

Mathematical Modeling of Reversible Bimolecular Catalyzed Transesterification Reaction Kinetics for PKO and Methanol synthesis

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Abstract

Continuous appraisal for alternative renewable energy sources particularly for bio-diesel production is a great concern to engineers and scientist globally. Actually, vegetable oils and C1 to C3 alcohol group alkali catalyzed transesterification reaction leads to bio-diesel production. The aspect of developing reaction time and disappearance rate (-R_A) mathematical models for effective various reactor types design seems impassive. Hence, in this work the authors developed a unified reaction time and disappearance rate (-R_A) predictive models as a function of reactants and product reaction rate constants (K₁ K₂), molar masses (MW), conversion (X_A), fractional volume change (ε) and density (ρ) dimensions using partial fraction and by parts integration methods. The developed models were simulated with Matlab codes programming approach exploiting the kinetics parameters of PKO, Methanol and biodiesel.

The results of the reaction time (t) at equilibrium, none equilibrium and disappearance rate (-R_A) show dependable relationship with the stipulated dimensions and were quite compatible with those of inferential laboratory physicochemical data reported. Thus;

$$-R_{\varepsilon A} = \frac{C_{AO}^2}{(1 + \varepsilon_A X_A)^2} [K_1(1 - X_A)(M - X_A) - K_2(N + X_A)(P + X_A)]$$

$$t_{\varepsilon} = \frac{1}{2K_1 \left(\frac{1}{X_{AE}} - 1 \right) C_{AO}} \ln \left(\frac{X_A - (2X_{AE} - 1)X_A}{X_{AE} - X_A} \right), \text{ and}$$

$$t = \frac{1}{C_{AO}} \left[\frac{1}{K_1} \left[\frac{1 + \varepsilon_A}{M - 1} \left(\ln \frac{1}{1 - X_A} \right) + \frac{1 + \varepsilon_A M}{1 - M} \ln \left(\frac{1}{M - X_A} \right) \right] \right. \\ \left. - \frac{1}{K_2} \left[\frac{1 - \varepsilon_A N}{P - N} \ln(N + X_A) + \frac{1 - \varepsilon_A P}{N - P} \ln(\rho + X_A) \right] \right]$$

Keywords:

Alkali Catalyzed Transesterification, Biodiesel, Mathematical Modelling, Reaction, Time Disappearance Rate.

Introduction

Significance of Study

Substantial inferential Laboratory works regarding alkali catalyzed transesterification of various equitable types and alcohol groups have been carried by engineers and scientists globally [1-17]. The researchers aim in this regard were primarily to optimize biodiesel production through the renewable energy sources. Another reason is focused on the possibility of eliminating environmental nuisance

chemical species emanating from the biodiesel production through the crude oil sources.

Noteworthy enough, the researchers used various vegetable oil types such as red palm oil, palm kernel oil, coconut oil and milk bush with alcohol groups from CH₃OH to C₃H₇OH – in alkali catalyzed transesterification processes thereby developing matrix component based kinetic analysis. Furthermore, these researchers need novel works were limited to inferential laboratory analysis and obtained values of reaction rates constants k₁ and k₉ establishing second order magnitude with units volume per mol per time [8-12]. The aspect of developing a feasible rate mathematical model that could be used

to design various industrial scale reactor types seems impressive. Interestingly, recent work of Abowei et al was able to mathematically express explicitly PKO and Methanol synthesis as reversible bimolecular reaction. The authors limited to the algebraic expression of the rate of reaction as typical of bimolecular reflections[15]. Hence in this work, we considered disappearance rate (-RA) and reaction time (t) mathematical modeling for alkali catalyzed transesterification of palm kernel oil and methanol processes positive definite integral techniques.

Structure, Uses, Physical and Chemical Properties

It is relevant to assess the extent of some previous works reported on palm kernel oil, methanol and biodiesel and glycerol structure, uses, physical and chemical properties including chemistry. Interestingly, alkali catalyzed palm kernel oil and methanol transesterification reaction process results into product formation of biodiesel and glycerol whose structures are given in figure 1.

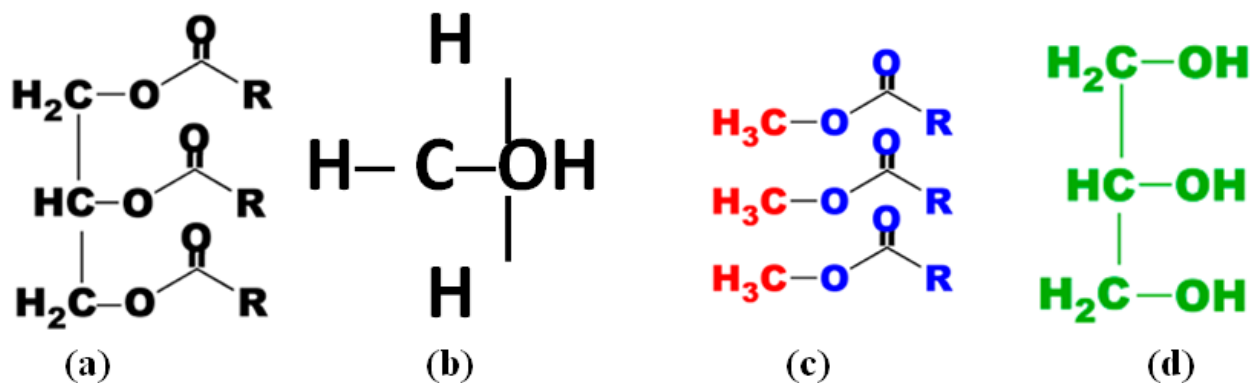


Figure 1: Palm Kernel Oil (a), Methanol (b), Biodiesel (c), Glycerol (d)[1-12]

The physical and chemical properties of palm kernel oil, methanol, bio-diesel and glycerol were qualitatively appraised

and widely published[1-12]. The physical and chemical properties of these chemical species are represented in table 1.

