Penerbit
Akademia Baru

Journal of Advanced Research in Materials Science
ISSN (online): 2289-7992 | Vol. 14, No.1. Pages 14-29, 2015

Modeling the Kinetics of Transesterification of Jatropha-based Methyl Esters with Trimethylolpropane

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Abstract – *Modeling transesterification kinetics of trimethylolpropane with jatropha-based methyl esters using acid catalyst had been performed. Nonlinear regression method was used for model development to determine the rate constants for both forward and reverse reactions. The model had previously been validated using data from literature on transesterification of trimethylolpropane with palm-based methyl esters using sodium methoxide catalyst. The model was based on the reverse mechanism of transesterification reactions and describes concentration changes of trimethylolpropane, monoesters and diesters production. The reaction rate constants were determined using MATLAB version 7.8. The rate determining step of transesterification of TMP is favored at higher temperatures, which is typical observation for an endothermic reaction. The developed model was also validated against data from the literature. A reasonable correlation between model simulations and experimental data was observed.*

Keywords: Biodegradable lubricant, Modeling, Transesterification kinetics, Jatropha-based methyl esters

1.0 INTRODUCTION

The detrimental environmental impact of large amounts of lubricants and industrial fluids from mineral oil-based lubricant has become an increasingly important issue [1]. The need for eco-friendly lubricant based on vegetable oil is growing due to advantages such as biodegradability, ecotoxicity, protection of water, nature and soils, excellent lubricity, low volatility, renewability of the source and protection of worker's health. The use of rapidly biodegradable lubricants, vegetable products as well as modified vegetable oil esters, could significantly reduce the environmental pollution compared to mineral oils.

Polyol esters based on vegetable oils have been produced from the transesterification of fatty acids (FA) or FA esters with polyhydric alcohols such as trimethylolpropane (TMP), neopentyl glycol (NPG) and pentaerythritol (PT). Among the polyhydric alcohols, trimethylolpropane is a well known polyhydric alcohols used in lubrication fields [2]. TMP based polyol esters from monocarboxylic acids have better physicochemical properties than conventional minerals oils [3]. Jatropha is a non-edible plant that was recently discovered to have great potential as feedstock for biodiesel and also biolubricant which can be alternative to other plant oil based lubricants as it is non-hazard and biodegradable, thus meeting the criteria of environmentally-friendly product [4]. Consequantly, jatropha oil methyl ester (JOME) was chosen as the starting material in the synthesis of polyol ester. Polyol esters have been utilized as base oil for various types of lubricating oil in various ways [5-8].

Transesterification of methyl esters with trimethylolpropane involve three steps reversible process. Firstly, TMP are converted to monoesters (M) and methanol (Met), which consecutively is converted to diesters (D) and methanol in the second step. In the third step, diester (D) is converted to triesters or TMP ester and methanol [9]. In all these reactions, methanol byproduct are produced and have to be removed to ensure completion of the reaction.

Kinetic data are vital for process assessment and development. Kinetic models are essential in the design of chemical reactors, in the study of chemical reactions and in catalyst development. Several studies on transesterification of methyl esters with trimethylolpropane have recently been published (9,10). Modeling of transesterification kinetic for palm oil methyl esters and trimethylolpropane had been developed using nonlinear regression method [9]. This model predicts both forward and reverse rate constants for the transesterification of methyl ester and polyhydric alcohol. Since mathematical modeling using this nonlinear regression method for transesterification of jatopha-based methyl esters with trimethylolpropane has not been reported yet, in this work, modeling of transesterification kinetics for jatropha-based methyl esters with trimethylolpropane using the mathematical model by acid catalyst was investigated. The reaction rate constants were determined using MATLAB version 7.8 and the ratios of rate constants and activation energy were compared with literature.

2.0 METHODOLOGY

2.1 MATERIALS

Jatropha Oil was purchased from Bionas Sdn Bhd. Potassium hydroxide pellets (purity > 99%), methanol (purity of 99.9%) and sulfuric acid (purity of 97%) were purchased from Merck Darmstadt, Germany. Trimethylolpropane [2-ethyl-2-(hydroxymethyl)-1,3-propanediol] (purity of 98%), N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA), (purity > 99%), ethyl acetate (purity of 99.9%) were obtained from Acros Organics, New Jersey, USA. Reference standards, (purity > 99.5 %) were purchased from Sigma Aldrich Chemicals Co. Steinheim. Sodium sulphate, ACS reagent grade, was obtained from R&M Chemicals.

