Simplified Rate Expression for Palm Kernel Oil (PKO) and Methanol Alkali Catalyzed Transesterification Reaction

Okewale A.D, Abowei M.F.N, Agbogun F.O, Owabor C.N

Abstract—The need for the development of simplified kinetics rates expression (-Rs) for Vegetable Oils Alkali Catalyzed Transesterification processes to enhance biodiesel production motivated this study. The study, therefore aimed at proposing unified simple rate expression that may be a useful prelude to design various reactor types for Alkali Catalyzed Transesterification of palm kernel oil (PKO) and Methanol reactions. The kinetics rate expression is proposed using simple explicit algebraic technique with the consideration that alkali catalyzed transesterification reaction of palm kernel oil and methanol is a reversible bimolecular reaction. The proposed kinetic reaction rate expression is developed as a function of conversion (X), reactants and products concentration and reaction rate constants (k1 and k2). The kinetics reaction rate expression obtained is further evaluated on the basis of reactants and product molar masses and densities. The developed models were simulated using Matlab codes programming techniques. The results for kinetic reaction rates (-Rα & -Rβα) decreases with decrease in fractional volume change (g) and increase in fractional conversion at constant reaction time. The results were quite compatible with those of inferential laboratory physicochemical characterization reported.

Index Terms—Simplified, Kinetic Rate Expression, Alkali Catalyzed Transesterification, Palm Kernel Oil Methanol Biodiesel.

I. INTRODUCTION

Researchers [1-4] globally have resolved unequivocally in tackling the high potential environmental perturbation problems resulting from utilization of non-renewable energy sources for industrial and domestic use. These environmental perturbation problems have led to increased awareness search for alternative renewable energy sources such as biogas and bio-fuels production. This renewable energy sources are expected to elevate global economy and minimize global environmental problems that were derived from the conventional fossil fuels [1]. Hence this work intensified on the development of Biodiesel from alkali catalyzed transesterification of palm kernel oil and methanol reaction which has great concern to engineers and scientist.

Actually, a great deal of novel research works [5-12] have been carried on biodiesel production via alkali catalyzed transesterification of vegetable oil types and various alcohol groups reaction, notably in methanol/ and ethanol processes. Those studies provided information on the chemistry, uses, reaction mechanisms and kinetics evaluation based on inferential laboratory data analysis procedures. The aspect of developing a feasible rate mathematical model that could be used to design various industrial scale reactor types seems impassive. Therefore, this work shall appraise quantitatively and qualitatively the development of feasible unified disappearance kinetic rate expression for alkali catalyzed transesterification of palm kernel oil and methanol reactions in the production of biodiesel. In other to establish the basis for the development of the unified rate expression, it is relevant to assess the extent of some previous works reported on palm kernel oil, methanol and biodiesel chemistry.

II. CHEMISTRY OF PALM KERNEL OIL, METHANOL AND BIODIESEL

A. Palm Kernel Oil (PKO)

Palm kernel oil is edible oil obtained from the palm tree whole physical appearance is presented in Fig. 1. Palm kernel oil is widely produced in the world and essentially through extraction processes [1].

Interestingly PKO is widely used as Biodiesel production, Cooking and frying oil, Margarines production, Shortenings, Non-dairy creamers, whipping creams; As cocoa butter substitute, In manufacture of soaps, Oleochemicals, In cosmetics, personal care products as skin conditioner, Viscosity increasing agent and Solvent. In addition, the cake residue obtained after extracting the oil is used as a feed for livestock and other medical functions due to its antidotes capabilities for poisoning and as surface protestant for minor wounds. Its structure, physical and chemical properties are presented below;