Table 1: Physical and Chemical Properties

| PROPERTIES | VALUES | | | |
|--|--------------------------------|----------------------------|--------------------------------|------------------------|
| | PKO | Methanol | Biodiesel | Glycerol |
| Density | .9898 g/l (40oC) | 0.79 – 0.80 g/l (20oC) | 0.871g/l (30oC) | 1.26 g/cm ³ |
| Kinematic viscosity | 30.1(40oC)[mm ² /s] | 0.544 – 0.59 mPa –s (25oC) | 2.99 mm ² /s (40oC) | 1.412 Pa•s |
| Molarmass | 182g/mol | 32g/mol | 186 g/mol | 92.094g/mol-1 |
| Melting point | 25 – 30oC | -97.8oC | 06oC | 17.8 °C |
| Boiling Point | 20oC | 64.7oC | 7.5oC | 290 °C |
| Colour | Burnt smell | Colourless | Pale Yellow | Colorless |
| Odour | Burnt brown | Odour Alcohol | Liquid mild | Odorless |
| Latent Heat of Vaporization | N/A | 37.43kJ/mol | N/A | 78.5kJ/mol |
| Refractive Index | 1.453 | 1.32652 | N/A | 1.4746 |
| Heat of Combustion | N/A | 726.1kJ/mol | 38.6 mj/kg | -1654.3 kJ/mol |
| Critical temperature | 31oC | 240oC | >220oC | 577 °C |
| Critical pressure | 74 bar | 79547 hPa | N/A | 74.02 |
| Flash point | 267oC | 9.7oC | 155oC | 160 °C |
| Relative evaporation rate (butyl acetate =1) | N/A | 4.1 | <1 | N/A |
| Relative evaporation rate (ether=1) | N/A | 6.3 | N/A | N/A |
| Vapor pressure | 0.19 to 2.16) kPa | 128 hPa (20oC) | N/A | 2.75 |

In addition, because of urged industrial and domestic application of PKO, Methanol, Biodiesel and Glycerol, great deal of works

on this aspect of uses are also reported accordingly by various researchers[1-12] as presented in table 2.

| Uses | | | |
|--|--|---------------------------|-------------------------------|
| PKO | Methanol | Biodiesel | Glycerol |
| * Biodiesel production | *Fuel | * Vehicular use | * FDA approved wound |
| * Cooking and frying oil | *denaturant for ethyl Alcohol | * Manufacturer acceptance | * Burn treatments |
| *Margarines production | * Solventfor Shellac | *Biodiesel in generator | * Electronic Cigarette liquid |
| * Shortenings Non-dairy Creamers | * Solvent for Varnishes Automobile Radiator anti – freeze, | *Transformer oil | * Antifreeze |
| * Whipping creams As cocoa butter substitute | *Denaturing additive to ethyl alcohol | *General heating oil | * Chemical intermediate |
| * In manufacture of soaps | *Denaturing poisons the ethyl alcohol | | *Vibration damping |
| * Oleochemicals | | | * Niche uses |
| * in Cosmetics | | | * Film industry |
| * Personnel care productas skin conditioner | | | * Ultrasonic couplant |
| *Cake residue obtained after extracting | | | * Internal combustion fuel. |
| Can beused as - feed for livestock -antidotes capabilities - Surface protection | | | |

Reaction Mechanism

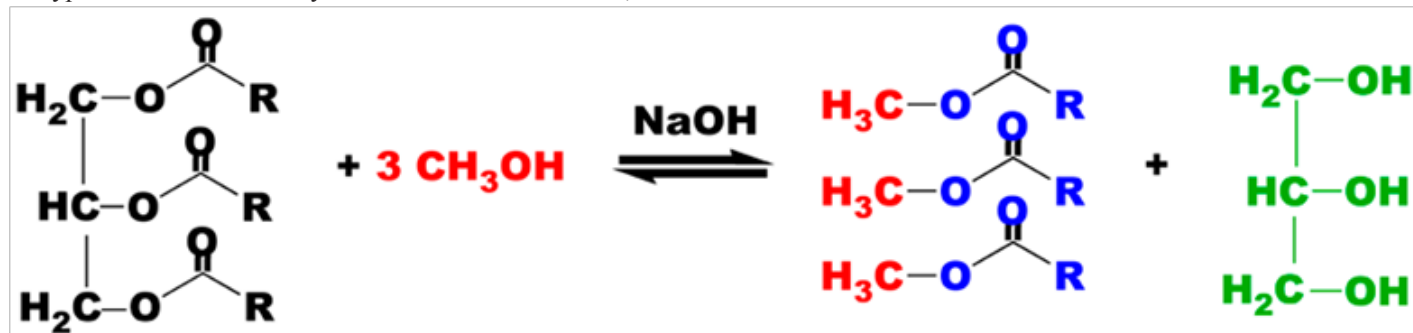
Interestingly, PKO and CH₃OH Catalyzed Reaction is a transesterification process in which researchers focussed their attention on the inferential laboratory analysis for the purpose of

establishing the order of reaction rate constants[9].

