MODELLING THE KINETICS OF ACID-BASE CATALYSIS FOR BIODIESEL PRODUCTION FROM WASTE UBE FRUIT OIL

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ABSTRACT

The production of biodiesel from waste ube oil was carried out through a two step process of esterification and transesterification reaction. The kinetics of the esterification of free fatty acid (FFA) in the waste ube oil with methanol, in the presence of Sulphuric acid at concentration of 10wt% relative to free fatty acids as catalyst concentration and methanol/oil ratio of 10:1. The energy of activation for the forward reaction decreased with increasing catalyst concentration from 4006.41 to 1346.15J/mol. The FFA was reduced from 77.84% to 0.97% in 2 hours. The kinetics of transesterification was studied with the model developed and simulated to give a result of 95.5% molar yield of biodiesel at reaction time of 60 minutes under catalyst concentration of 1%, methanol/oil ratio of 6:1 and temperature of 55^0C.

KEYWORDS: Kinetics, Catalysts, biodiesel, ube, oil, dacryodes eduli, acid-base, catalysis,esterification, transesterification, modelling.

1. INTRODUCTION

The current global challenges in ozone layer deplation, environmental degradation occassioned by exploration and exploitation of the natural oil has made vegetable oils and products synthesized from natural raw materials stage a strong come back in the recent decades as a veritable means of fuel production. In the early days of diesel engines, vegetable oils were tested as a possible motor fuel but the idea never succeeded due to incompatibility problems such as deterioration of the oil with time, high viscosity and fouling of engine. Recently, it was discovered that vegetable oil can be transformed into a product which is much more adequate as a diesel fuel than the original oil itself [1].

Although the importance of biodiesel as an alternative fuel has grown in the last twenty years, the chemical kinetics of trans-esterification, the most common means of producing biodiesel, remain controversial. Most efforts in the literature have focused on finding the best fit of empirical data to simple models of reaction order. Some of these results are contradictory [2].

Raw Ube oil has an olive green color, is semi-solid at room temperature , and frequently separates into two layers: a liquid upper and a semi-solid bottom layer . The presence of the greenish hue is suggested to be due to the presence of chlorophyll pigments. Once bleached and degummed, the oil has a yellowish-brown coloring [3].

The waste ube oil has a very high free fatty acid (FFA) this is as result of the rancidity of the oil due to the degree of biodegration occassioned by the wastage. The high FFA content of the oil makes it impossible for transesterification to be used on the oil because saponification of the oil by the base catalyst will not allow the transesterification to proceed. Glycerolysis requires a very high temperature of 200^oC and a fairly slow process. Acid catalysis is a very slow process which may take 48 hours to complete the reaction and problem of separation of the fatty acid methyl ester and water. The aim of this work is to develop the kinetics of both the acid and base catalysis reaction from which a model that will simulate the optimum conditions can be developed. The kinetics of each of the shall be developed separately.

2.0. MATERIALS AND METHODS

The oil used was obtained from waste ube fruit through solvent extraction process and the FFA composition was determined to be 77.84% FFA, the composition of the FFA as determined using thin layer chromatography equiped with flame ionization detector (TLC-FID) is as follows: stearic acid (7.2%), oleic acid (40.96%), palmitic (3.24), lineoleic (1.38), the acid value was determined as per the UNE-5500. The crude oil was degummed using Phosphoric acid and water. The degummed oil was esterified using methanol/oil ratio of 6:1, 10wt% Sulphuric acid at temperature of 60^0C in 2 hours.

The upper layer was separated from the lower layer using separating funnel and followed by washing of the sample with distilled water to remove any residual catalyst.. The influence of temperature on the esterification rate was studied at a fixed methanol/oleic acid ratio of 6:1 and temperature ranges of 30, 40, 50 and 60^0C. The transesterification reaction was carried out using Potassium hydroxide (KOH) at the range of 0.5% to 1.5%, methanol/oilratio between 3:1 to 9:1 at temperature of 55^0C and time of 60minutes in a batch process.

3.0. RESULTS AND FINDINGS

3.1   Esterification Reaction.

The elimination of FFA relies on the well-known esterification reaction.

R_1-COOH + R_2-OH R_1-COOR$_2$ + H_2O

The reaction was catalyzed by acids.

Kinetic Model

The kinetic model used in this work relied on the following Assumptions:

1. The esterification reaction was a reversible heterogenous process the rate of which is under operating conditions used was controlled by that of the chemical reaction.
2. The chemical reaction occured in oil phase.
3. The methanol/ube oil mole ratio used was high enough for the methanol concentration to remain constant throughout the process.

The reaction was assumed to be homogenous, first-order in the forward direction and second-order in the reverse direction and thus conform to the following kinetic law:

$$-\frac{dC_A}{dt} = K_1 CA - K_2 C_w C_E \qquad (1)$$

Where C_A is the concentration of FFA in mg KOH / g oil (Acid Value)

C_E is the concentration of FAME

C_W is the concentration of water

K_1 = Kinetic constan t for the forward reaction

K_2 = Kinetic constant for the reverse reation

If C_E and C_W are assumed to be zero at $E = 0$, and $A = A_o – E$

Where E = Acidity removed, then according to carberry,

$$\frac{dE}{dt} = K_1 (A_0 - E) - K_2 E^2 \qquad (2)$$

where A_0 = Initial Concentration of FFA.