1) Chemical Structure
2) **Properties**

<table>
<thead>
<tr>
<th>Properties</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density at 40/25°C[kg/m3]</td>
<td>898</td>
</tr>
<tr>
<td>Kinematic viscosity at 40°C[mm2/c]</td>
<td>30.1</td>
</tr>
<tr>
<td>Free fatty acid[lauric]</td>
<td>1.189</td>
</tr>
<tr>
<td>Odour</td>
<td>Burnt smell</td>
</tr>
<tr>
<td>Colour</td>
<td>Burnt brown</td>
</tr>
<tr>
<td>Solubility</td>
<td>Soluble in non-polar solvent</td>
</tr>
<tr>
<td>Iodine value [mm iodine/g oil]</td>
<td>19.3</td>
</tr>
<tr>
<td>Saponification value [mm KOH/g oil]</td>
<td>250</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.453</td>
</tr>
<tr>
<td>Pour point</td>
<td>20°C</td>
</tr>
<tr>
<td>Saponification Value (mgKOH/g)</td>
<td>280.5±56.1</td>
</tr>
<tr>
<td>Acid value (mgKOH/g)</td>
<td>2.7±0.3</td>
</tr>
<tr>
<td>Free fatty (FFA) (mgKOH/g)</td>
<td>1.35±0.15</td>
</tr>
<tr>
<td>Ester value (mEq/kg)</td>
<td>277.8±56.4</td>
</tr>
<tr>
<td>Peroxide value (mEq/kg)</td>
<td>14.3±0.0</td>
</tr>
<tr>
<td>Iodine value (mgKOH/g)</td>
<td>13.86±5.02</td>
</tr>
<tr>
<td>Specific Gravity value (S.G)</td>
<td>0.904</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.412</td>
</tr>
<tr>
<td>Inorganic materials (%)</td>
<td>1.05%</td>
</tr>
</tbody>
</table>

**TABLE I: PHYSICAL AND CHEMICAL PROPERTIES OF CRUDE PALM KERNEL OIL [9-11]**

B. **Methanol**

Methanol, also known as methyl alcohol, wood alcohol, wood naphtha or wood spirits, is a chemical compound with chemical formula CH₃OH. Its uses entail fuel, denaturant for ethyl alcohol, biodiesel production via transesterification reaction, solvent for shellac and varnishes, automobile radiator anti-freeze, denaturing additive to ethyl alcohol and Denaturing poisons the ethyl alcohol. The structural formula of methanol is:

![Methanol Structure](https://example.com/methanol_structure.png)

**Fig. 3. Methanol Structure [2]**

1) **Properties**

Methanol physical properties were extrapolated from Material Safety data sheet (MSDS) as sited in the reports of Fibow Petroleum & Environmental Engineering Consult on methanol disposal analysis by Abowei M.F.N. [14]

**TABLE II: PHYSICAL AND CHEMICAL PROPERTIES OF METHANOL [14]**

<table>
<thead>
<tr>
<th>Properties</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Liquid</td>
</tr>
<tr>
<td>Colour</td>
<td>Colourless</td>
</tr>
<tr>
<td>Odour</td>
<td>Characteristic odour Mild Pleasant odour Alcohol</td>
</tr>
<tr>
<td>Melting Point</td>
<td>-97.8°C</td>
</tr>
<tr>
<td>Latent Heat of Vaporization</td>
<td>37.43kJ/mol</td>
</tr>
<tr>
<td>Refractive Index</td>
<td>1.32652</td>
</tr>
<tr>
<td>Heat of Combustion</td>
<td>726.1kJ/mol</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>64.7°C (1013 hPa)</td>
</tr>
<tr>
<td>Critical temperature</td>
<td>240°C</td>
</tr>
<tr>
<td>Critical pressure</td>
<td>79547 hPa</td>
</tr>
<tr>
<td>Flash point</td>
<td>9.7°C</td>
</tr>
<tr>
<td>Relative evaporation rate</td>
<td>4.1</td>
</tr>
<tr>
<td>Relative evaporation rate</td>
<td>6.3</td>
</tr>
<tr>
<td>Vapor pressure</td>
<td>128 hPa (20°C)</td>
</tr>
<tr>
<td>Vapor Pressure at 50°C</td>
<td>552 hPa</td>
</tr>
<tr>
<td>Relative vapor density at 20°C</td>
<td>1.1</td>
</tr>
</tbody>
</table>

