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Kinetic Modeling of Transesterification of Jatropha *curcas* Seed Oil Using Heterogeneous Catalyst

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Abstract
A mathematical model describing chemical kinetics of transesterification of jatropha *curcas* oil using calcium oxide (CaO) as heterogeneous catalyst has been developed. The model is based on the resverse mechanism of transesterification reactions and describes dynamic concentration changes of all the reactants and products. The study was conducted at the following reaction conditions: methanol to oil ratio (10:1); catalyst concentration (8wt %); time (1hr); temperature (55°C) and stirrer speed (700rpm). It was observed that the changes in concentration of all reactants and products as a function of time and temperature were highly significant between 0-25 minutes. The study also revealed that conversion of triglyceride to diglyceride was the rate determining step (RDS) and the effective rate constants for all the six reactions (reversible and irreversible) were favoured by high temperature. The observed kinetics was first order and the temperature dependent terms obtained using Arrhenius law revealed Activation energy of 14.80kJ/mol and frequency factor of 20.697s^{-1}. The predictive power of the developed model was checked by fitting experimental data and revealed good correlation.

1. Introduction

Diesel fuel has an important role in the industrial economy of any country. This fuel run a major part of the transport sector and its demand is increasing steadily, requiring an alternative fuel which is technically feasible, economically competitive, environmentally acceptable and readily available (Zhang et al., 2003).

Biodiesel, synthesized by transesterification of vegetable oils and fats, is a realistic alternative of diesel fuel because it provides a fuel from renewable resources and has lower emissions than petroleum diesel (Staat and Vallet, 1994). It is biodegradable, non-toxic and has a low emission profile of greenhouse gases. Chemically, biodiesel is fatty acid methyl or ethyl esters and they are called biodiesel only when used as fuel in diesel engines and heating systems (Meher et al., 2004).

Methyl esters of fatty acids are produced by alcoholysis (transesterification with alcohols) of triglycerides with methanol in the presence of an acid or a base catalyst. The reaction proceeds in three steps in which triglyceride (TG) reacts with methanol to produce diglyceride (DG) which further reacts with methanol to yield monoglyceride (MG) and that finally reacts with methanol to produce methyl ester and glycerol. (Freedman *et al,* 1986).

Conventional synthesis techniques of biodiesel rely on soluble base homogeneous catalysts (sodium and potassium hydroxide). Acid homogeneous catalysts are also used but require longer reaction time as compared to the alkaline-based transesterification reaction. However, homogeneous catalysts are difficult to recover and lead to downstream waste treatment, increasing the cost of biodiesel production. Base catalysts have limitation for high free fatty acid (FFA) containing oils leading to soap formation and consumption of the catalyst. They are also sensitive to water content in the oil. Acid catalysts are usually used for oils with high FFAs. On the other hand, heterogeneous catalysts could improve the synthesis methods by eliminating the additional processing costs associated with homogeneous catalysts (Abebe *et al,* 2011; Galen *et al,* 2004).Therefore, the use of heterogeneous catalyst as replacement to homogeneous in transesterification reactions has for long gained acceptability .It is of interest to study the kinetics of the reaction in order to evaluate its industrial applicability.

Knowledge of transesterification reaction kinetics enables prediction of the extent of chemical reaction (or the conversion) and understanding on the changes in reactants and products concentration at any time under particular conditions. It is an also essential requirement by both process and chemical engineers in the design and optimization of reactor system (Levensipel, 2000).

The objective of this work was to develop a new kinetic model of transesterification process of Jatropha *curcas* oil in a heterogeneous catalyst including a reverse mechanism of three consecutive chemical reactions and check it on different experimental data generated. The development was based on a fundamental concept that the transesterification process proceed via nth-order kinetics.