On integration eqn(2) yields

$K_2 \alpha t = \ln[A_0 + E(\beta - 0.5)]/[A_0 + E(\beta + 0.5)] \qquad (3)$

Where $\alpha = \sqrt{\frac{K^2}{4} + K \cdot A_0} \qquad (4)$

$\beta = \frac{\alpha}{K} \qquad and \quad K = \frac{K_1}{K_2} \qquad (5)$

K_1 and K_2 were determined by trial and error, using variable β values until a plot of the right handside of eqn (3) consisting of a straight line with a negligible intercept was obtained. The influence of temperature on the specific reaction rate was determined by fitting K_1 and K_2 to the Arhenius equation,

$$K = Ae^{[\frac{-\Delta E}{RT}]} \qquad (6)$$

Using plots of lnK as a function of the reciprocal temperature to get the activation energy for both reactions. Figs. 1 and 2 shows the fitting of the experimental data obtained at a methanol/oleic acid mole ratio of 6:1, a catalyst concentration of 10% and a temperature of 60°C. From the results obtained it could be deduced that since the oil has a very high acid value (155.28), it will require longer time (120minutes) for the free fatty acid to be hydrolized completely. (Fig. 3 shows the

kinetic constants obtained) as expected, K_1 increased with increasing temperature; on the other hand, K_2 was negligible irrespective of the temperature, which indicates that the hydrolysis reaction hardly took place. Based on the small value of K_2, Kocsisova and Sendzikiene have proposed fitting experimental data to a first-order kinetic law.

The influence of temperature on the specific reaction rate was determined by fitting K_1 and K_2 to the Arrhenius equation,

$$K = Ae^{\frac{-\Delta E}{RT}} \qquad (7)$$

using plots of lnK as a function of the reciprocal temperature
(Fig. 4). However, both the frequency factor, A, and the energy of activation, ΔE, were obtained by non-linear regression, using the software Mintab v. 16. The results are shown in Table 1. The energy of activation for the forward reaction obtained was 4006.41 J/mol while for the reverse reaction was 1346.15J/mol.

Table 1 Energies of activation and frequency factors for the esterification of FFA in Ube oil

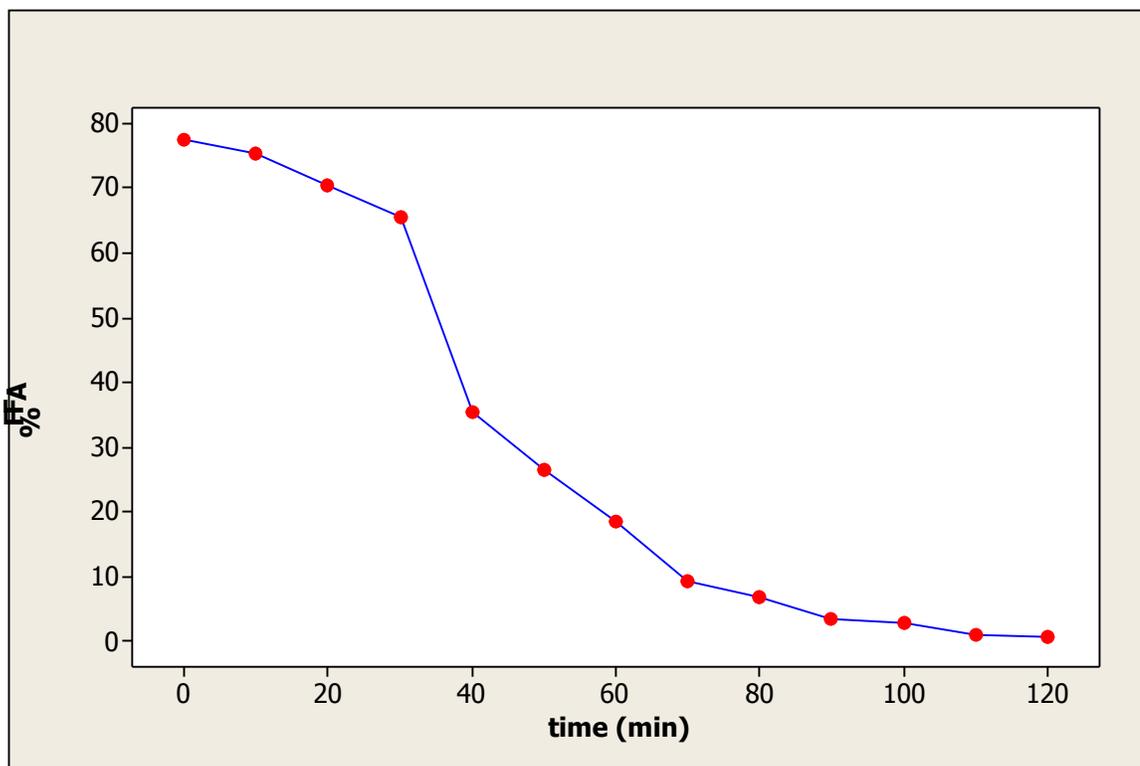| S/N	K	A	E (J/mol)
1	K_1	1.33547×10^4	4006.41
2	K_2	2.6923×10^4	1346.15