**TABLE III: PHYSICAL PROPERTIES OF BIODIESEL AND ASTM DIESEL FUEL [11-12]**

<table>
<thead>
<tr>
<th>Properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative density</td>
<td>0.79 – 0.80 (20°C)</td>
</tr>
<tr>
<td>Relative density of saturated gas/air mixture</td>
<td>1</td>
</tr>
<tr>
<td>Specific gravity / density</td>
<td>790 – 800 kg/m³ (20°C)</td>
</tr>
<tr>
<td>Molecular mass</td>
<td>32.04g/mol</td>
</tr>
<tr>
<td>Solubility</td>
<td>Soluble in water: 100g/100ml (20°C)</td>
</tr>
<tr>
<td>Log Pow</td>
<td>-0.77 (Experimental value)</td>
</tr>
<tr>
<td>Auto-ignition temperature</td>
<td>455°C (1013 hPa, DIN 51794; Self – ignition Temp)</td>
</tr>
<tr>
<td>Viscosity, dynamic</td>
<td>0.544 – 0.59 mPa–s (25°C)</td>
</tr>
<tr>
<td>Explosion limits</td>
<td>5.5 – 36.5 vol %</td>
</tr>
</tbody>
</table>

C. **Biodiesel**

Biodiesel is a chemical species whose production is drive from renewable energy sources and otherwise called methyl esters or transformer oil. Its chemical structure, relative chemical and physical properties and uses are highlighted herein. Biodiesel is used mainly as; Vehicular use and manufacturer acceptance, Railway usage, Cleaning oil spills, Biodiesel in generator, Transformer oil and General heating oil. The structure is presented as:

![Biodiesel Structure](https://example.com/biodiesel_structure.png)

**Fig. 4. Biodiesel Structure [2]**

2) **Physical and Chemical Properties**

**TABLE III: PHYSICAL PROPERTIES OF BIODIESEL AND ASTM DIESEL FUEL [11-12]**

<table>
<thead>
<tr>
<th>Properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour and Odour</td>
<td>2.99</td>
</tr>
<tr>
<td>Density at 30°C (kg/m3) or g/mL</td>
<td>0.875</td>
</tr>
<tr>
<td>Viscosity at 40°C</td>
<td>1.55</td>
</tr>
<tr>
<td>Specific gravity (kg/m3 or g/mL)</td>
<td>06</td>
</tr>
<tr>
<td>Flash point °C</td>
<td>7.5</td>
</tr>
<tr>
<td>Pour point</td>
<td>0.31</td>
</tr>
<tr>
<td>Cloud point</td>
<td>15.35</td>
</tr>
<tr>
<td>Acid value (mg NaOH/g)</td>
<td>165</td>
</tr>
<tr>
<td>Iodine value</td>
<td>0.02</td>
</tr>
<tr>
<td>Saponification value (mg NaOH/g)</td>
<td>0.03</td>
</tr>
<tr>
<td>Ash content (%)</td>
<td>54.57</td>
</tr>
<tr>
<td>Water content (%)</td>
<td>38.6</td>
</tr>
<tr>
<td>Octane Number</td>
<td>&gt;220</td>
</tr>
<tr>
<td>H. value (M/Kg)</td>
<td>&gt;200oC</td>
</tr>
<tr>
<td>Autogeneration Temperature</td>
<td>&lt;2</td>
</tr>
<tr>
<td>Vapour Pressure mm Hg</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Volatiles: % by Volume</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Solubility in H2O, % by Volume</td>
<td>* Stable and hazardous</td>
</tr>
<tr>
<td>Evaporation Rate Butyl Acetate =1</td>
<td>* Strong Oxidizing agents</td>
</tr>
<tr>
<td>Stability and relativity</td>
<td>* highly Combustible produces CO2 &amp; * CO along with thick smoke</td>
</tr>
</tbody>
</table>

D. **Sodium Hydroxide**

Sodium hydroxide is one of the most common inorganic bases or alkalis. It is also called caustic soda or lye and it is a white solid ionic compound consisting of sodium cations...
Na⁺ and hydroxide anions OH⁻. Its structure is simply Na‘OH and pictorially as presented in Fig. 4 and its uses encompasses; Alkali Catalyzed Transesterification process, Chemical pulping, Tissue digestion, Dissolving amphoteric metals and compounds, Esterification and transesterification reagent, Food preparation, Cleaning agent, Water treatment as pH, regulation, In cement mixes, mortars, concrete, grouts, Flavonoids, Summer-winter heat storage, paper industry, petroleum industry, textiles industry, manufacture of soaps and detergents and Bayer process of aluminum production.