In any case, the stoichiometry and kinetics rate analysis of this reaction were reported thus;

Stoichiometry

The hypothetical stoichiometry of the reaction is as follows;

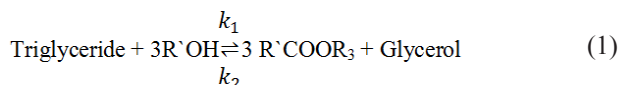


Triglyceride

3 molecules of methyl esters

Glycerol

And the overall reaction for the transesterification is summarized thus;



Similarly the kinetics describing the reaction mechanism is limited and is hypothetically presented by previous as follows;



The overall reaction was now



Where TG = glyceride (PKO), ROH = methanol, E = ethyl ester, DG = diglyceride and MG = monoglyceride.

The researchers in their work proved second-order reaction rate constant and arrived at the governing equations characterizing the stepwise reactions for transesterification of triglycerides [8-12].

$$\frac{dTG}{dt} = -K_1TG.A + K_2DG.E - K_7TG.A^3 + K_8GL.E^3 \quad (6)$$

$$\frac{DDG}{dt} = K_1TG.A - K_2DG.E - K_3DG.A + K_4MG.E \quad (7)$$

$$\frac{dMG}{dt} = K_3DG.A - K_4MG.E - K_5MG.A + K_6MG.E \quad (8)$$

$$\frac{dGL}{dt} = K_5MG.A - K_6GL.E + K_7TG.A^3 - K_8GL.E^3 \quad (9)$$

$$\frac{dE}{dt} = K_1TG.A - K_2DG.E + K_3DG.A - K_4MG.E + K_5MG.A \quad (10)$$

$$-K_6GL.E + K_7TG.A^3 - K_8GL.E^3 \quad (11)$$

$$\frac{dA}{dt} = -\frac{dE}{dt} \quad (12)$$

Where K_1 to K_8 are reaction rate constants, TG, DG, MG, GL, A and E are the concentrations in weight percent of triglyceride, diglyceride, monoglyceride, glyceride, methanol and ester respectively. In addition the kinetic analysis as presented in equations 1 to 12 where summarized based on matrix transformation module as thus;

$$\begin{bmatrix} a_{11} & a_{12} & a_{13} & a_{14} & a_{15} & a_{16} & a_{17} & a_{18} \\ a_{21} & a_{22} & a_{23} & a_{24} & a_{25} & a_{26} & a_{27} & a_{28} \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ a_{n1} & a_{n2} & a_{n3} & a_{n4} & a_{n5} & a_{n6} & a_{n7} & a_{n8} \end{bmatrix} \begin{pmatrix} K_1 \\ K_2 \\ \cdot \\ \cdot \\ K_7 \\ K_8 \end{pmatrix} = \begin{pmatrix} D_1 \\ D_2 \\ \cdot \\ \cdot \\ D_n \end{pmatrix} \quad (13)$$

From equation 13 obviously, there is need to develop a feasible unified reaction time and disappearance rate equations that can be used for various industrial reactor types designs this had seemed not critically looked into. Hence this work is focused on mathematically modeling of reaction time at equilibrium, non-equilibrium and disappearance rate that can be exploited to

facilitate design of industrial base reactor.

Materials and Methods

Materials

The Materials exploited in this work entails mainly desktop research component such as; Laptop, Matlab software, work spreadsheet and other associated computational tools for the simulation of the developed mathematical models.

Model Formulation

Partial fraction and by-parts integral coupled with simple algebraic techniques were exploited in the development of the simulative mathematical models. In this work consideration is based on the fact that the reaction mechanism as equation 1 demonstrated reversible bi-molecular reaction of second-order magnitude [13]. Now putting A = PKO, B = NaOH, R = Glycerol and S = Methyl Ester; then equation can be rewritten as;



From the reaction stoichiometry as in equation 14, a kinetic rate can be mathematically defined, thus;

$$-R_A = \frac{-dC_A}{dt} = K_1C_A C_B - K_2C_R C_S \quad (15)$$

Where $-RA$ = Disappearance rate, K_1 & K_2 = reaction rate constants; C_A , C_B , C_R & C_S are concentrations of PKO, NaOH, Glycerol & Methyl Ester respectively.

Disappearance (-RA) Rate Model

Interestingly, from the reaction stoichiometry as in equations 1 and 14, alkali catalyzed transesterification of PKO and methanol reaction shows exothermic and therefore voidage (ϵ) term can be inculcated into equation 16 as;

$$-R_{\epsilon A} = K_1 \left(\frac{C_{AO} - C_{AO}X_A}{1 + \epsilon_A X_A} \right) \left(\frac{C_{BO} - C_{AO}X_A}{1 + \epsilon_A X_A} \right) - K_2 \left(\frac{C_{RO} + C_{AO}X_A}{1 + \epsilon_A X_A} \right) \left(\frac{C_{SO} + C_{AO}X_A}{1 + \epsilon_A X_A} \right) \quad (16)$$

$$\text{Where; } C_A = C_{AO} \left(\frac{1 - X_A}{1 + \epsilon_A X_A} \right) \quad (17)$$

$$-R_{\epsilon A} = \frac{C_{AO}^2}{(1 + \epsilon_A X_A)^2} \left[K_1(1 - X_A) \left(\frac{C_{BO}}{C_{AO}} - X_A \right) - K_2 \left(\frac{C_{RO}}{C_{AO}} + X_A \right) \left(\frac{C_{SO}}{C_{AO}} + X_A \right) \right] \quad (18)$$