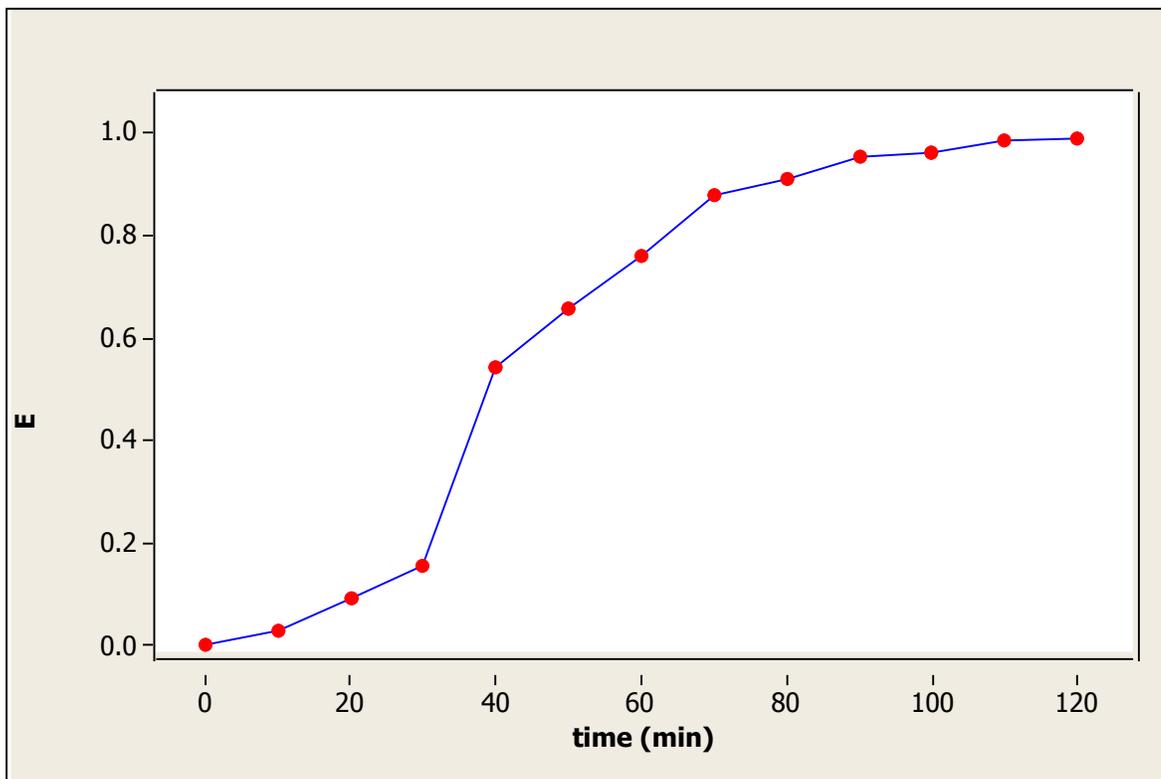Fig. 1 Conversion of FFA with respect to time
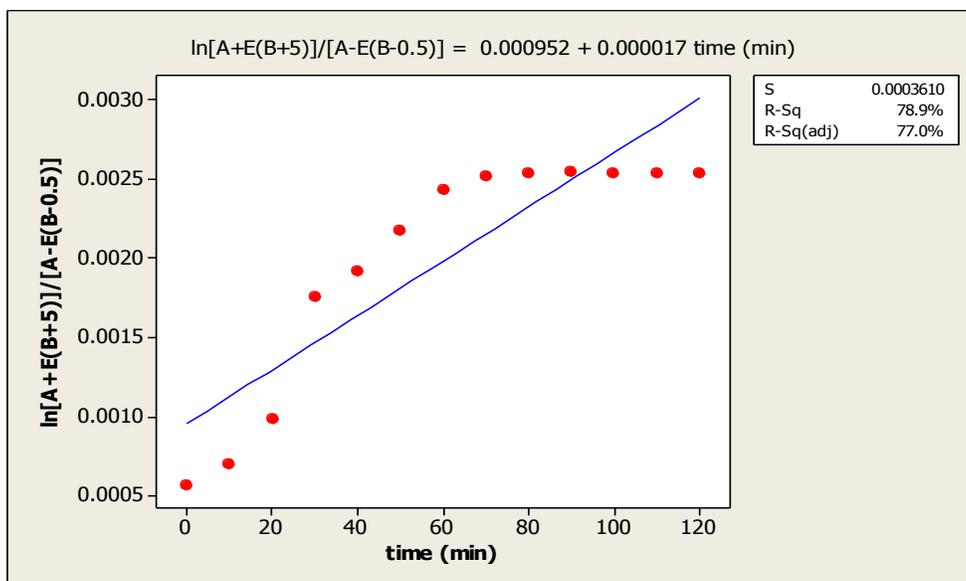
Fig. 2 Plot of Conversion of FFA Vs Time