1.1. Kinetic Modeling

The mechanism proposed for transesterification of jatropha oil is composed of a series of reversible decompositions of triglyceride to diglyceride, diglyceride to monoglyceride, and monoglyceride to glycerol. However, the kinetics of such reactions is first order with respect to the reacting components' concentration as shown in Equations (1) to (3) (Burno *et al*, 2006 ; Issiyarrku, 2005).

$$TG + AL \rightleftharpoons DG + ME \tag{1}$$

$$DG + AL \rightleftharpoons MG + ME \tag{2}$$

$$MG + AL \rightleftharpoons ME + GL \tag{3}$$

K_1, K_3 and K_5represent rate constants for forward reactions in Equations (1), (2) and (3) respectively. Similarly, K_2, K_4 and K_6 represent rate constants for backward reactionsalso in Equations (1), (2) and (3) respectively. TG = concentration of triglyceride, AL = concentration of alcohol, DG = concentration of diglyceride, ME = concentration of methylester, MG = concentration of monoglyceride, GL = concentration of glycerol

Each step consumes 1 mole of alcohol and produces 1 mole of ester and the overall equation is shown in Equation (4).

$$TG + 3AL \rightarrow 3ME + GL \tag{4}$$

To determine the rate constants, differential equations were established by applying rate law on Equations (1)-(3).Based on the above mechanism and model assumptions the rate equations of various species were described by using component mass balances as shown in Equations (5)-(10). Where symbol A, B, C, D, E and F represents the concentration of TG, AL, DG, ME, MG and GL respectively.

$$r_A = \frac{dC_A}{dt} = -K_1AB + K_2CD \tag{5}$$

Since the concentration of alcohol was always in excess relative to concentration of other reactant species. This implies that Equation (5) was assumed to proceed via pseudo first order kinetics with respect to concentration of triglyceride (A) and Equation (5) becomes (6).

$$r_A = \frac{dC_A}{dt} = -k_1A + K_2CD \tag{6}$$

k_1 = K_1B and refer to as effective rate constant. Similarly, other rate expressions were also derived in the same manner by making similar assumption of excess concentration of alcohol as follows:

$$r_C = \frac{dC_C}{dt} = k_1A - k_2CD - k_3C + k_4ED \tag{7}$$

$$r_D = \frac{dC_D}{dt} = k_1A - k_2CD + k_3C - k_4ED + k_5E - k_6FD \tag{8}$$

$$r_E = \frac{dC_E}{dt} = k_3C - k_4ED + k_5E + k_6FD \tag{9}$$

$$r_B = \frac{dC_B}{dt} = k_1A - k_2CD - k_3C + k_4ED - k_5E + k_6FD \tag{10}$$

Equations (5)-(10) are system of Ordinary Differential Equations (ODE) and were solved for values of k_1-k_6 using MATLAB software (Version 2010a).

1.2. Activation Energy and Frequency Factor

The temperature dependent terms (Activation energy and frequency factor) for the rate determining step (RDS) were calculated using well known Arrhenius equations given in Equation (11).

$$k = k_o e^{\frac{-E_a}{RT}} \tag{11}$$

Linearization of Equation (11) resulted in Equation (12). A plot of *ln k* against *(1/T)* gives slope=E_a/R and intercept = lnk_o.

$$\ln k = (^{-E_a}/_{RT}) + lnk_o \tag{12}$$

k = rate constant (the unit depends on the reaction order); k_o = pre-exponential factor (same unit as that of k); E_a = activation energy (J·mol^{-1}); R = gas constant (8.314 J·mol^{-}

$^{1}\cdot K^{-1}$); and T = temperature (K).