Again putting $M = \frac{C_{BO}}{C_{AO}}$; $N = \frac{C_{RO}}{C_{AO}}$; $P = \frac{C_{SO}}{C_{AO}}$ to equation 31 results in;

$$-R_{\epsilon A} = \frac{C_{AO}^2}{(1 + \epsilon_A X_A)^2} [K_1(1 - X_A)(M - X_A) + K_2(N + X_A)(P + X_A)] \quad (19)$$

Conversely the reaction time for transesterification process can be calculated as;

$$-R_{\epsilon A} = C_{AO} \frac{dX_A}{dt} = \frac{C_{AO}^2}{(1 + \epsilon_A X_A)^2} [k_1(1 - X_A)(M - X_A) - K_2(N + X_A)(P + X_A)] \quad (20)$$

$$\frac{dX_A}{dt} = \frac{C_{AO}^2}{(1 + \epsilon_A X_A)^2} [k_1(1 - X_A)(M - X_A) - K_2(N + X_A)(P + X_A)]$$

Equation 19 and 20 are the Abowei et al modified rate expression for the bimolecular reversible vegetable oils and C1 to C3 alcohol catalyzed transesterification reaction in the production of biodiesel and glycerin.

Now considering the coefficients of the transesterification reaction as in equation 1, thus

$$\varepsilon = \frac{\Sigma P - \Sigma R}{\Sigma R} \quad (21)$$

Where ΣP and ΣR are coefficients of product and reactants respectively; then $\Sigma R=4$, $\Sigma P=2$ and upon substitution into equation 21 gives

$$\varepsilon = 2-4/4 = -1/2$$

This shows that the reaction for palm kernel oil and methanol is an exothermic and the kinetic rate model as developed in equation 19 and 20 needs to be inculcated.

Reaction time (t) evaluation

From equation 33 at isothermal situation, it is possible that

$$-R_A = C_{AO} \frac{dX_A}{dt} = C_{AO}^2 \{K_1(1-X_A)(M-X_A) - K_2(N+X_A)(P+X_A)\} \quad (22)$$

At equilibrium situation with restrictions that $C_{AO} = C_{BO}$ and $C_{NO} = C_{PO} = 0$; $dC_{AO}/dt = 0$; Hence from equation 22 we establish the fractional conversion of A at equilibrium conditions to be;

$$K_C = (N+X_{AE})(P+X_{AE}) / (1-X_{AE})(M+X_{AE}) \quad (23)$$

$$\text{Where } K_C = K_1/K_2 \quad (24)$$

Equation 22 to 24 can be rewritten as;

$$\frac{1}{K_2} \frac{dX_A}{dt} = C_{AO} [K_C(1-X_A)(M-X_A) - (N+X_A)(P+X_A)] \quad (25)$$

Substituting equation 23 into 25 gives

$$\frac{1}{K_2} \frac{dX_A}{dt} = C_{AO} \left[\frac{(N+X_{AE})(P+X_{AE})}{(1-X_{AE})(M+X_{AE})} [(1-X_A)(M-X_A)] - (N+X_A)(P+X_A) \right] \quad (26)$$

Further simplification of equation 26 gives;

$$\frac{1}{K_2} \frac{dX_A}{dt} = C_{AO} \left[\frac{(N+X_{AE})(P+X_{AE})(1-X_A)(M-X_A) - (1-X_{AE})(M+X_{AE})(N+X_A)(P+X_A)}{(1-X_{AE})(M+X_{AE})} \right] \quad (27)$$

Equation 27 upon adoption of induction and algebraic manipulations with subsequent integrations resulting to;

$$\ln \left(\frac{X_A - (2X_{AE}-1)X_A}{X_{AE} - X_A} \right) = 2K_1 \left(\frac{1}{X_{AE}} - 1 \right) C_{AO} t \quad (28)$$

$$t = \frac{1}{2K_1 \left(\frac{1}{X_{AE}} - 1 \right) C_{AO}} \ln \left(\frac{X_A - (2X_{AE}-1)X_A}{X_{AE} - X_A} \right) \quad (29)$$

Where X_A & C_{AO} = PKO Fractional conversion and concentration respectively;

At non equilibrium situation with the consideration of non-isothermal exothermic situation, then equation 29 could be solved as follows;

Integration Partial Fraction Method

$$\int \frac{(1+\varepsilon_A X_A) dX_A}{K_1(1-X_A)(M-X_A)} - \int \frac{(1+\varepsilon_A) dX_A}{K_2(N+X_A)(P+X_A)} = C_{AO} \int dt. \quad (30)$$

$$\text{Putting } B = \int \frac{1+\varepsilon_A X_A}{K_1(1-X_A)(M-X_A)} dX_A \quad (30)$$

$$\text{and } C = \int \frac{1+\varepsilon_A X_A}{K_2(N+X_A)(P+X_A)} dX_A \quad (31)$$