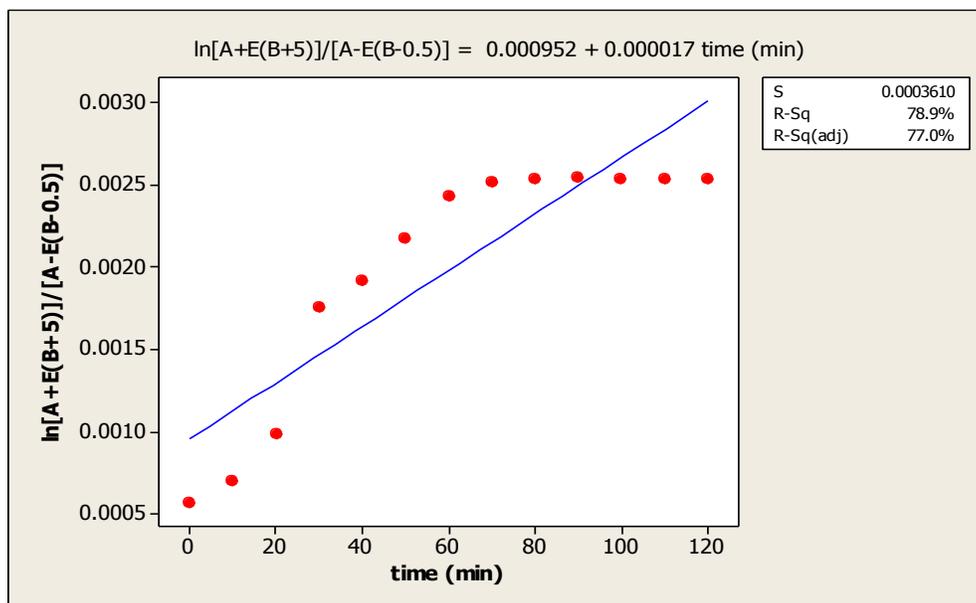Fig. 3 Determination of the Kinetic Constants

Fig. 4. Influence of temperature on the specific reaction rate

3.2 Transesterification Reactions
Kinetic Model
 Model Formation Assumptions
The following assumptions were made for the development of the kinetic model.
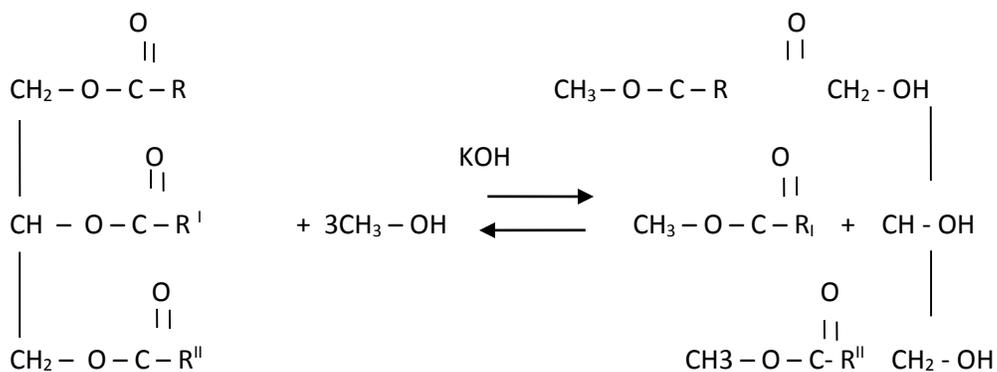1.   The forward and reverse reactions proceeded at different reaction rate.
2.   That there was no concentration gradient
3.   The pressure in the reactor was kept constant.
4.   The work done by the shaft is negligible.
5.   The FFA composition is negligible.