1.3. Determination of Reaction Order

The reaction order was determined by assuming that the forward reaction proceed via nth- order kinetics and the backward reaction followed second order overall kinetics. It was also assumed that the concentrations of alcohol was always in excess relative to the concentration of the other reactants at any given time during the reaction such that k value becomes effective rate constant (Levespiel, 1999) and Coker, 2001). Based on this assumption, the reaction order (n) and rate constant (k) were then obtained by solving Equation (13).

$$r_{TG} = \frac{dC_{TG}}{dt} = -kC_{TG}^{n}\ , \qquad (13)$$

2. Materials and Method

2.1. Materials

Pre-treated jatropha *curcas* seed oil with composition shown in Table 1 was obtained from National Research Institute for Chemical Technology (NARICT), Zaria, Nigeria. Methanol, calcium oxide and other chemicals/reagents were obtained from ROMPTECH chemicals and scientific Co. Ltd. Zaria, Nigeria. All chemicals/reagents were of analytical grades with purity>99%.

Table 1. *Properties of the pretreated jatropha seed oil used in this work as compared to acceptable limit*

Parameter	Unit	Value	Limits
Density	kg/m^3	870.1	864-880
Viscosity @ 24.3°C	MPa.S	151.4	140.1-160
Neutralization No	mg KOH/g	0.93	0.6-0.99
Free Fatty Acid	mg KOH/g	0.7	1-1.5
Saponification Value	mg/g	180.5	170-202.6
Moisture Content	%	1.2	1-2
Kinematic Viscosity	m^2/s	0.174	
Monoglyceride	wt (%)	-	0-0.24
Diglyceride	wt (%)	2.50	1.1-3.5
Triglyceride	wt (%)	95.16	92-99.1
Iodine Value	mg Iodine/g	94.1	93-106

2.2. Reaction Procedure

The reaction was conducted in a 1-litre three-necked reactor-equipped with a reflux condenser, thermometer and sampling port. The reactor was heated on a magnetic heating mantle equipped with PID temperature controller capable of controlling the temperature within ±0.2°C of the setting point. Mixing was provided by magnetic stirrer at a speed of 700rpm.Prior to use, the calcium oxide was placed in small stainless steel pans and was heated in a muffle furnace from room temperature to 150 ◦C for 4 hours to remove any moisture that might be present. Initially, the reactor was charged with 50g of pretreated jatrophaoil and heated to 45°C.8wt % of the pretreated calcium oxide (based on the oil weight)was dissolved in methanol and the mixture was heated until the temperature reached 45°C. The methanol to oil molar ratio used was 10:1. The heated mixture (calcium oxide + methanol) wasthen added to the heated jatrophaoil in the reactor and the temperature was maintained at45°C for 1 hour.Same procedure was repeated and the temperature was varied from 45°C to 50°C and 55°C.

2.3. Sampling and Analysis

The biodiesel produced was characterized as a function of time using the following procedure. Approximately 5ml of reaction sample was collected in a measuring cylinder containing 3 drops of 1.1NHCl acid solution to neutralize the alkaline catalyst. The collected samples were then immediately placed in an ice bath thus preventing further reaction from occurring. Each sample was taken at 5 minutes intervals and diluted with 20times tetrahydrofuran (THF) to ensure uniform mixture of transesterification products. The transesterification products were then analyzed using Gas chromatography-Mass Spectrometer (GC-MS).The (GC-MS) was equipped with a Chrompack CP9001 chromatograph, 5CB capillary column (50 m x0.32 mm, 1.2 *m*m thickness) and a flame ionization detector. Injector and detector temperatures were set at523 K. Oven temperature started at 358 K for 90 s, then increased to 393 K at a rate of 16 K s^{-1}, further increased to 458 K at a rate of 50.9 K s^{-}1 and finally held constant at 458 K for 275 s. The XChrom software was used to analyze the gas chromatography data. n-Octane was used as internal standard in the gas chromatography analysis. Standard calibration curves for the methyl esters were prepared using n-Octane as an internal standard. Using these calibration charts, the integrated areas were converted to weight percentages for each component present in the sample.