2.1 EXPERIMENTAL

2.1.1 Reaction conditions for Kinetic Study of Transesterification of Neopentyl Polyols

The kinetic study of transesterification of trimethylolpropane with Jatropha oil methyl ester was performed using method previously described in [9] for determination of rate constants of the reaction. The reaction conditions employed in the kinetic studies are pressure (25 kPa), catalyst (1% H_2SO_4), molar ratio of TMP /FAME (4:1), temperature (423, 433, 443, 453, 463, 473, 483, 513 K), based on method described in [11, 12] for transesterification of trimethylolpropane with Jatropha oil methyl ester (JOME). Calculated amounts of TMP and FAME were added to the reaction flask that was brought to a predetermined temperature using the constant temperature bath. A calculated amount of catalyst was quickly added to the reactants, and timing of the reaction was begun. Samples (0.5 ml each) were removed from the reaction mixture at various intervals, depending upon reaction conditions. The reactions were sampled initially at 5-min intervals, and later samples were taken at 30-min intervals during the course of five hours. Samples were immediately quenched in iced water, thus stopping the reaction. Then the samples were quantitatively analyzed by GC which provides the composition (wt%) of TMP, monoester, diesters and triesters.

2.1.2 Kinetic Modeling

In this work, nonlinear regression had been used for the prediction of rate constants of TMP transesterification for both forward and reverse reactions using Matlab. The model from previous work by Kamil et. al. [9] had been used to predict the kinetics and reaction rates of transesterification of trimethylolpropane (TMP) with Jatropha-based methyl ester. The experimental data were determined from experimental work in this study, based on study by Kamil et. al. [11]. The general mechanism proposed for the transesterification of TMP are composed of a series of reversible formation of neopentyl polyols to monoester, monoesters to diesters, and diesters to neopentyl polyol esters, as shown in Scheme 1.

The transesterification process of trimethylolpropane (TMP) with fatty acid methyl ester (FAME) is modeled as a three-step process (Scheme 1). In the first step, TMP are converted to monoesters (M) and methanol (Met), which in turn is converted to diesters (D) and methanol in the second step. In the third and final step, D is converted to triesters (TE) or TMP ester and methanol. Methanol is a byproduct that is removed to ensure completion of the reaction. The kinetic model adopted in the present work was that, there are six steps in Scheme 1 that are formed from three reversible steps.

$$\text{TMP} + \text{FAME} \xrightarrow{k1} \text{M} + CH_3OH \quad (1)$$

$$\text{M} + CH_3OH \xrightarrow{k2} \text{TMP} + \text{FAME} \quad (2)$$

$$\text{M} + \text{FAME} \xrightarrow{k3} \text{D} + CH_3OH \quad (3)$$

$$\text{D} + CH_3OH \xrightarrow{k4} \text{M} + \text{FAME} \quad (4)$$

$$\text{D} + \text{FAME} \xrightarrow{k5} \text{TE} + CH_3OH \quad (5)$$

$$\text{TE} + CH_3OH \xrightarrow{k6} \text{D} + \text{FAME} \quad (6)$$

The overall reaction is:

$$\text{TMP} + 3\text{FAME} \rightleftharpoons \text{TE} + 3CH_3OH \quad (7)$$

Scheme 1. General mechanism of transesterification of trimethylolpropane (TMP) with fatty acid methyl esters (FAME)

For rate constants determination, differential equations were established by applying rate law in equations (Equation 1) – (Equation 6), for TMP transesterification. All the differential equations of the systems were solved using laplace transformation and the computer simulations were performed using Matlab version 7.8 for transesterification of TMP with JOME. MATLAB program was used to compute the rate constants for each reaction. The Matlab program was written in order to compute the rate constants (k_1, k_2, k_3, k_4, k_5 and k_6) from each particular steps of the transesterification to produce polyol esters. There were two major steps involved in fitting the nonlinear regression models in MATLAB, which involve fitting of the preliminary program and main program. Fitting of nonlinear regression model involves estimation of parameters or initial guess values using toolbox that fits the equation [14]. The values were adjusted so that the curve comes closer to the points [14].

First, fitting of preliminary program involves specific programs which were written to provide estimates of the fitted values for the model from a set of parameter estimates (initial guess values for preliminary program). The program is composed of preliminary programs in which the constants η_i, β_i, α_i ,ω_i and χ_i which correspond to polyol, monoester, diester, triester and byproduct concentration, were calculated. These constants were determined using nonlinear regression by minimizing the standard error of estimate (SEE) or the root-mean-square of residuals for N data points as follows:

$$SEE \quad = \quad \sqrt{\frac{{}^{a}_{N}(C_i - E_i)^2}{N}} \tag{8}$$

Where Ci = f(Ei), Ci = calculated values of the weight% of polyol, monoesters, diesters, triesters and byproduct and Ei = experimental values of the weight % of polyol, monoesters, diesters, triesters and byproduct. A correlation, r >0.9 was achieved for the constants determination at optimum temperature through the adjustment of initial guess values and was used as the basis for calculation of constants at other temperatures. Minimization of errors was initiated by providing initial guesses for each kinetic parameter. The best estimates for nonlinear regression were obtained using toolbox *lsqnonlin* or *fminsearch* from MATLAB.

Second, determination of initial set of parameter estimates for the main program. The initial guess values were selected based on the values that fit the graphs of concentration vs. time for polyol, monoesters, diesters and polyol esters. The main programs are based on the rate of concentration change of neopentyl polyols, monoester and diester which yield the rate constants of each step. The rate constants (k_1, k_2, k_3, k_4, k_5 and k_6) for the forward and reverse reactions were determined using nonlinear regression by minimizing the standard error of estimate (SEE) or the root-mean-square using the selected toolbox.