The Kinetics of Waste Ube oil trans-esterification is a chemical conversion process in which triacylglycerol reacts with an alcohol (Methanol) in the presence of a catalyst (KOH) to produce Waste Ube Oil Methyl ester (biodiesel) and glycerol as by – products.
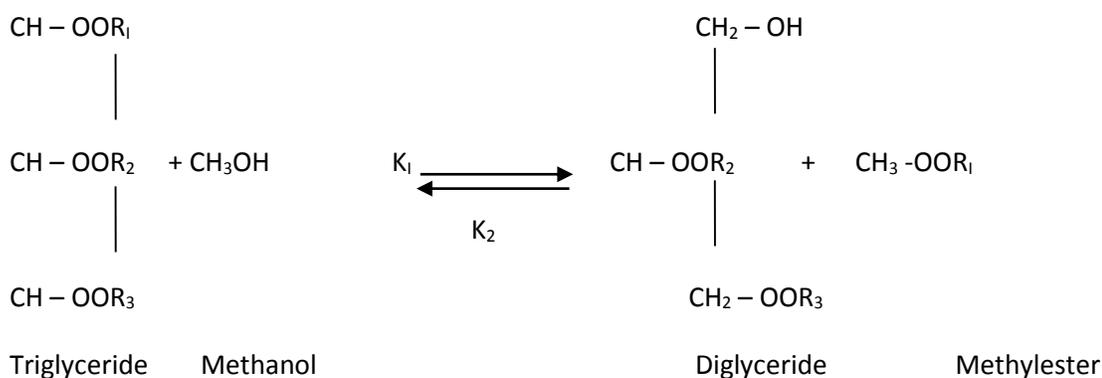The reaction kinetics involves three step wise reactions
   1. Reaction of Methanol with triglycerides to produce diglycerides.
   2. Reaction of methanol with diglycerides to produce monoglycerides.
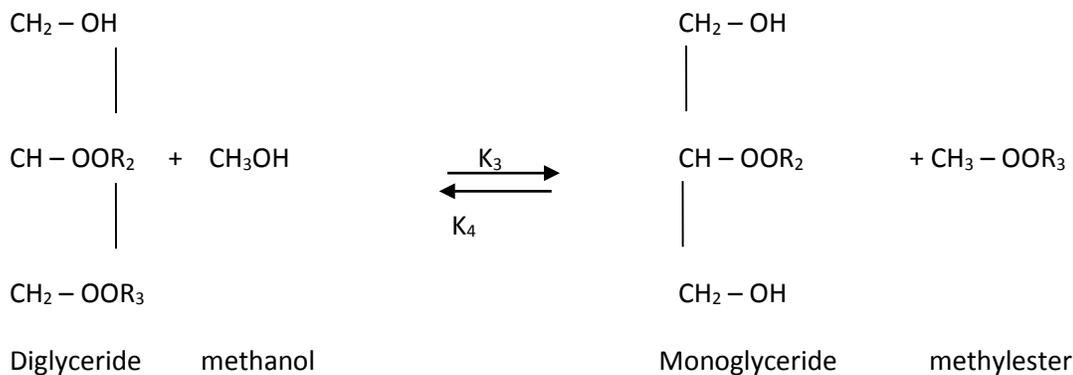   3. Reaction of Methanol with monoglycerides to produce glycerol.
In the three reactions above, one molecule of fatty acid methyl ester is produced from each of the reaction.
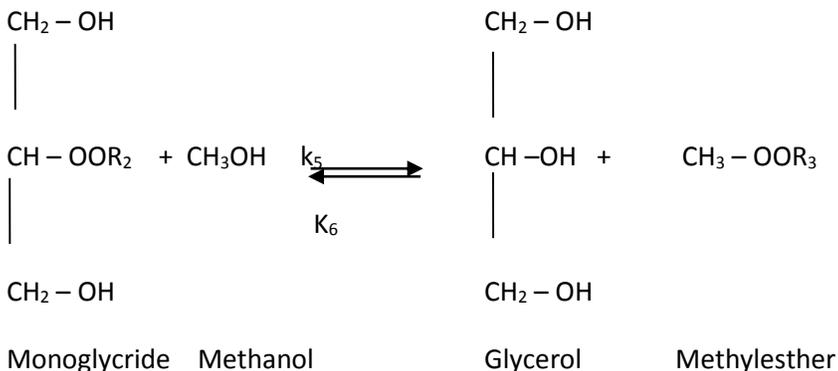
$$\begin{matrix} & \overset{\displaystyle O}{\overset{\displaystyle \|}{}} \\ CH_2 - O - C - R \end{matrix}$$

$$CH_2 - O - C - R \qquad\qquad CH_3 - O - C - R \qquad CH_2 - OH$$

$$\begin{matrix} & O \\ & \| \\ CH - O - C - R^{\,I} \end{matrix} \quad + \; 3CH_3 - OH \quad \xrightarrow{\;\; KOH \;\;} \quad \begin{matrix} O \\ \| \\ CH_3 - O - C - R_I \end{matrix} \; + \; CH - OH$$

$$CH_2 - O - C - R^{\,II} \qquad\qquad CH3 - O - C - R^{\,II} \quad CH_2 - OH$$

STEP (1)

$$\begin{matrix} CH - OOR_I \\ | \\ CH - OOR_2 \quad + CH_3OH \\ | \\ CH - OOR_3 \end{matrix} \qquad K_I \underset{K_2}{\overset{}{\rightleftarrows}} \qquad \begin{matrix} CH_2 - OH \\ | \\ CH - OOR_2 \quad + \quad CH_3 - OOR_I \\ | \\ CH_2 - OOR_3 \end{matrix}$$

Triglyceride   Methanol   Diglyceride   Methylester

STEP (2)

$$\begin{matrix} CH_2 - OH \\ | \\ CH - OOR_2 \quad + \quad CH_3OH \\ | \\ CH_2 - OOR_3 \end{matrix} \qquad K_3 \underset{K_4}{\overset{}{\rightleftarrows}} \qquad \begin{matrix} CH_2 - OH \\ | \\ CH - OOR_2 \qquad + CH_3 - OOR_3 \\ | \\ CH_2 - OH \end{matrix}$$