3. Results and Discussion

3.1. Properties of Jatropha Oil

The physio-chemical properties of the pre-treated jatropha oil used in this work are presented in Table 1.It is evident that all the properties are within the acceptable limits. However, the low water content (0.5%) and free fatty acid (0.7%) suggest that the oil is suitable for direct transesterification reaction without any further treatment. High water content in the oil in excess of 1.5% reacts with the triglyceride to form free fatty esters and could also lead to the hydrolysis of alkyl ester produced during transesterification reaction (Emin, 2008). The high value of triglyceride (95.16%) and viscosity (151.4 MPa.s) in the oil is an indication that the oil has high potential of biodiesel yield and also not suitable for direct combustion (Pramanik, 2003).

3.2. Analysis of Transesterification Products

Heterogeneous-catalyzed transesterification of jatropha oil was studied at three reaction temperatures (45, 50, and

55°C).The optimum reaction conditions were methanol to oil ratio of 10, catalyst concentration of 8wt% (based on the weight of oil), reaction time of 1 hour and stirrer speed of 700 rpm. The transesterification reaction is a stepwise reaction consisting of a number of consecutive, reversible reactions as shown in Equations (1-3).

Typical concentration profiles of triglyceride (TG), diglyceride (DG), monoglyceride (MG), methyl ester (ME), and glycerol (GL) for the reaction at the stated reaction conditions and reaction temperatures of 45,50 and 55°C are shown in Figures 2,3 and 4. These figures indicate changes in concentrations of triglycerides and formation of esters and glycerol as well as the intermediate compounds such as diglycerides and monoglyceridesat any given time during the reaction.

An analysis of Figures 2, 3 and 4 can prove that the TG concentration continuously decreases, until it approached value close to zero at the end of the reaction. On the other hand, ME concentration increases rapidly during the first 25 minutes of the reaction reaching a maximum and after that slightly increases and remain constant. However, the concentration of MG slowly increases and its utilization was not completed throughout the reaction time.

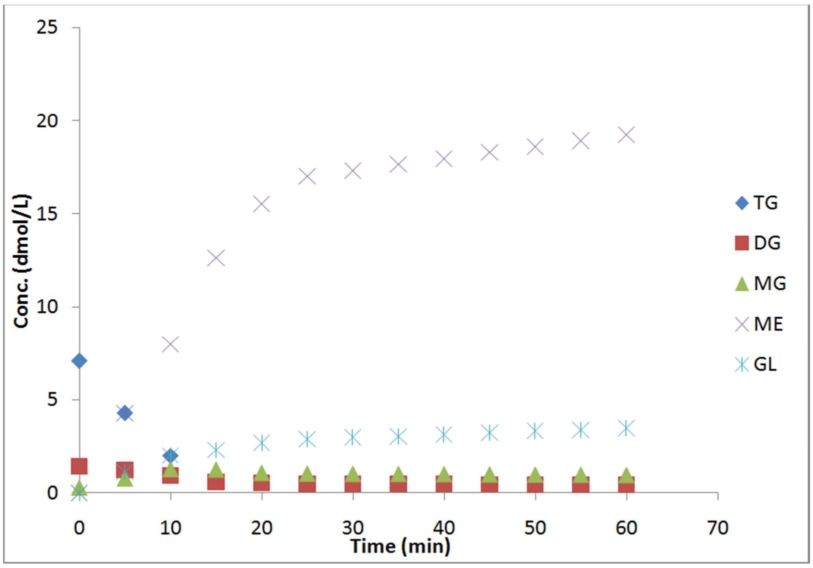

Figure 1. *Effect of reaction time on concentration of TG,DG, MG, ME and GL at 45°C*

After 25 min, insignificant changes in the concentration of each component were observed. There are two explanations for this phenomenon. First, the change in concentrations drops as the reaction approaches equilibrium. Second, methyl ester and glycerol are immiscible with each other even at a higher stirring speed of 700 rpm (Vicente *et al.*, 2005). Also, the glycerol-rich phase is formed as the reaction proceeds even in the presence of a co-solvent (Zhou *et al.*, 2003). Once glycerol forms, the catalyst is transferred into a glycerol phase, thus lowering the catalyst concentration in the ester phase thereby lowering the reaction rate.