MATLAB has many built-in functions and toolboxes with curve fitting capabilities. The best estimates for nonlinear regression were obtained using toolbox *lsqnonlin* or *fminsearch* [12, 15]. *fminsearch* is generally referred to as unconstrained nonlinear optimization where it finds the minimum of a scalar function of several variables, starting at an initial estimate. *lsqnonlin* is an optimization toolbox which solves nonlinear least squares problems, including nonlinear fitting problems [14].

Activation energies for different steps were calculated based on Arrhenius equations as shown below,

$$k = Ae^{\frac{-E}{RT}} \tag{9}$$

Where k = rate constant (the unit depends on the reaction order); A = pre-exponential factor (same unit as that of k); E = activation energy (J mol $^{-1}$); R = gas constant (8.314 J mol^{-1} K^{-1}); and T = temperature (K).

3.0 RESULTS AND DISCUSSION

3.1 Transesterification Analysis of Jatropha-based TMP ester

Figure 1 shows product distribution curves for the transesterification of JOME with TMP at 483 K. The molar ratio of JOME/TMP was 4:1 and the catalyst used was 1.0wt% sulfuric acid. Both, D and TE curves showed zero initial slopes suggesting that D and TE were not formed directly from TMP. Conversely, M was formed directly from TMP because of its nonzero initial slope. There was only small concentration of D and a zero concentration of M in the product, towards the end of the reaction. TE began to form only after 15 minutes of reaction. The rate was slow at the beginning, followed by a sudden increase in rate, and finally reaches equilibrium in 300 minutes.

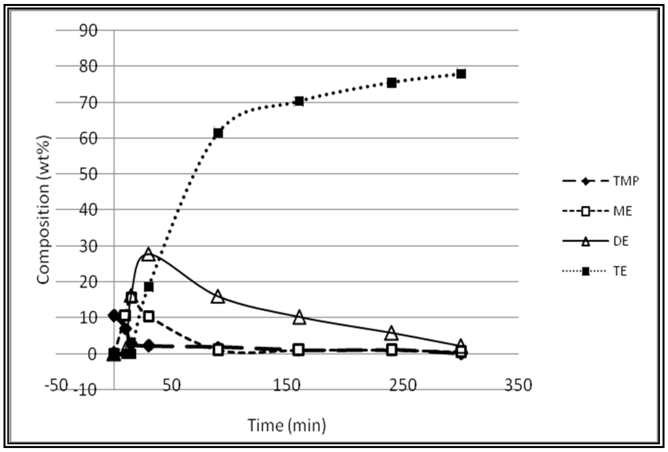


Figure 1: Concentration profile for the transesterification of JOME with TMP at 483K. Monoesters (M), diesters (D), triesters (TE), trimethylolpropane (TMP).

The rate of TE production slowed down as D had to compete with both TMP and M for JOME. M was formed from TMP, followed by the formation of M to form D. Subsequently, D production increased along with decreased of TMP and M. The process continued until concentration of D reached maximum, decreased and finally reached equilibrium.

The sudden increase in the rate of TE formation overlapped with the point when the concentration of D was at a maximum. The concentration of product that passes through a maximum concentration of intermediate is typical of an irreversible series reaction [17]. The sudden surge in the rate of TE formation coincided with the point when the concentration of D was at a maximum. This maximum concentration formed by the intermediate is typical of an irreversible series reaction [18].

As shown in Figure 1, the reaction had reached completion at approximately 200 minutes at 483 K. The final product contained approximately 90 wt % triesters after removal of unreacted JOME. Previously, Yunus et al. [13] reported approximately 98wt% triester after removal of palm oil methyl ester (POME), the excess reactant. The reaction had reached completion in less than 20 minutes at 80°C. The molar ratio of POME to TMP was 10:1 and the catalyst employed was sodium methoxide. Uosukainen et al. [18] stated that conversion up to 99% was observed in 10 hours at 120℃, 5.3 kPa for trimethylolpropane rapeseed esters. However, the polyol esters were a mixture of mono, di and triesters.

On the other hand, the conversion to TMP ester at 423 K was remarkably low, as shown in Figure 2. M formed as the reaction started and plateau off at around 30min. Similarly, D formation increased greatly up to 100min and almost plateaus off, thereafter. This indicates that decomposition of M to form D and decomposition of D to form TE was very slow. This could be seen from the gradual formation of TMP ester up to 300 min, as shown from the figure.