Diglyceride   methanol   Monoglyceride   methylester

STEP (3)

$$CH_2 - OH \qquad\qquad\qquad CH_2 - OH$$

$$CH - OOR_2 \ + \ CH_3OH \quad \xrightleftharpoons[K_6]{k_5} \quad CH - OH \ + \qquad CH_3 - OOR_3$$

$$CH_2 - OH \qquad\qquad\qquad CH_2 - OH$$

Monoglycride   Methanol   Glycerol   Methylesther

The three stepwise reactions and the overall can be written symbolically as

$$TG \ + \ ROH \quad \xrightleftharpoons[K_2]{K_1} \quad DG \ + \ ME$$

$$DG \ + \ ROH \quad \xrightleftharpoons[K_4]{K_3} \quad MG \ + \ ME$$

$$MG \ + \ ROH \quad \xrightleftharpoons[K_6]{K_5} \quad GL \ + \ ME$$

And overall

$$TG \ + \ 3ROH \quad \xrightarrow{\underset{Catalyst}{NaOH}} \quad GL \ + \ 3ME$$
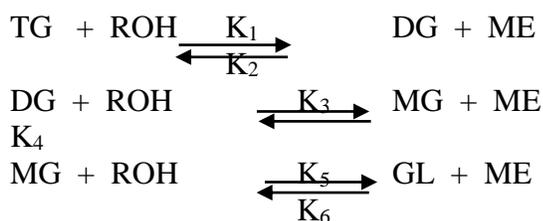
The rate equation will therefore involve mathematical expression describing the rate of progress of the reaction. In order to derive the various rate equations for each of the species in the Ube oil transesterification reaction, the overall chemical equation can be simplified into their single elementary reactions.

$$TG + ROH \quad \xrightarrow{K_1} \quad DG + ME$$
$$DG + ME \quad \xrightarrow{K_2} \quad TG + ROH$$
$$DG + ROH \quad \xrightarrow{K_3} \quad MG + ME$$
$$MG + ME \quad \xrightarrow{K_4} \quad DG + ROH$$
$$MG + ROH \quad \xrightarrow{K_5} \quad GL + ME$$
$$GL + ME \quad \xrightarrow{K_6} \quad MG + ROH$$
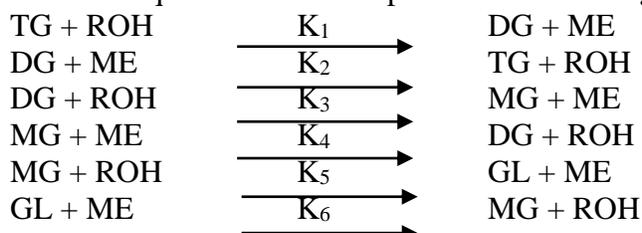
Where
TG = Triglyceride
DG = Diglyceride
MG = Monoglyceride
GL = Glycerol
ME = Methyl Ester
ROH = Alcohol
$K_1, K_2, K_3, K_4, K_5,$ and K_6 are constants

The following rate equations are therefore established.

$$dC_{TG}/dt = -K_1 C_{DG} C_{ROH} + K_2 C_{DG} C_{ME} \qquad\qquad 1$$
$$dC_{DG}/dt = K_1 C_{TG} C_{ROH} - K_{2TG} C_{ROH} - K_3 C_{MG} C_{ROH} + K_4 C_{MG} C_{ME} \qquad\qquad 2$$
$$dC_{MG}/dt = K_3 C_{DG} C_{ROH} - K_4 C_{DG} C_{ROH} - K_5 C_{GL} C_{ME} + K_6 C_{GL} C_{ME} \qquad\qquad 3$$
$$dc_{ME}/dt = K_1 C_{TG} C_{ROH} - K_2 C_{TG} C_{ROH} + K_3 C_{DG} C_{ROH} - K_4 C_{DG} C_{ROH} + K_5 C_{MG} C_{ROH} - K_6 C_{MG} C_{ROH} \qquad\qquad 4$$

$$dc_{ROH}/dt = -K_1 C_{DG} C_{ME} + K_2 C_{DG} C_{ME} - K_3 C_{MG} C_{ME} + K_4 C_{MG} C_{ME} - K_5 C_{GL} C_{ME} + K_6 C_{GL} C_{ME} \qquad 5$$
$$dc_{GL}/dt = K_5 C_{MG} C_{ROH} - K_6 C_{MG} C_{ROH} \qquad\qquad 6$$
$$r_{TG} = -K_1 C_{TG} C_{ROH} - K_2 C_{DG} C_{ME} \qquad\qquad 7$$
$$r_{DG} = K_1 C_{TG} C_{ROH} - R_2 C_{DG} C_{ME} - K_3 C_{DG} C_{ROH} + K_4 C_{MG} C_{ME} \qquad\qquad 8$$
$$r_{MG} = K_3 C_{MG} C_{ME} - K_4 C_{MG} - K_S C_{MG} C_{ROH} + K_6 C_{GL} C_{ME} \qquad\qquad 9$$
$$r_{GL} = K_S C_{MG} C_{ROH} - K_6 C_{GL} C_{ME} \qquad\qquad 10$$
$$r_{ROH} = -k_1 G_G C_{ROH} - k_2 C_{DG} C_{ME} + K_3 C_{DG} C_{ROH} + K_4 C_{MG} C_{ME} + K_6 C_{GL} C_{ME} \qquad\qquad 11$$
$$r_{Me} = -r_{ROH} \qquad\qquad 12$$