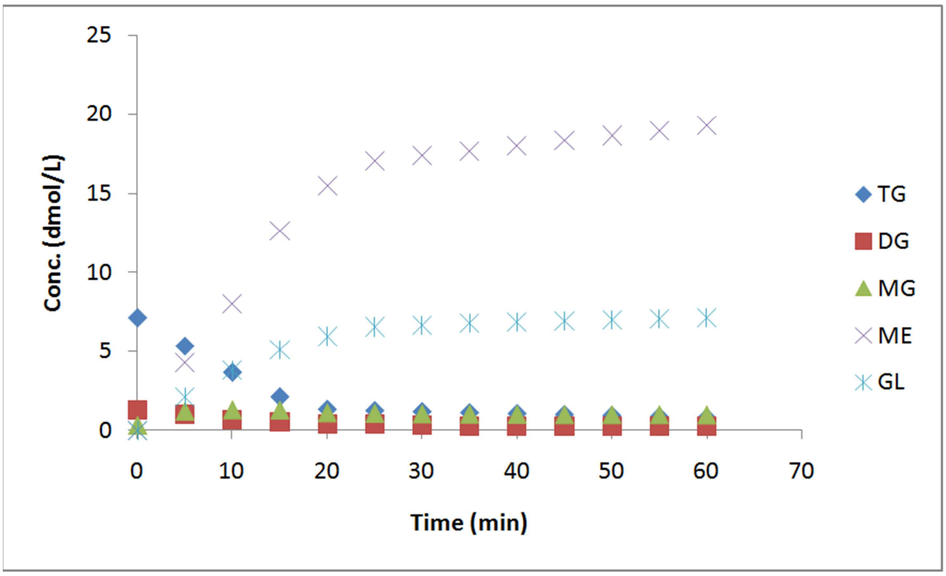

Figure 2. *Effect of reaction time on concentration of TG,DG, MG, ME and GL at 50°C*

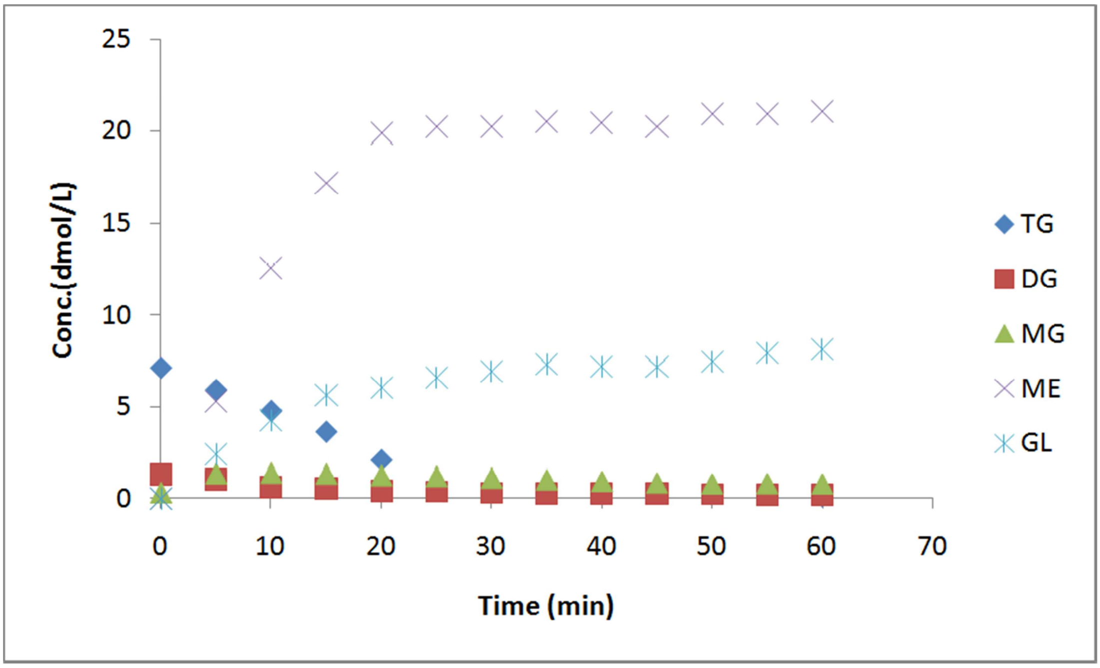

Figure 3. *Effect of reaction time on concentration of TG,DG, MG, ME and GL at 55°C*