1) Chemical Structure

The chemical structure of Glycerol is presented as;

\[
\begin{align*}
&\text{H}_2\text{C} \text{OH} \\
&\text{H} \text{C} \text{OH} \\
&\text{H}_2\text{C} \text{OH}
\end{align*}
\]

Fig. 6. Glycerol Structure [2]

III. KINETIC EVALUATION OF PALM KERNEL OIL AND METHANOL SYNTHESIS

Series of research works have been reported [9] in the alkali catalyzed triglycerides and alcohol transesterification process with respect to reaction kinetics in laboratory scale. The stoichiometry and kinetics evaluation of this study were reported as:

A. Stoichiometry of Reaction

The stoichiometry of the reaction is presented thus;

\[
\text{Triglyceride} + 3\text{R'OH} \rightleftharpoons 3\text{R'COOR} + \text{Glycerol}
\]

And the overall reaction for the transesterification is summarized thus;

\[
\frac{k_1}{k_2} \text{Triglyceride} + 3\text{R'OH} \rightleftharpoons 3\text{R'COOR} + \text{Glycerol}
\]

B. Kinetic Evaluation

Similarly, the kinetics describing the reaction mechanism is limited and is hypnotically presented as follows;

\[
\begin{align*}
&\frac{k_3}{k_4} \text{DG} + \text{E} \\
&\frac{k_5}{k_6} \text{MG} + \text{E}
\end{align*}
\]

The overall reaction was now

\[
\frac{k_7}{k_8} \text{TG} + 3\text{ROH} \rightleftharpoons \text{GL} + 3\text{E}
\]

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

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

\[
\frac{d\text{DG}}{dt} = -K_1 \text{DG}.A + K_2 \text{DG}.E - K_3 \text{DG}.A^3 + K_4 \text{GL}.E^3
\]  
(6)

\[
\frac{d\text{DG}}{dt} = K_1 \text{DG}.A - K_2 \text{DG}.E + K_3 \text{DG}.A + K_4 \text{MG}.E
\]  
(7)

\[
\frac{d\text{MG}}{dt} = K_3 \text{DG}.A - K_4 \text{MG}.E + K_5 \text{MG}.E + K_6 \text{MG}.A
\]  
(8)

\[
\frac{d\text{GL}}{dt} = K_5 \text{MG}.A - K_4 \text{GL}.E + K_7 \text{TG}.A^3 - K_8 \text{GL}.E^3
\]  
(9)

\[
\frac{d\text{A}}{dt} = -\frac{d\text{A}}{dt}
\]  
(12)

Where K₁ to K₄ are reaction rate constants, TG, DG, MG, GL, A and E are the concentrations in weight percent of triglyceride, triglyceride, monoglyceride, glyceride, methanol and ester respectively; in addition, the kinetic analysis as presented in (1) to (12) where summarized based on matrix transformation module as thus;

\[
\begin{bmatrix}
    a_{11} & a_{12} & a_{13} & a_{14}a_{15}a_{16} & a_{17} & a_{18} \\
    a_{21} & a_{22} & a_{23} & a_{24}a_{25}a_{26} & a_{27} & a_{28} \\
    \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
    a_{n1} & a_{n2} & a_{n3} & a_{n4}a_{n5}a_{n6} & a_{n7} & a_{n8}
\end{bmatrix}
\begin{bmatrix}
    K_1 \\
    K_2 \\
    K_3 \\
    K_4 \\
    K_5 \\
    K_6
\end{bmatrix}
\]

\[
= 
\begin{bmatrix}
    D_1 \\
    D_2 \\
    \vdots \\
    D_n
\end{bmatrix}
\]  
(13)

From (13) obviously, there is need to develop a feasible unified kinetic rate equation that can be used for various industrial reactor types design as this has seem not critical looked into.