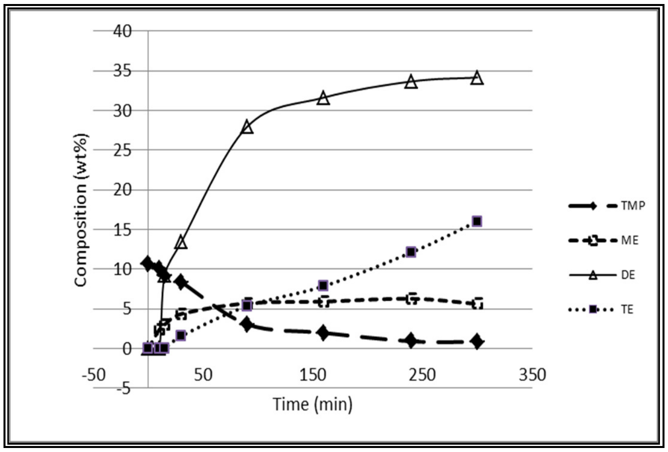


Figure 2: Concentration profile for the transesterification of JOME with TMP at 423K. Monoesters (M), diesters (D), triesters (TE), trimethylolpropane (TMP).

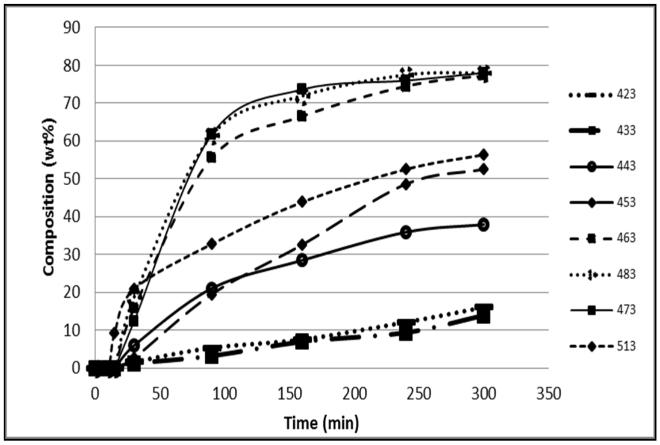


Figure 3: The effect of temperature and time on the composition of polyol esters in the synthesis of Jatropha-based TMP esters at 423 K – 513 K.

Figure 3 illustrate the influence of temperature on Jatropha oil TMP ester synthesis. The effect of temperature on polyol ester formation for the reaction of JOME and trimethylolpropane was determined, at a molar ratio of 4:1 catalyzed by 1wt% H_2SO_4 at eight temperatures ranging from 423 K – 513 K. The selected temperature range was chosen from the literature [19], [20]. The polyol esters formation is essentially completed in 5 hr for temperature ranged at 463 K – 483 K. The results of this study showed that maximum conversion to triesters was obtained at temperature range of 463 K to 483 K. The conversion was reduced at temperature outside of this range. At low temperature, the reactions were slow and incomplete. Similarly, as the temperature was increased to 513 K, the polyol esters formation was gradual. Although the rate of reaction at 513 K was much faster compared to the rate at other temperature, the equilibrium value of TE formation was much lower. At higher temperature (513 K), in the presence of moderate vacuum, methyl esters boil at a considerably lower temperature and can be pulled off by the vacuum at high temperature.

3.2 Derivation of Rate Expression for Jatropha-based TMP ester

The transesterification process of jatropha-based methyl ester and trimethylolpropane is modeled as a three-step process as shown in Scheme 1. In the first step, TMP are converted to monoesters (M) and methanol (Met), which in turn is converted to diesters (D) and methanol in the second step. In the third and final step, D is converted to triesters or polyol esters (TE) and methanol. Methanol is a byproduct that is removed to ensure completion of the reaction.

The kinetic model adopted in the present work was that, there are six steps in Scheme 1 that are formed from three reversible steps of Equations 1, 2 and 3. Each reaction step, forward as well as backward, are shown. The differential equations characterizing the stepwise reactions are as follow.

$$\frac{dC_T}{dt} = r_{1TMP} + r_{2TMP} = -k_1 C_{TMP} C_J + k_2 C_M C_{Met}$$

$$\frac{dC_M}{dt} = k_1^{'} C_{TMP} - k_2 C_M C_{Met} - k_3^{'} C_M + k_4 C_D C_{Met}$$

$$\frac{dC_D}{dt} = k_3^{'} C_M - k_4 C_D C_{Met} - k_5^{'} C_D + k_6 C_{TE} C_{Met}$$

Where $k_i' = k_i C_J$, $i=1,3,5$. k_1 to k_6 are reaction rate constants $(\text{wt\%})^{-2}(\text{min})^{-1}$; C_{TMP}, C_J, C_M, C_D, C_{TE} and C_{Met} are weight percentage of trimethylolpropane, jatropha oil methyl ester, monoester, diester, triester(polyol ester) and methanol respectively in the reaction mixture**.**

a) Determination of rate constants for jatropha-based TMP ester

i) *Determination of k_1 and k_2*

Rate of concentration change of TMP is rate of formation of TMP in equation 2, subtract the rate of disappearance of TMP in equation 1.

$$\frac{dC_{TMP}}{dt} = -k_1 C_{TMP} C_J + k_2 C_M C_{Met} \tag{10}$$

Since the JOME concentration used in the reaction was in excess, it can be considered as a constant. Therefore, effective rate constant, $k'_1 = k_1 C_J$.

$$\frac{dC_{TMP}}{dt} = -k_1^{'} C_{TMP} + k_2 C_M C_{Met} \tag{11}$$

To solve equation 11, C_M and C_{Met} need to be expressed as a function of time.