3.3. Rate Determining Step (RDS)

The effective rate constants (*k*) defined in Equations (6)-(10) were calculated using concentration-time data shown in Figures 2, 3 and 4 at specified reaction conditions and reaction temperatures of 45 50 and 55°C. A program was written in MATLAB software (version 2010a)for solving the six ordinary differential equation (ODE) having six unknowns and the values of the effective rate constants calculated are presented in Table 2.

Table 2. *Effective rate constants of transesterification of jatropha oil different temperatures*

Reaction	Rate constant (unit)	Temperature (°C)		
		45	50	55
TG→ DG	$k_1(min^{-1})$	0.077	0.084	0.091
DG→ TG	$k_2(L.dmol^{-1}.min^{-1})$	0.004	0.005	0.006
DG→ MG	$k_3(min^{-1})$	0.190	0.274	0.392
MG→ DG	$k_4(L.dmol^{-1}.min^{-1})$	0.001	0.003	0.006
MG→ GL	$k_5(min^{-1})$	0.158	0.340	0.717
GL→ MG	$k_6(L.dmol^{-1}.min^{-1})$	0.003	0.003	0.003

Since the reaction order and hence the units of k for forward and backward reactions are not the same, a direct comparison of forward and backward rate constants cannot be made. However, it is evident from Table 2 that the rate constant values for forward reactions (k_1, k_3, k_5) were far greater than backward reactions (k_2, k_4, k_6). It means that the forward reactions dominate and the reverse reactions can be neglected for these experimental conditions. The effective rate constant for triglyceride conversion to diglyceride was the lowest of all the forward reactions at all reaction temperatures and can be considered as the rate determining step (RDS). It could also be seen that the effective rate constants for the RDS increased from 0.077 to 0.084then to 0.091 min^{-1}as the reaction temperature increased from 45 to 50 and to 55°C, respectively. This also indicates that the RDS of transesterification of jatropha oil is favored at higher temperatures and is a typical observation for an endothermic reaction.

3.4. Modeling and Simulation

The effective rate constants (k_1-k_6) calculated were later substituted in the kinetic rate equations (6)-(10)to calculate concentrations of TG, DG, MG ME and GL. This followed by simulation and graphical representation shown in Figures 4, 5 and 6. In all these Figures, the accuracy of the effective rate constants were determined by comparing the experimental values (dots) with calculated values (solid lines). Correlation of the two values (experimental and calculated revealed high correlation coefficient with value well above 0.957. This indicates that the calculated effective rate constants (k_1-k_6) were accurate. However, the deviation between model and experimental data of TG profiles was more significant in Figures 4 & 5.However, this slight deviation does not change the overall very good prediction of the model for these operational conditions.

