synthesis of biolubricant from sesame seed oil via response surface methodology. Egyptian Journal of Petroleum, 27(3), 265-275. doi:10.1016/j.ejpe.2017.04.001
- [12] Aziz, N. A., Yunus, R., Rashid, U., & Syam, A. M. (2014). Application of response surface methodology (RSM) for optimizing the palm-based pentaerythritol ester synthesis. Industrial Crops and Products, 62, 305-312. doi:10.1016/j.indcrop.2014.08.040
- [13] Annisa, A. N., & Widayat, W. (2018). A Review of Bio-lubricant Production from Vegetable Oils Using Esterification Transesterification Process. MATEC Web of Conferences, 156, 06007. doi:10.1051/matecconf/201815606007
- [14] D. Kania, Y. Robiah, O. Rozita, A.R. Suraya, M.J. Badrul. Journal of Petroleum Science and Engineering, 135, 177-184 (2015).
- [15] Panchal, T. M., Patel, A., Chauhan, D., Thomas, M., & Patel, J. V. (2017). A methodological review on bio-lubricants from vegetable oil based resources. Renewable and Sustainable Energy Reviews, 70, 65-70. doi:10.1016/j.rser.2016.11.105
- [16] Jain, S., Sharma, M., & Rajvanshi, S. (2011). Acid base catalyzed transesterification kinetics of waste cooking oil. Fuel Processing Technology, 92(1), 32-38. doi:10.1016/j.fuproc.2010.08.017
- [17] Freedman, B., Pryde, E. H., & Mounts, T. L. (1984). Variables affecting the yields of fatty esters from transesterified vegetable oils.

Journal of the American Oil Chemists Society, 61(10), 1638-1643. doi:10.1007/bf02541649

- [18] Hamid, H. A., Yunus, R., & Choong, T. S. (2018). Utilization of MATLAB to Simulate Kinetics of Transesterification of Palm Oil-Based Methyl Esters with Trimethylolpropane for Biodegradable Synthetic Lubricant Synthesis. Energyo. doi:10.1515/energyo.0022.00007
- [19] Hamid, H. A., Yunus, R., Rashid, U., Choong, T. S., & Al-Muhtaseb, A. H. (2012). Synthesis of palm oil-based trimethylolpropane ester as potential biolubricant: Chemical kinetics modeling. Chemical Engineering Journal, 200-202, 532-540. doi:10.1016/j.cej.2012.06.087
- [20] Kamil, R. N., & Yusup, S. (2010). Modeling of reaction kinetics for transesterification of palm-based methyl esters with trimethylolpropane. Bioresource Technology, 101(15), 5877-5884. doi:10.1016/j.biortech.2010.02.084
- [21] Sulaiman, S.Z., A.L. Chuah and A. Fakhru'l-Razi, 2007. Batch production of trimetylolpropane ester from palm oil as lubricant base stock.. J. Applied Sci., 7: 2002-2005.
- [22] Nurdin, S., Misebah, F. A., Haron, S. F. and Yunus, R. (2015). Transesterification Kinetics of Jatropha Methyl Ester and Trimethylolpropane for Biolubricant Synthesis Using Paphia undulata Shell Waste. J. of Advances in Environmental Biology (AEB)/ISI/SCOPUS, 9 (1), 35-43.
- [23] Yunus, R., Fakhrui-Razi, A., Ooi, T. L., Biak, D. R., & Iyuke, S. E. (2004). Kinetics of transesterification of palm-based methyl esters with trimethylolpropane. Journal of the American Oil Chemists Society, 81(5), 497-503. doi:10.1007/s11746-004-0930-7
- [24] Chang, T., Masood, H., Yunus, R., Rashid, U., Choong, T. S., & Biak, D. R. (2012). Activity of Calcium Methoxide Catalyst for Synthesis of High Oleic Palm Oil Based Trimethylolpropane Triesters as Lubricant Base Stock. Industrial & Engineering Chemistry Research, 51(15), 5438-5442. doi:10.1021/ie2028365