Now applying partial fractions technique resulting to; for B keeping $1/K_1$ as a multiplying factor; thus;

$$\frac{A}{1-X_A} + \frac{L}{(M-X_A)} = \frac{1+\varepsilon_A X_A}{(1-X_A)(M-X_A)} \quad (32)$$

$$\frac{A(M-X_A) + L(1-X_A)}{(1-X_A)(M-X_A)} = \frac{1+\varepsilon_A X_A}{(1-X_A)(M-X_A)} \quad (33)$$

$$A(M-X_A) + L(1-X_A) = 1 + \varepsilon_A X_A \quad (34)$$

Let $X_A = M$, then $0 + L(1-M) = 1 + \varepsilon_A M$; thus,

$$L = (1 + \varepsilon_A M) / (1-M) \quad (35)$$

Let $X_A = 1$; then $A(M-1) + L(0) = 1 + \varepsilon_A$; thus

$$A = (1 + \varepsilon_A) / (M-1) \quad (36)$$

For C; keeping $1/K_2$ as a multiplying factor; thus

$$\frac{Q}{(N+X_A)} + \frac{R}{P+X_A} = \frac{1 + \varepsilon_A X_A}{(N+X_A)(P+X_A)} \quad (37)$$

$$Q(P+X_A) + R(N+X_A) = 1 + \varepsilon_A X_{AA} \quad (38)$$

Let $X_A = -P$; then $Q(0) + R(N-P) = 1 - \varepsilon_A P$; thus

$$R = (1 - \varepsilon_A P) / (N-P) \quad (39)$$

Let $X_A = -N$; then $Q(0) + R(P-N) = 1 - \varepsilon_A N$; thus

$$Q = (1 - \varepsilon_A N) / (P-N) \quad (40)$$

$$C_{AO} t = \frac{1}{K_1} \left[\frac{1+\varepsilon_A}{M-1} \left[-\ln(1-X_A) + \frac{1+\varepsilon_A M}{1-M} \ln(M-X_A) \right] - \frac{1}{K_2} \left[\frac{1-\varepsilon_A N}{P-N} \ln(N+X_A) + \frac{1-\varepsilon_A P}{N-P} \ln(P+X_A) \right] \right] \quad (41)$$

$$C_{AO} t = \frac{1}{K_1} \left[\frac{1+\varepsilon_A}{M-1} \left[\ln\left(\frac{1}{1-X_A}\right) + \frac{1+\varepsilon_A M}{1-M} \ln\left(\frac{1}{M-X_A}\right) \right] - \frac{1}{K_2} \left[\frac{1-\varepsilon_A N}{P-N} \ln(N+X_A) + \frac{1-\varepsilon_A P}{N-P} \ln(P+X_A) \right] \right] \quad (42)$$

$$t = \frac{1}{C_{AO}} \left[\frac{1}{K_1} \left[\frac{1+\varepsilon_A}{M-1} \left(\ln\left(\frac{1}{1-X_A}\right) + \frac{1+\varepsilon_A M}{1-M} \ln\left(\frac{1}{M-X_A}\right) \right) - \frac{1}{K_2} \left[\frac{1-\varepsilon_A N}{P-N} \ln(N+X_A) + \frac{1-\varepsilon_A P}{N-P} \ln(P+X_A) \right] \right] \right] \quad (43)$$

Integration by Parts Technique

$$\frac{dX_A}{dt} = \frac{C_{AO}}{1+\varepsilon_A} [K_1(1-X_A)(M-X_A) - K_2(N+X_A)(P+X_A)] \quad (44)$$

Expanding right hand side of equation (44) gives;

$$\left. \begin{aligned} \text{Let } D &= K_1(1-X_A)(M-X_A) \\ &= K_1[M - X_A - X_A M + X_A^2] \\ &= K_1 M - K_1 X_A - K_1 X_A M + K_1 X_A^2 \end{aligned} \right\} \quad (45)$$

$$\left. \begin{aligned} \text{Let } E &= K_2(N + X_A)(P + X_A) \\ &= K_2[NP + NX_A + X_AP + X_A^2] \\ &= K_2NP + K_2NX_A + K_2X_AP + K_2X_A^2 \end{aligned} \right\}$$

Substituting the expanded terms in D and E into equation (44) becomes;

$$\frac{dX_A}{dt} = \frac{C_{AO}}{1 + \varepsilon_A X_A} [K_1M - K_1X_A - K_1X_AM + K_1X_A^2 - K_2NP - K_2NX_A - K_2X_AP - K_2X_A^2]$$

$$= \frac{C_{AO}}{1 + \varepsilon_A X_A} [K_1M - K_2NP - K_1X_A - K_1X_AM - K_2NX_A - K_2X_AP + K_1X_A^2 - K_2X_A^2]$$

Further rearrangement of equation (47) gives;

$$\int \frac{1 + \varepsilon_A X_A}{K_1M - K_2NP - (K_1 + K_1M + K_2P)X_A + (K_1 - K_2)X_A^2} dX_A = C_{AO} \int dt \quad (48)$$

Applying Integration by parts and simplifying gives;

$$\left[\frac{1 + \varepsilon_A X_A}{-(K_1 + K_1M + K_2N + K_2P + 2(K_1 - K_2)X_A)} - \ln [K_1M - K_2NP - (K_1 + K_1M + K_2N + K_2P)X_A + (K_1 - K_2)X_A^2] \right] - \left[\frac{X_A + 2\varepsilon_A X_A}{K_1M - K_2NP - (K_1 + K_1M + K_2N + K_2P)X_A + (K_1 - K_2)X_A^2} \right] = C_{AO}t \quad (49)$$

$$t = \frac{1}{C_{AO}} \left[\frac{1 + \varepsilon_A X_A}{-(K_1 + K_1M + K_2N + K_2P + 2(K_1 - K_2)X_A)} - \ln [K_1M - K_2NP - (K_1 + K_1M + K_2N + K_2P)X_A + (K_1 - K_2)X_A^2] \right] - \left[\frac{X_A + 2\varepsilon_A X_A}{K_1M - K_2NP - (K_1 + K_1M + K_2N + K_2P)X_A + (K_1 - K_2)X_A^2} \right] \quad (50)$$

Equation 49 and 50 are the Abowei et al proposed generalized mathematical models for the prediction of reaction time vegetable oils and C1 to C3 alkali catalyzed transesterification reaction process in the production of bio- diesel.