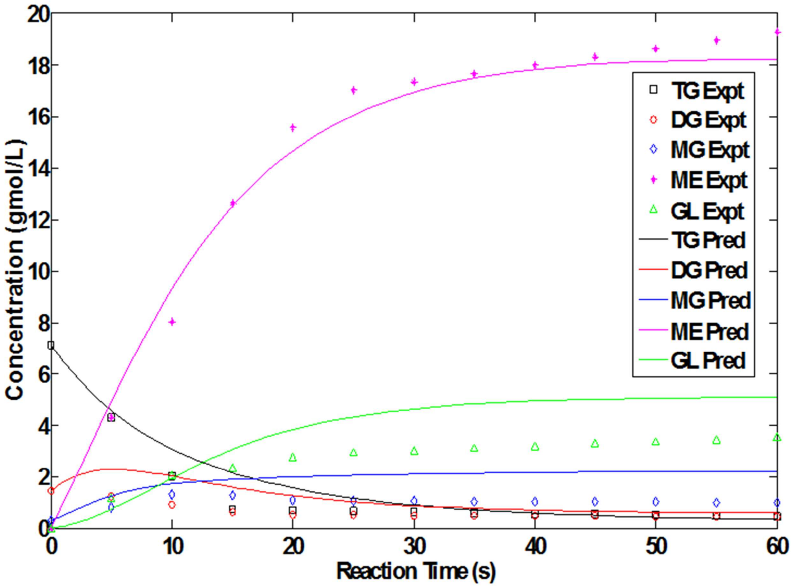

Figure 4. *Calculated MG, DG, TG, ME and GL concentrations vs. experimental MG,DG TG, ME and GL concentration at 45°C*

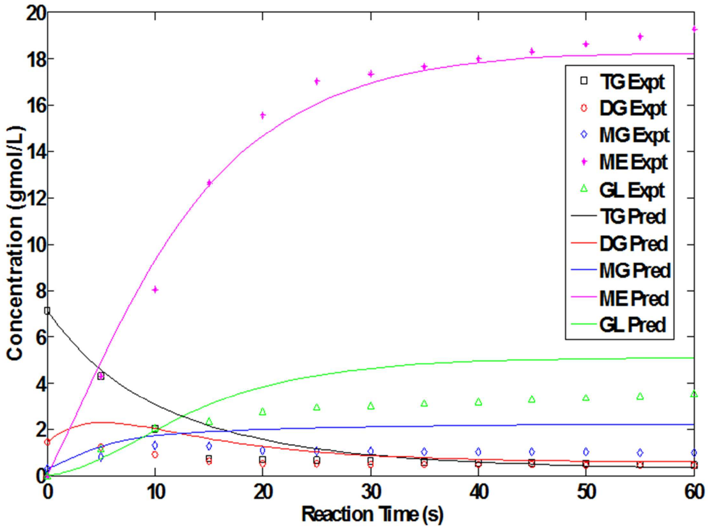

Figure 5. *Calculated MG, DG, TG, ME and GL concentrations vs. experimental MG,DG TG, ME and GL concentration at 50°C*

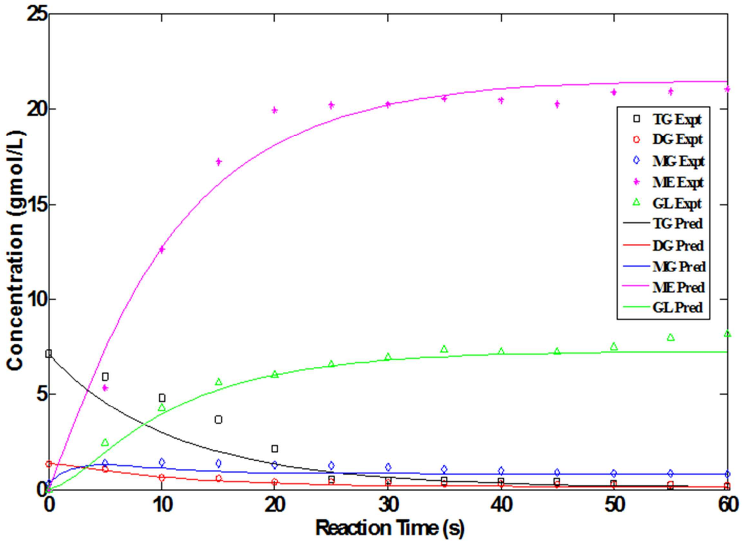

Figure 6. *Calculated MG, DG, TG, ME and GL concentrations vs. experimental MG,DG TG, ME and GL concentration at 55°C*

3.5. Determination of Kinetic Parameters

The activation energy determines the extent of dependency of rate constants on reaction temperature at a given condition. The activation energy and frequency factor for the RDS (TG→DG) were calculated from the Arrhenius equation by plotting *ln k*vs*1/T* as shown in Figure 7.