IV. MATERIALS AND METHODS

A. Materials

The Materials exploited in this work encompassed mainly desk top research component such as; Laptop, Mathlab software, work spreadsheet and other associated computational tools for the simulation of the developed unified kinetic rate models.

B. Development of Kinetic Reaction Rate (-RA)

Coupled simple algebraic and induction principle technique is exploited in the development of the unified kinetic rate expression. In this work consideration is based on the fact that the reaction mechanism as (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;

\[
A + 3B \rightarrow R + S
\]

\[
k_3
\]  
(14)

From the reaction stoichiometry as in (14), a unified empirical kinetic rate can be mathematically, thus;

\[-R_A = \frac{-d\text{DG}}{dt} = K_1 \text{CA}.B - K_2 \text{C.R}.S
\]  
(15)

Where \(-R_A = \) Disappearance rate, K₁ & K₂ = reaction rate constants; Cₐ, Cₐ, Cₐ & Cₐ are concentrations of PKO, NaOH, Glycerol & Methyl Ester respectively.

C. Simplified Kinetics Rate (-RA) Model

In-case, for Isothermal situation as typical of reversible bi-molecular reaction status, noting that;

\[C_{\text{AO}} = C_{\text{AO}}(1 - X\lambda)
\]  
(16)

Then, Equations (16) and (15) combined give;

\[-R_A = K_1(C_{\text{AO}} - C_{\text{AO}}X\lambda)(C_{\text{BO}} - C_{\text{AO}}X\lambda) - K_2(C_{\text{BO}} + C_{\text{AO}}X\lambda)(C_{\text{SO}} + C_{\text{AO}}X\lambda)
\]  
(17)

Further application of simple factorization techniques to (17) gives;

\[-R_A = K_1 \left[C_{\text{AO}}^2(1 - X\lambda)(\frac{C_{\text{BO}}}{C_{\text{AO}}} - X\lambda)\right] - K_2 \left[C_{\text{AO}}^2(\frac{C_{\text{BO}}}{C_{\text{AO}}} + X\lambda)\right]
\]  
(18)

\[-R_A = K_1 \left[C_{\text{AO}}^2(1 - X\lambda)(\frac{C_{\text{BO}}}{C_{\text{AO}}} - X\lambda)\right] - K_2 \left[C_{\text{AO}}^2(\frac{C_{\text{BO}}}{C_{\text{AO}}} + X\lambda)\right]
\]  
(19)

\[-R_A = C_{\text{AO}}^2 \left[K_1 \left((1 - X\lambda)\left(\frac{C_{\text{BO}}}{C_{\text{AO}}} - X\lambda\right)\right) - K_2 \left(\frac{C_{\text{BO}}}{C_{\text{AO}}} + X\lambda\right)\right]
\]  
(20)

Putting \(M = \frac{C_{\text{BO}}}{C_{\text{AO}}}\); \(N = \frac{C_{\text{RO}}}{C_{\text{AO}}}\) and \(P = \frac{C_{\text{SO}}}{C_{\text{AO}}}\) into (20) resulting;

\[-R_A = C_{\text{AO}}^2 \left[K_1 \left((1 - X\lambda)(M - X\lambda)\right) - K_2 [(N + X\lambda)(P + X\lambda)]\right]
\]  
(21)

1) Reaction time (t) evaluation

Also, from (15) and (21); it is possible that;

\[-R_A = C_{\text{AO}} \frac{dx_A}{dt} = C_{\text{AO}} \left[K_1 \left((1 - X\lambda)(M - X\lambda)\right) - K_2 [(N + X\lambda)(P + X\lambda)]\right]
\]  
(22)

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

\[K_c = \frac{(N + X\lambda)(P + X\lambda)(M - X\lambda)}{(1 - X\lambda)(M + X\lambda)}
\]  
(23)

Where \(K_c = \frac{K_1}{K_2}
\]  
(24)