Substituting the rate equations into the performance equation establishes the modeled ordinary differential equations (MODES) for the trans-esterification of waste ube oil.

$$dC_{TG}/dt = -K_1 C_{TG} C_{ROH} + K_2 C_{DG} C_{ME} \qquad\qquad 13$$
$$dC_{DG}/dt = K_1 C_{TG} C_{ROH} - K_2 C_{DG} C_{ME} - K_3 C_{DG} C_{ROH} + K_4 C_{MG} C_{ME} \qquad\qquad 14$$
$$dC_{MG}/dt = K_3 C_{DG} C_{ROH} - K_4 C_{MG} C_{ME} - K_5 C_{MG} C_{ROH} \qquad\qquad 15$$
$$dC_{GL}/dt = k_5 C_{MG} C_{ROH} - K_6 C_{GL} C_{ME} \qquad\qquad 16$$
$$dC_{ROH}/dt = -K_1 C_{TG} C_{ROH} + K_2 C_{DG} C_{ME} - K_3 C_{DG} C_{ROH} + K_4 C_{MG} C_{ME} - K_2 C_{MG} C_{ROH} + K_6 C_{GL} C_{ME} + (C_{ROHO} - C_{ROH}) \qquad\qquad 17$$
$$dc_{ME}/dt = K_1 G_G C_{ROH} - K_2 C_{DG} C_{ME} + K_3 C_{DG} C_{ROH} - K_4 C_{MG} C_{ME} + K_5 C_{MG} C_{ROH} - K_6 C_{GL} C_{ME} \qquad\qquad 18$$

$$K1 = C_{DG} C_{ME}/C_{TG} C_{ROH} \qquad\qquad 19$$
$$K2 = C_{TG} C_{ROH}/C_{DG} C_{ME} \qquad\qquad 20$$
$$K3 = C_{MG} C_{ME}/C_{DG} C_{ROH} \qquad\qquad 21$$
$$K4 = C_{DG} C_{ROH}/C_{MG} C_{ME} \qquad\qquad 22$$
$$K5 = C_{ML} C_{ME}/C_{MG} C_{ROH} \qquad\qquad 23$$
$$K6 = C_{MG} C_{ROH}/C_{GL} C_{ME} \qquad\qquad 24$$

Simulation Methodology

A Computer program for solving the differential equation was employed on the program Matlab 7.5 to solve the system of differential equations for the trans-esterification of waste ube oil. The system of design equations was solved for residence time up to 60 minutes. Generally for numerical technique, the step size of step time (t) used in simulation affects the obtained results. The values of the various rate constants was calculated from the experimental results obtained.

Table 2 Tabulation of Rate Constants

Rate Constant	Values
K_1	1.415
K_2	0.350
K_3	2.776
K_4	2.191
K_5	3.236
K_6	0.143

The results obtained from the simulation are presented in Figures 5, 6 and 7 which predicts the composition profile during trans- esterification of ube oil at 55°C using the k values at molar ratio of 3:1, 6:1 and 9:1 for methanol: oil. The composition of FAME was higher at 3:1 compared to 6:1 and 9:1.

Concentration Profile

The concentration curves for the Trans esterification of waste ube oil at 55ºC with varying reaction ratios (3:1, 6:1 and 9:1) are presented in Figure 5, 6 and 7. The plots show the rate of consumption of triglycerides and formation of methyl esters and glycerol as well as the intermediates. It showed curves for the production of methyl esters and glycerol. This is an indication of a slow reaction rate at the beginning which is followed by a sudden surge and finally a lower rate as the reaction approaches completion. At the molar ratio 0f 3:1, it took 100 minutes for the reaction to produce $2mol/dm^3$ of methyester, at molar ratio of 6:1 it took 15 minutes to reach $2mol/dm^3$ of methyl ester produced while at 9:1 molar ratio it took 10 minutes to reach $2mol/dm^3$. In general, the concentration of the products increases with time. As the reaction progresses. The yield increased with an increase in molar ratio. From the three graphs it could be deduced that optimum yield is achieved at 50 minutes with molar ratio of 9:1 and catalyst concentration of 1%.
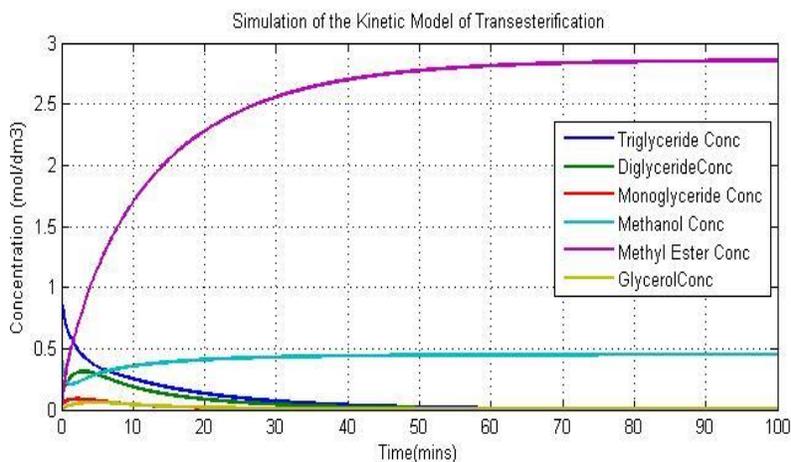