Development of function C_M

The formula for the change in concentration of C_M can be expressed as exponential terms [21]. The change in concentration of C_M is shown in equation 12 below. The equation is expected to fit curves of various shapes, such as figures presented in Figure 4. Figure 4 illustrates fitting of Equation 12 to monoester concentration profile for jatropha based TMP transesterification using acid catalyst.

$$C_M = C_{M_0} + \frac{\beta_1(e^{-\beta_2 t} - e^{-\beta_3 t})}{\beta_3 - \beta_2} - \frac{\beta_4(e^{-\beta_5 t} - e^{-\beta_6 t})}{\beta_6 - \beta_5} - \frac{\beta_7(e^{-\beta_8 t} - e^{-\beta_9 t})}{\beta_9 - \beta_8} \qquad (12)$$

where β_i can be determined from experimental results using nonlinear regression.

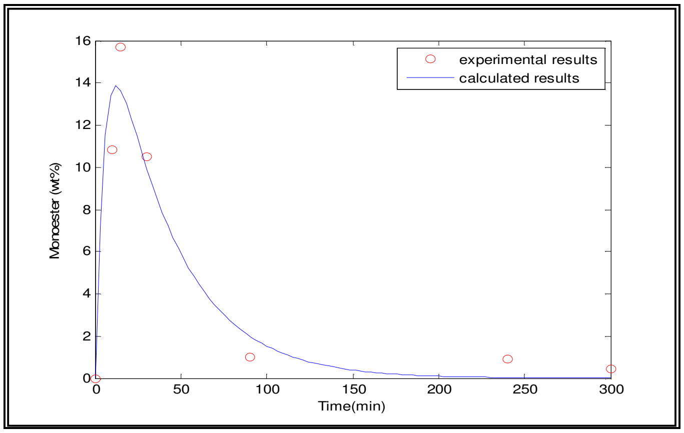


Figure 4: Typical monoester concentration profile for TMP transesterification using acid catalyst.

The formula for methanol concentration is illustrated in equation 13 below:

$$C_{Met} = C_{Met_0} + \frac{\omega_1(e^{-\omega_2 t} - e^{-\omega_3 t})}{\omega_3 - \omega_2} - \frac{\omega_4(e^{-\omega_5 t} - e^{-\omega_6 t})}{\omega_6 - \omega_5} \qquad (13)$$

The substitution of Equations 12 and 13 into Equation 11 is for the determination of rate constants, k_1 and k_2.

ii) Determination of k_3 and k_4

The rate of concentration change of monoesters is the rate of formation of monoesters in Equations 1 and 4 subtract rate of disappearance of monoesters in Equations 2 and 3.

$$\frac{dC_M}{dt} = +k_1^{'} C_{TMP} - k_2 C_M C_{Met} - k_3^{'} C_M + k_4 C_D C_{Met} \qquad (14)$$

Similar to Equation 3, the concentration of TMP and diesters can be expressed as the equations below.

$$C_{TMP} = C_{TMP_0} + \frac{\eta_1 (e^{-\eta_2 t} - e^{-\eta_3 t})}{\eta_3 - \eta_2} \tag{15}$$

$$C_D = C_{D_0} + \frac{\alpha_1 (e^{-\alpha_2 t} - e^{-\alpha_3 t})}{\alpha_3 - \alpha_2} - \frac{\alpha_4 (e^{-\alpha_5 t} - e^{-\alpha_6 t})}{\alpha_6 - \alpha_5} - \frac{\alpha_7 (e^{-\alpha_8 t} - e^{-\alpha_9 t})}{\alpha_9 - \alpha_8} \tag{16}$$

where η_i and α_i can be determined from experimental results using nonlinear regression.

The substitution of Equations 13, 15, 16 into Equation 14 is for determination of rate constants, k_3 and k_4.

iii) *Determination of k_5 and k_6*

Rate of concentration change of diesters is rate of formation of diesters in Equations 3 and 6 subtract the rate of disappearance of diesters Equations 4 and 5:

$$\frac{dC_D}{dt} = +k_3^{'} C_M - k_4 C_D C_{Met} - k_5^{'} C_D + k_6 C_{TE} C_{Met} \tag{17}$$

The concentration of polyol esters can be expressed as:

$$C_{TE} = \frac{\chi_1 (e^{-\chi_2 t} - e^{-\chi_3 t})}{\chi_3 - \chi_2} \tag{18}$$

where χ_i can be determined from experimental results using nonlinear regression.

The substitution of Equations 12, 13, 18 into Equation 17 is for determination of rate constants, k_5 and k_6.

3.3 Determination of Reaction Rate Constants

The rate constants were determined from the differential equations which were established by applying rate law on the series of (Equation 1) – (Equation 6) stated in Scheme 1. The differential equations were solved using laplace transformation. Matlab program was utilized for the determination of rate constants of each reaction using nonlinear regression method.