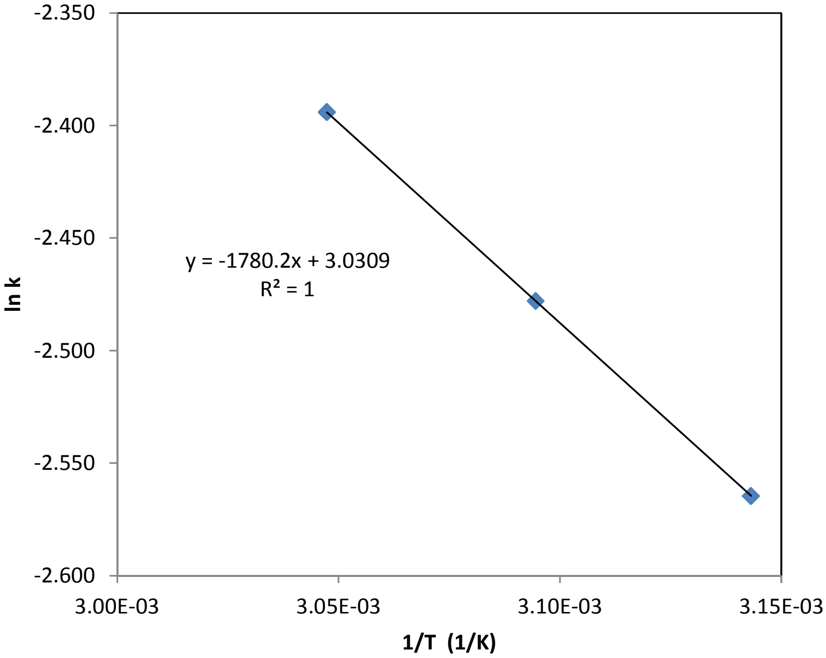

Figure 7. *Temperature dependency on rate constant from Arrhenius equation*

The values of the activation energy and frequency factor were 14.801J/mol and 20.697s^{-1} respectively. It is evident in the value of activation energy that the reaction is mass transfer resistance and that the product diglyceride is less stable and has higher potential energy than the reactant triglyceride. In this type of reaction, heat is usually absorbed from the surroundings in the reactant mixture (Issariyakul, 2006).

3.6. Development of Kinetic Rate Equation

Solution to Equation (12) using concentration-time data of RDS at 55°C revealed that the reaction was first order (n=1) and conversion of triglyceride to methyl ester in the presence of excess alcohol proceeds via first order kinetics. Substituting values of E_a, k_o, R and n in Equation (11) and (13) respectively. The rate equation for the transesterification of jatropha *curcas* seed oil using CaO as heterogeneous catalyst is given by Equation (14).

$$r_{TG} = \frac{dC_{TG}}{dt} = 20.697 * C_{TGo} * \exp\left(\frac{-14.80}{8.314*T}\right)(1 - X_{TG}) \quad (14)$$

$$C_{TG} = C_{TGo}(1 - X_{TG})$$

4. Conclusions

In this study, kinetic modeling of transesterification of jatropha *curcas* seed oil using heterogeneous catalyst was conducted and the conclusions derived from this study are as follows:

1. A new mathematical model describing kinetics of transesterification of jatropha oil using CaO as heterogeneous catalyst and stated reaction conditions has been developed as shown in Equation (14).
2. The rate determining step (RDS) for the transesterification reaction was the conversion of triglyceride to diglyceride and was being favoured by high temperature.
3. The kinetic of the reaction revealed first order (n=1) having Activation energy and frequency factor of 14.80 kJ/mol and 20.697 respectively.

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