Computational Data Evaluation Method

Simulative parameters such as molar mass, concentration of reactant and product species and computational algorithm are formulated;

Molar Mass (MW)

Atomic weights of C = 12, O = 16 and H = 1; and coupled with stoichiometric coefficient are exploited for the computation of reactant and product species molar masses using equation (1) thus;

For A = PKO; B = CH₃OH; R = Biodiesel; and S = Glycerol; then

$$\left. \begin{aligned} MW_A &= (12 \times 6) + (16 \times 6) + (1 \times 14) = 182 \text{ g/mol} \\ MW_B &= (12 \times 3) + (16 \times 3) + (4 \times 3) = 96 \text{ g/mol} \\ MW_R &= (12 \times 6) + (16 \times 6) + (18 \times 1) = 186 \text{ g/mol} \\ MW_S &= (12 \times 3) + (16 \times 3) + (8 \times 1) = 92 \text{ g/mol} \end{aligned} \right\} \quad (51)$$

Concentrations C_{AO}, C_{BO}, C_{RO} & C_{SO}

Applying dimensional analysis approach, concentration is computed as;

$$\text{Concentration} = (\text{Mols}) / \text{Volume} = \text{Density} / (\text{Molar Mass}) \quad (52)$$

and from table 1 to 5

$$\rho_A \cong 0.904 \text{ g/cm}^3; \rho_B \cong 0.8 \text{ g/cm}^3; \rho_R \cong 0.875 \text{ g/cm}^3; \rho_S \cong 1.263 \text{ g/cm}^3$$

Hence substituting these parameters and those in 37 into 38 gives;

$$\left. \begin{aligned} C_{AO} &= 0.904/182 = 0.00496 \text{ mols/cm}^3 \\ C_{BO} &= 0.800/96 = 0.00822 \text{ mols/cm}^3 \\ C_{RO} &= 0.875/186 = 0.00470 \text{ mols/cm}^3 \\ C_{SO} &= 1.263/92 = 0.01372 \text{ mols/cm}^3 \end{aligned} \right\} \quad (53)$$

Conversely, from equation 39 it is possible that;

$$\left. \begin{aligned} M &= C_{BO}/C_{AO} = 0.00822/0.00496 \cong 1.657 \\ N &= C_{RO}/C_{AO} = 0.00470/0.00496 \cong 0.947 \\ P &= C_{SO}/C_{AO} = 0.01372/0.00496 \cong 2.766 \end{aligned} \right\} \quad (54)$$

Table 3: Summary of Operating Parameters.

| S/No. | Parameter | Value | Reference |
|-------|-----------------|--|--------------------|
| 1. | K ₁ | 1.61 X 10 ⁻³ m ³ /mols.min | Ahiekpor etal 2010 |
| 2. | K ₂ | 1.0 X 10 ⁻⁵ m ³ /mols.min | Ahiekpor etal 2020 |
| 3. | C _{AO} | 4.96 mols/m ³ | Calculated |
| 4. | C _{BO} | 8.22 mols/m ³ | Calculated |
| 5. | C _{RO} | 4.70 mols/m ³ | Calculated |
| 6. | C _{SO} | 13.74 mols/m ³ | Calculated |
| 7. | M | 1.657 | Calculated |
| 8. | N | 0.947 | Calculated |
| 9. | P | 2.766 | Calculated |
| 10. | ε | 0.05 | Calculated |

Algorithm Formulation

We herein formulated computational algorithm simulate the disappearance kinetic rate of reaction exploiting the developed models in equation 21, 29 and 32 using the data in table six for isothermal and non-isothermal conditions. The summarized algorithm outline flow chart computation model is given in figure 2.

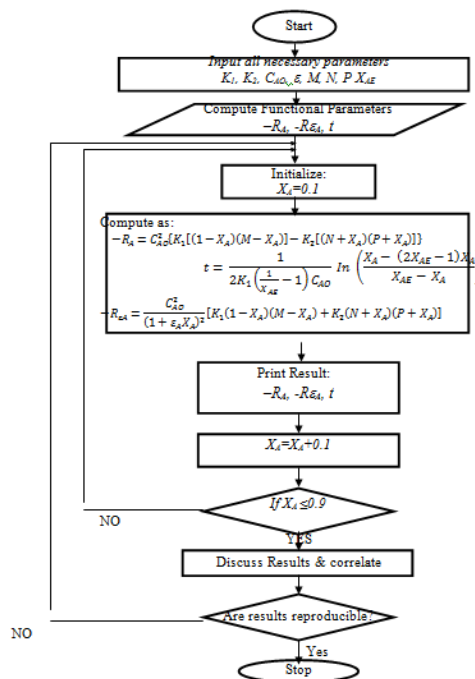


Figure 2: Summarized Algorithm outline Flow Chart Computational Model.

Results and Discussion

The formulated kinetic disappearance rate models were simulated using Matlab codes programming techniques and results obtained are presented in table 4.