The simulation results for the transesterification of JOME with TMP for TMP, M and D is shown in Figure 5. The rate constants determined for the reaction of JOME and TMP at a 4:1 molar ratio using 1wt% sulfuric acid catalyst at various temperatures are shown in Table 1. As expected, the value of k increased with increase in temperature. An increase in temperature result in an increase rate of reaction since the particles gain more kinetic energy and lead to more productive collisions. At lower temperature (423 K – 453 K), the forward rate constants, k_3 was the largest and k_5 the smallest. The following sequence existed among the rate constants of the three steps involved in TMP transesterification at lower temperature, $k_3 > k_1 > k_5$. However, at higher temperature (463 K – 483 K) the sequence changed. It was observed that the forward rate constant, k_1 was the largest, next k_3 and followed by k_5, which is the smallest rate constant. The rate constant magnitudes follow the sequence $k_1>k_3>k_5$. Yunus et al. [13] reported that the same sequence ($k_1>k_3>k_5$) was observed for the transesterification of trimethylolpropane with palm-based methyl esters using sodium methoxide catalyst.

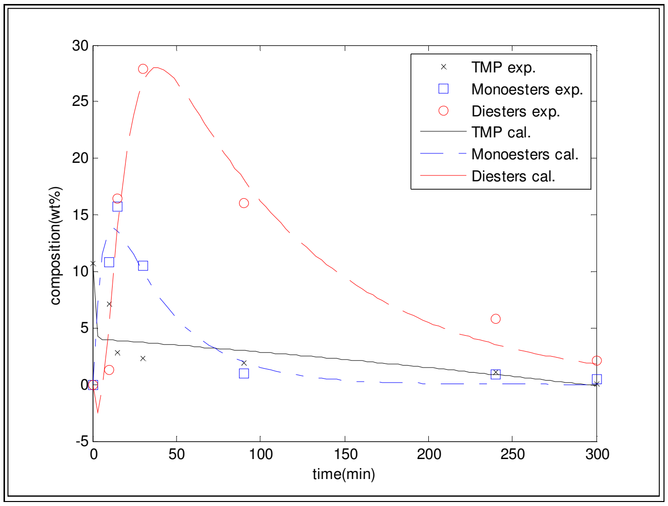


Figure 5: Plot of experimental data (exp) and calculated values (cal) for transesterification of JOME with TMP at 483 K, JOME-to-TMP molar ratio at 4:1 and catalyst 1.0wt% sulfuric acid. [× TMP r= 0.8959; □ Monoester r= 0.9711; ○ Diester r= 0.9709.]

The magnitude of the rate constants affects the final products of the transesterification process of TMP ester production. At lower temperature (423 K – 453 K), the value of rate constants k_1, k_3, and k_5 are much lower than the rate constants value, at higher temperature (463 K – 483 K). The higher the value of rate constant, the faster is the reaction. This is consistent with the concentration profile for the transesterification of JOME with TMP at 483 K, Figure 1, which shows higher TE concentration formed as compared to the concentration profile for the transesterification of JOME with TMP at 423 K, Figure 2.

The reaction rate constants were determined at temperature range of 463 K to 483K. At this temperature range, rate constant k_5 for the conversion to triester is the lowest of all the rate constants for forward reactions at all reaction temperatures (See Table 1). This indicates that the rate determining step (RDS) for overall acid catalyzed transesterification of trimethylolpropane is the fifth step, i.e., conversion of diester to polyol ester. The rate constants of the RDS of TMP transesterification in Table 1 increased from 0.1707 to 0.2848 to 0.3280 (wt%)$^{-2}$ (min)$^{-1}$ when the reaction temperature was increased from 463 K to 473 K to 483 K, respectively. This indicates that the RDS of transesterification of TMP is favored at higher temperatures. This is a typical observation for an endothermic reaction.

Table 1: Average Reaction Rate Constants at Different Temperatures for the Transesterification Kinetics of Jatropha Oil Methyl Esters with Trimethylolpropane.

Temperature (K)	Forward and Reverse Rate constants (wt%)$^{-2}$ (min)$^{-1}$					
	k_1	k_2	k_3	k_4	k_5	k_6
423	0.0111	0.0975	0.0181	0.0697	-0.004*	0.0200

433	0.0277	0.0589	0.0411	-0.1130*	0.006	0.0202
443	0.03	0.1219	0.0718	0.0386	0.0096	0.0200
453	0.0752	0.1404	0.1731	0.6307	0.0148	0.0200
463	0.5179	0.0077	0.2708	-0.0034*	0.1707	0.0199
473	0.5177	0.0166	0.3143	-0.0085*	0.2848	0.0149
483	0.517	0.0126	0.3907	-0.0080*	0.3280	0.0195
513	0.5175	0.0068	0.2402	-0.0070	0.2856	0.0198

* - negative value

Some disadvantage of nonlinear regression method has been reported. It has been stated that nonlinear regression can report a best fit rate constant that is negative [22]. As shown in Table 1, several rate constants especially k_4 has negative values. These values are undesirable and are scientifically meaningless. Nevertheless, the negative value rate constants represent only approximately 10 % of the whole data and the other 90% of the data were assumed to be correctly fitted as shown by the high regression values ($R^2 > 0.9$). The assumption made is that these negative values are positive.