Equation (22) to (24) can re-written as;

\[\frac{1}{K_c} \frac{dx_A}{dt} = C_{\text{AO}} \left[K_c \left((1 - X\lambda)(M - X\lambda) - (N + X\lambda)(P + X\lambda)\right)\right]
\]  
(25)

Substituting (23) into (25) gives
\[
\frac{1}{K_0} \frac{dX_A}{dt} = C_{AO} \left( \frac{(N+X_{AE})(P+X_{AE})}{(1-X_{AE})(M+X_{AE})} \left(1 - X_A \right)(M - X_A) - (N + X_A)(P + X_A) \right)
\]

This shows that the reaction is exothermic and the kinetic rate model as developed in (32) and (33) needs to be inculcated with the exothermic concept resulting;

\[
-R_A = \frac{C_{AO}}{1 - 0.5X_A} \left[ X_1(1 - X_A)(M - X_A) - K_2(N + X_A)(P + X_A) \right]
\]

And,

\[
\frac{dX_A}{dt} = \frac{C_{AO}}{1 - 0.5X_A} \left[ k_1(1 - X_A)(M - X_A) - K_2(N + X_A)(P + X_A) \right]
\]

V. COMPUTATIONAL METHOD FOR KINETIC RATE ANALYSIS

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

A. 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 (1) thus;

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

\[
MW_A = (12 \times 6) + (16 \times 6) + (1 \times 14) = 182 g/mol
\]

\[
MW_B = (12 \times 3) + (16 \times 3) + (4 \times 3) = 96 g/mol
\]

\[
MW_R = (12 \times 6) + (16 \times 6) + (18 \times 1) = 186 g/mol
\]

B. Concentrations CAO, CBO, CRO & CSO

Applying dimensional analysis approach, concentration is computed as;

\[
\text{Conc} = \frac{\text{Mols}}{\text{Volume}} = \frac{\text{Density}}{\text{Molar Mass}}
\]

And from Table I to V; \( \rho_A \equiv 0.904 \text{ g/cm}^3; \rho_B \equiv 0.8 \text{ g/cm}^3; \rho_R \equiv 0.875 \text{ g/cm}^3; \rho_S \equiv 1.263 \text{ g/cm}^3 \)

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

\[
C_{AO} = 0.904 \text{ /182 = 0.00496 mols/cm}^3
\]

\[
C_{BO} = 0.800 \text{ /96 = 0.00822 mols/cm}^3
\]

\[
C_{RO} = 0.875 \text{ /186 = 0.00470 mols/cm}^3
\]

\[
C_{SO} = 1.263 \text{ /92 = 0.01372 mols/cm}^3
\]

Conversely, from n (39) it is possible that;

\[
M = \frac{C_{BO}}{C_{AO}} = 0.00822 \text{ /0.00496 = 1.657}
\]

\[
N = \frac{C_{RO}}{C_{AO}} = 0.00470 \text{ /0.00496 = 0.947}
\]
\[ p = \frac{C_{SO}}{C_{AO}} = \frac{0.01372}{0.00496} = 2.766 \]

Table VI: Summary of Operating Parameters

<table>
<thead>
<tr>
<th>S/No.</th>
<th>Parameter</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>K1</td>
<td>1.61 × 10⁻³ m³/mol·min</td>
<td>Ahiekpor et al 2010</td>
</tr>
<tr>
<td>2.</td>
<td>K2</td>
<td>1.0 × 10⁻⁵ m³/mol·min</td>
<td>Ahiekpor et al 2020</td>
</tr>
<tr>
<td>3.</td>
<td>CAO</td>
<td>4.96 mol·m³</td>
<td>Calculated</td>
</tr>
<tr>
<td>4.</td>
<td>CBO</td>
<td>8.22 mol·m³</td>
<td>Calculated</td>
</tr>
<tr>
<td>5.</td>
<td>CRO</td>
<td>4.70 mol·m³</td>
<td>Calculated</td>
</tr>
<tr>
<td>6.</td>
<td>CSO</td>
<td>13.74 mol·m³</td>
<td>Calculated</td>
</tr>
<tr>
<td>7.</td>
<td>M</td>
<td>1.657</td>
<td>Calculated</td>
</tr>
<tr>
<td>8.</td>
<td>N</td>
<td>0.947</td>
<td>Calculated</td>
</tr>
<tr>
<td>9.</td>
<td>P</td>
<td>2.766</td>
<td>Calculated</td>
</tr>
<tr>
<td>10.</td>
<td>ε</td>
<td>0.05</td>
<td>Calculated</td>
</tr>
</tbody>
</table>