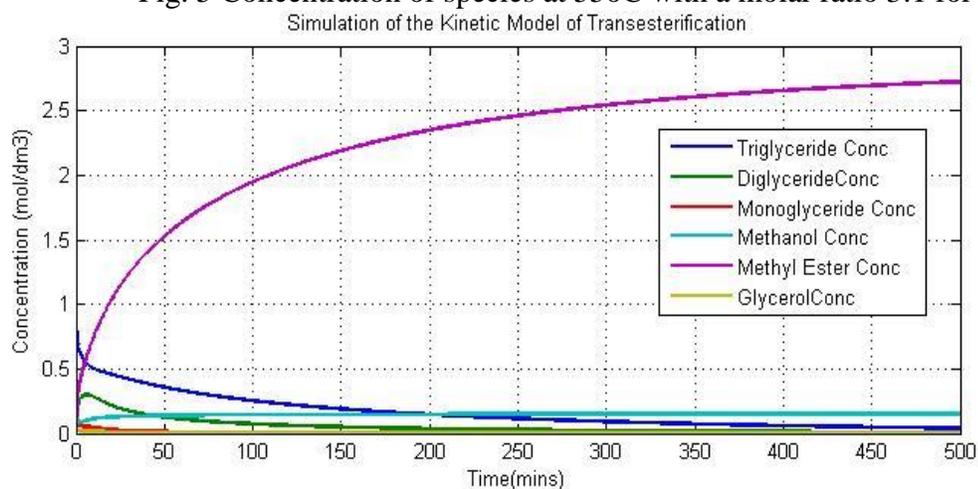Fig. 5 Concentration of species at 55oC with a molar ratio 3:1 for methanol: oil

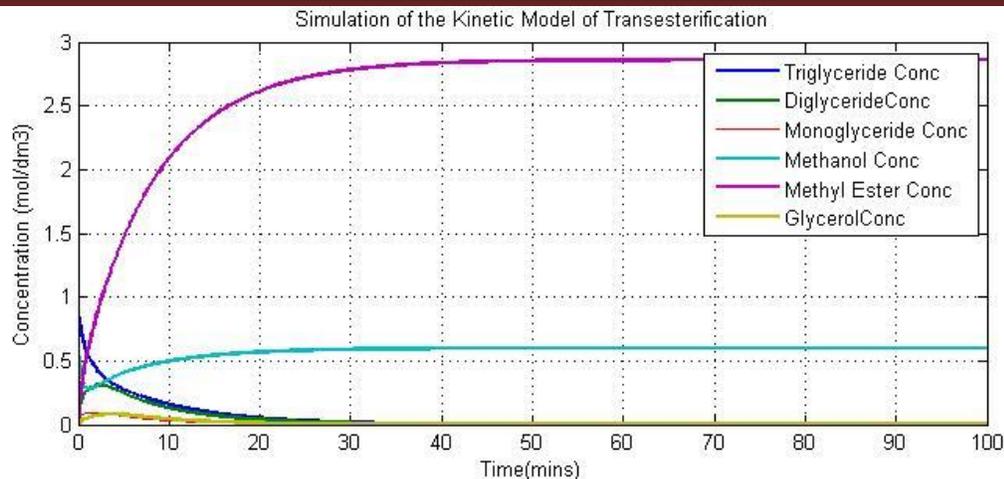Fig. 6 Concentration of species at 50ºC with a molar ratio 6:1 for methanol: oil

Fig. 7 Concentration of species at 50oC with a molar ratio 9:1 for methanol: oil

CONCLUSION

The high FFA content of the waste ube fruit oil makes transesterification reaction to be unsuitable for the production of biodiesel therefore leaving only the option of esterification followed by transesterification reaction. The essence of esterification reaction was to reduce the FFA from 77.84% to less than 1%. The FFA in ube oil can be removed effectively by esterification with methanol using a 10% Sulphuric acid concentration relative to FFA, a methanol/oil ratio of 6:1 temperature of 60^0C at speed of 250rpm and time of 2hours. The simulation of the kinetic model of the transesterification process showed that the optimum yield was achieved at 50minutes with molar ratio of 9:1 and catalyst concentration of 1%.

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