Results

Table 4: Simulated Results of $-R_A$, $R_{\varepsilon A}$ and t as function of fractional conversion.

| X_A | $-R_A, \text{mols}/\text{m}^3 \cdot \text{min}$ | $R_{\varepsilon A}, \text{mols}/\text{m}^3 \cdot \text{min}$ | Time t , min | $1 + \varepsilon_A X_A, \varepsilon = -0.5$ |
|-------|---|--|----------------|---|
| 0.1 | 0.0548 | 0.0557 | 69.87 | 0.95 |
| 0.2 | 0.0453 | 0.0461 | 69.87 | 0.90 |
| 0.3 | 0.0367 | 0.0374 | 69.87 | 0.85 |
| 0.4 | 0.0288 | 0.0297 | 69.87 | 0.80 |
| 0.5 | 0.0218 | 0.0229 | 69.87 | 0.75 |
| 0.6 | 0.0155 | 0.0170 | 69.87 | 0.70 |
| 0.7 | 0.0100 | 0.0119 | 69.87 | 0.65 |
| 0.8 | 0.0053 | 0.0077 | 69.87 | 0.60 |
| 0.9 | 0.0013 | 0.0043 | 69.87 | 0.55 |

Discussions

Effect of Fractional Conversion on Reaction Kinetic Rates

Graphical relationship is established to ascertain the effect of fractional conversion (X_A) on reaction kinetic rates at isothermal and non-isothermal cases. The results generally depicts dependency relationship of fractional conversion and reaction kinetic Rate as in table 7 and figure 9. The kinetic Rate as in ($-R_A$) is inversely proportional to the fractional conversion in both isothermal and non-isothermal cases. This means that at higher fractional conversion, the kinetic reaction rate ($-R_A$) is very small in the alkali catalyzed esterification process of PKO and methanol synthesis.

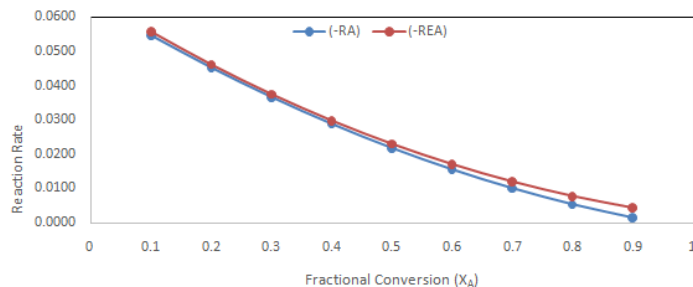


Figure 3 : Graph of Reaction Rates against Fractional Conversion

The results also show approximately quadratic functional feature reflecting the analysis of the model equations in 21 and 32. Thus Case I for isothermal condition; equation 21 is reduced to the form

$$-R_A = 22 [K_1(1 - X_A)(1.65 - X_A) - K_2(0.947 + X_A)(2.766 + X_A)] \quad (55)$$

And upon the substitution of the K_1 and K_2 values as in table 6 into equation 55 gives;

$$-R_A = 22 [1.6 \times 10^3(1 - X_A)(1.65 - X_A) - 1 \times 10^{-5}(0.947 + X_A)(2.766 + X_A)] \quad (56)$$

Case II for non-isothermal condition: thus;

$$-R_{\varepsilon A} = \frac{c_{A0}^2}{1 + \varepsilon_A X_A} [K_1(1 - X_A)(1.65 - X_A) - K_2(0.947 + X_A)(2.766 + X_A)] \quad (57)$$

Conversely with the introduction of the K_1, K_2 & $\varepsilon = -0.5$ Values into equation 43 resulting to;

$$-R_{\varepsilon A} = \frac{22}{1 - 0.5X_A} [K_1(1 - X_A)(1.65 - X_A) - K_2(0.947 + X_A)(2.766 + X_A)] \quad (58)$$

Fractional Conversion & Reaction Time Effect

Fractional conversion X_A and reaction time (t) at equilibrium condition was studied and presented in figure 4. The result shows linear independent relation with fractional conversion. Reaction time(t) exhibited same uniformity as conversion increases.

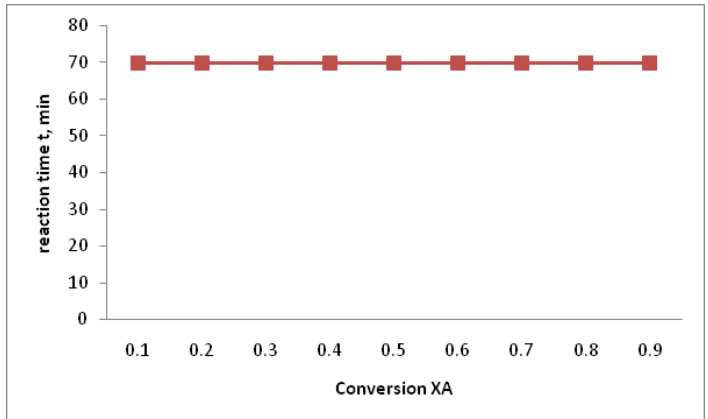


Figure 4: Fractional Conversion versus Reaction time effect.

In other words kinetic reaction time (t) is independent of fractional conversion in the alkali catalyzed transesterification of PKO and methanol reaction process. This relationship is authenticated with the analysis of equation 29 recalling. Thus;

$$t = \frac{1}{2K_1 \left(\frac{1}{X_{AE}} - 1\right) C_{AO}} \ln \left(\frac{X_A - (2X_{AE} - 1)X_A}{X_{AE} - X_A} \right) \quad (29)$$

Now putting $X_{Ac} = 0$ as with restrictions that $C_{AO} = C_{BO}$ and $C_{RO} = C_{SO}$; then;

$$\left. \begin{aligned} t &= \frac{1}{-2K_1 C_{AO}} \ln(-2) \\ t &= \frac{1}{-2K_1 C_{AO}} \ln\left(\frac{1}{2}\right) \\ t &= \frac{0.346}{K_1 C_{AO}}, \text{min.} \end{aligned} \right\} \quad (45)$$

Upon further substitution of the parameters K_1 and CAO values gives $t = 69.87 \cong 70$ min.