3.4 Activation Energy, E_a

Activation energy can be defined as the minimum energy required to start a chemical reaction. It also determines the extent of dependency of rate constants on reaction temperature at a given condition. The activation energies (E_a) were estimated from Arrhenius equation [$\log_{10}k = (-E_a/2.303R)/T+C)$], where T is expressed in K and R is the universal gas constant. The slope, which equals $-E_a/2.303R$, can be determined. The frequency factor, C was determined from the y-intercept. Arrhenius plot for the transesterification of TMP with JOME for temperature range from (423 K – 483 K) is shown in Figure 6 and the activation energies in Table 2.

As shown in Figure 6, the plots of log k vs 1/T for temperature range (423 K – 483 K) are not linear and have low regression values of 0.902, 0.960 and 0.861 for k_1, k_2 and k_3 respectively. However, the plots were more linear as the temperature range in Figure 6 was split into two, lower temperature range (423 K – 453 K) and higher temperature range (463 K -483 K), as shown in Figure 7 (a) and (b), respectively. The splitting of the temperature resulted in the change of slope or the activation energies at the corresponding temperature range. Levenspiel [17] stated that for multiple reactions, a change in the observed activation energy with temperature indicates a shift in the controlling mechanism of the reaction. The shift in the controlling mechanism of the reaction could be the explanation for the change of reaction rate sequence observed earlier. It was observed that the reaction rate sequence changed from $k_3>k_1>k_5$ to $k_1>k_3>k_5$ as temperature was increased to higher range. The sequence at higher temperature $k_1>k_3>k_5$ appear to follow the ease for the reaction take place due to steric hindrance. It is easier to substitute the first alcohol group on TMP compared to substitution of the third group when the other two alcohol group has been substituted. It was also observed that reaction rate sequence is consistent with the activation energy, Ea sequence. The activation energy, Ea sequence at higher temperature range is $Ea_1<Ea_3<Ea_5$ whereas, at lower temperature range $Ea_3<Ea_1<Ea_5$ which are coherent with the reaction rate sequence at corresponding temperature.

Table 3 showed the activation energy at temperature range of 423 K -453 K and 463 K – 483 K. The activation energies at temperature range of 423 K – 453 K are between 16.7 to 27.9 kcal/mol. However, as the temperature was increased to higher range (463 K – 483 K), the activation energy reduced to 0.03 to14.5 kcal/mol. Activation energy, Ea shows how strong the rate of reaction depends on reaction temperature. Lower Ea indicates that the reactions are not very sensitive to reaction temperature.

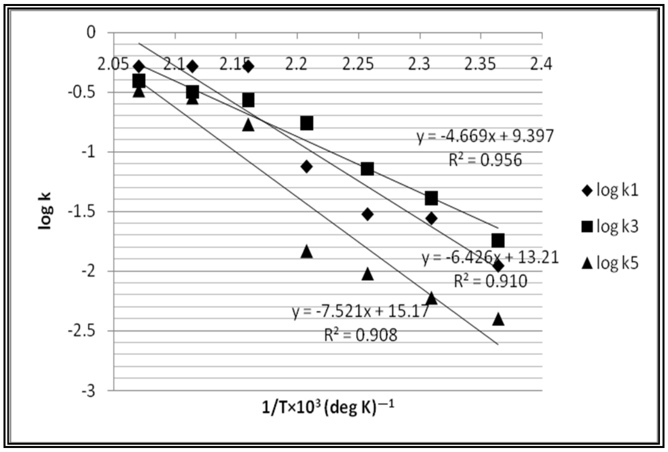
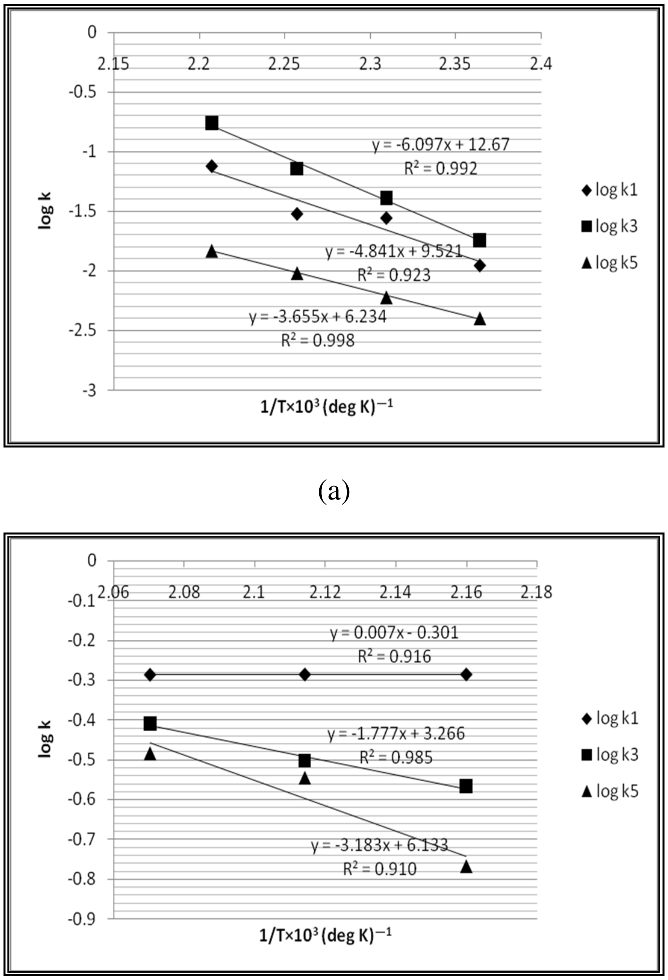