Kinetic Reaction Rates versus and Reaction Time

Kinetic rates and time shows linear independency as in figure 11. Kinetic reactions rates at both isothermal and non-isothermal conditions show decrease with increase in fractional conversion at constant reaction time frame. This analysis is also well depicted in table 4.

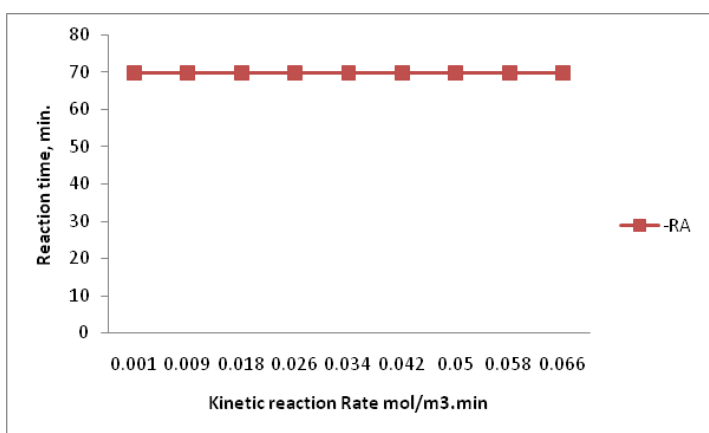


Figure 5: Kinetic rate versus reaction.

Fractional Volume change Versus Conversion

Alkali catalyzed transesterification of PKO and methanol reaction process demonstrated exothermic status with fractional volume change or voidage $\epsilon = -0.5$ as in equation 34. Fractional volume change increases with decrease in fractional conversion as show in figure 6.

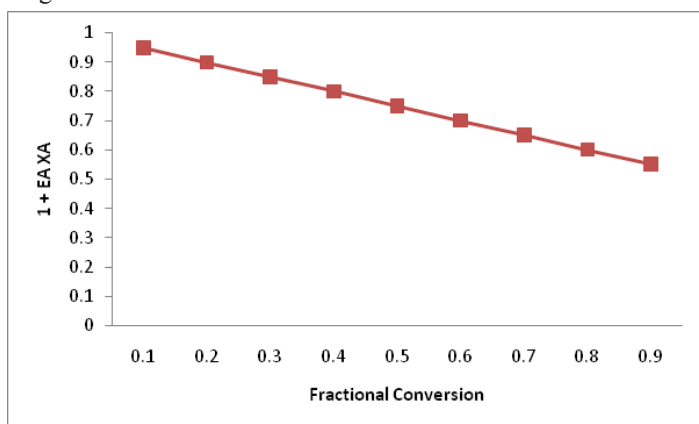


Figure 6: Fractional volume change versus Fractional Conversion.

Interestingly, fractional volume change ($1 + \epsilon_n X_A$) decreases with decrease in kinetic reaction rate ($-R_A$) for both isothermal and non-isothermal conditions but increase in fractional conversion X_A . This observation is very feasible as presented in table 4 as well.

Conclusion And Recommendation

Generally the results of simulation obtained for kinetic reaction rate for both isothermal equilibrium and non-isothermal conditions demonstrated dependable functionality with reaction time, fractional volumetric change voidage (ϵ) and fractional conversion (X_A). Results for kinetic reaction rates ($-R_A$ & $-R_{eA}$) decreases with decrease in fractional volume change (ϵ) and increase in fractional conversion at constant reaction time. The results obtained were obvious and comparable with similar works, demonstrating at least the novel realities of the formulated models. Therefore, the models can be exploited for the design of hypothetical reactor types for alkali transesterification of PKO and methanol reaction process in the production of biodiesel (transformer oil).

Nomenclature

| S/No | Symbol | Description | Unit |
|------|--------------------------|--------------------------|--------------------------|
| 1. | PKO | Palm Kernel Oil | N/A |
| 2. | TG | Glycerol | N/A |
| 3. | MG | Monoglyceride | N/A |
| 4. | E | ethyl ester | N/A |
| 5. | DG | Diglyceride | N/A |
| 6. | K_1, K_2, K_3, K_4 | 2nd Order Reaction Rate | Vol/mols.min |
| 7. | $a_{11} - a_{n8}$ | Matrix Components | N/A |
| 8. | A | PKO | N/A |
| 9. | B | NaOH | N/A |
| 10. | R | Glycero | N/A |
| 11. | S | Methyl ester | N/A |
| 12. | C_{AO} | Concentration | mols/m ³ |
| 13. | C_{BO} | Concentration | mols/m ³ |
| 14. | C_{RO} | Concentration | Concentration |
| 15. | C_{SO} | Concentration | mols/m ³ |
| 16. | X_A | Fractional Conversion | N/A |
| 17. | $-R_A, R_{eA}$ | Kinetic Reaction Rate | mols/m ³ .min |
| 18. | $M, N \& P$ | Constants | N/A |
| 19. | KC | Equilibrium Constant | N/A |
| 20. | ϵ | Fractional volume Change | N/A |
| 21. | XAE | Equilibrium conversion | N/A |
| 22. | NW_A, NW_B, NW_R, NW_S | Molar Mass | Mols/g |

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