Figure 6: Arrhenius plot showing the temperature dependency of the reaction rate constants for temperature range of 423 K – 483 K.

Table 2: Activation Energies for Transesterification of TMP with JOME at temperature range of 423 K – 483 K.

Reaction	Rate constant	E_a(kcal/mol)	R^2
TMP↔M	k_1	20.024	0.960
M↔D	k_3	26.083	0.902
D↔TE	k_5	28.762	0.861



(a)

(b)

Figure 7 (a) and (b): Arrhenius plot showing the temperature dependency of the reaction rate constants for temperature ranging from 423 K – 453 K and 463 K -483 K, respectively.

Yunus et al. [13] reported activation energies for transesterification reactions of palm oil methyl esters (POME) with trimethylolpropane, using sodium methoxide catalyst, range from 33.3 to 33.9 kcal/mol, whereas the transesterification reactions of palm kernel oil methyl esters (PKOME) with trimethylolpropane, using sodium methoxide catalyst, range from 17.2 to 17.6 kcal/mol. In this study, the activation energies for transesterification of JOME with TMP, range from 0.03 to 14.5 kcal/mol, is lower than the activation energies of transesterification of POME with TMP. This indicates that the transesterification reaction between JOME with TMP using sulfuric acid catalyst at 483 K are less sensitive to temperature than the transesterification reaction between POME with TMP.

Change in activation energy was observed as the temperature was increased from 423K-453K range to 463K-483K range for transesterification of TMP with JOME, as shown in Table 3. Besides the change in activation energy, a change in the reaction rate sequence and the order of reaction were also noticed. It was observed that the reaction rate sequence changed from $k_3>k_1>k_5$ at temperature range of 423K-453K to $k_1>k_3>k_5$ as temperature was increased to

463K-483K range. Change in the observed activation energy with temperature indicates a shift in the controlling mechanism of the reaction, for multiple reactions [17]. Additionally, Emtir et al. [23] observed change in the order of reaction as the temperature was increased for the esterification reaction between glycerol and oleic acid in the presence of pyridine as a cosolvent. A second-order rate equation was fitted to the experimental data at 453 K while a third-order rate equation was fitted for the data obtained at higher temperatures (473 K and 493 K). In general, it can be concluded that for transesterification reaction between TMP and JOME, the temperature should be selected in the range of 463K-483K. This is consistent with the findings of other researches which suggested temperature in the range of 453K-473K for transesterification process to produce polyol esters [24].

Table 3: Activation Energies for Transesterification of TMP, Monoesters (M) and Diesters (D) with Jatropha Oil Methyl Esters (JOME).

Temperature (K)	Reaction	Rate constant	E_a (kcal/mol)	R^2
423 - 453	TMP↔M	k_1	22.1	0.923
	M↔D	k_3	27.9	0.992
	D↔TE	k_5	16.7	0.998
463 -483	TMP↔M	k_1	0.03	0.916
	M↔D	k_3	8.1	0.985
	D↔TE	k_5	14.5	0.910

4.0 CONCLUSSION

Kinetics of transesterification of jatropha-based methyl ester (JOME) with trimethylolpropane (TMP) was investigated. The mechanism of TMP transesterification is believed to occur via three stepwise and reversible reactions. The rate constants for the forward and reverse reaction for the formation of intermediates ME and DE and final product were determined utilizing nonlinear regression method and MATLAB version 7.8 at various temperatures. Activation energy was determined from plots of log k vs 1/T. The activation energy values ranged from 0.03 to 14.5kcal/mol for TMP ester. The conversion of diester to triester was found to be the rate determining step of the overall reaction, with activation energy of 14.5kcal/mol. The rate constants of the RDS of TMP transesterification increased when the temperature was increased. This indicates that the rate determining step (RDS) of transesterification of TMP is favoured at higher temperatures, which is typical observation for an endothermic reaction. The developed model was also validated against data from the literature. A good correlation between model simulations and experimental data was observed.

ACKNOWLEDGEMENT

The authors would like to acknowledge financial support by Ministry of Higher Education (MOHE) on Long Term Research Grant Scheme (LRGS) 0153AB-I41 and the necessary facilities from University Teknologi Petronas to conduct the research work.

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