C. Algorithm Formulation

We herein formulated computational algorithm simulate the disappearance kinetic rate of reaction exploiting the developed models in (21), (29) and (32) using the data in tale six for isothermal and non-isothermal conditions. The summarized algorithm outline flow chart computation model is given in Fig. 8.

Flow Chart of Programme for Isothermal \(-R_A\), Non-Isothermal \(-R_{EA}\), and \(t\)

Fig. 8: Summarized Algorithm outline Flow Chart Computational Model.

VI. RESULTS AND DISCUSSION

The formulated kinetic disappearance rate models were simulated using Matlab codes programming techniques and results obtained are presented in Table VII:

A. Results

Table VII: Simulated Results of \(-R_A, R_{EA}\) and \(t\) as Function of Fractional Conversion

<table>
<thead>
<tr>
<th>(X_A)</th>
<th>(-R_A, \text{mols}/\text{m}^3 \cdot \text{min})</th>
<th>(R_{EA}, \text{mols}/\text{m}^3 \cdot \text{min})</th>
<th>Time (t, \text{min})</th>
<th>(1 + \varepsilon X_A, \varepsilon = -0.5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.0548</td>
<td>0.0557</td>
<td>69.87</td>
<td>0.95</td>
</tr>
<tr>
<td>0.2</td>
<td>0.0453</td>
<td>0.0461</td>
<td>69.87</td>
<td>0.90</td>
</tr>
<tr>
<td>0.3</td>
<td>0.0367</td>
<td>0.0374</td>
<td>69.87</td>
<td>0.85</td>
</tr>
<tr>
<td>0.4</td>
<td>0.0288</td>
<td>0.0297</td>
<td>69.87</td>
<td>0.80</td>
</tr>
<tr>
<td>0.5</td>
<td>0.0218</td>
<td>0.0229</td>
<td>69.87</td>
<td>0.75</td>
</tr>
<tr>
<td>0.6</td>
<td>0.0155</td>
<td>0.0170</td>
<td>69.87</td>
<td>0.70</td>
</tr>
<tr>
<td>0.7</td>
<td>0.0100</td>
<td>0.0119</td>
<td>69.87</td>
<td>0.65</td>
</tr>
<tr>
<td>0.8</td>
<td>0.0053</td>
<td>0.0077</td>
<td>69.87</td>
<td>0.60</td>
</tr>
<tr>
<td>0.9</td>
<td>0.0013</td>
<td>0.0043</td>
<td>69.87</td>
<td>0.55</td>
</tr>
</tbody>
</table>

B. Discussions

1) 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 VI and Fig. 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.

Fig. 9: Graph of Reaction Rates against Fractional Conversion

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

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

And upon the substitution of the \(K_1\) and \(K_2\) values as in Table VI into (41) gives;

\[ -R_A = 22 [1.6 × 10^{-5} (1 - X_A) (1.65 - X_A) - 1 × 10^{-5} (0.947 + X_A) (2.766 + X_A)] \]

Case II for non-isothermal condition: thus;

\[ -R_{EA} = \frac{C_{SO}}{1 + \varepsilon X_A} [K_1 (1 - X_A) (1.65 - X_A) - K_2 (0.947 + X_A) (2.766 + X_A)] \]
Conversely with the introduction of the K1, K2 & ε = -0.5 Values into (43) resulting to:

\[-R_{eA} = \frac{22}{1-0.5X_A} [K_1(1 - X_A)(1.65 - X_A) - K_2(0.947 + X_A)(2.766 + X_A)] \quad (44)\]

2) Fractional Conversion & Reaction Time Effect

Fractional conversion X_A and reaction time (t) at equilibrium condition was studied and presented in Fig. 10. The result shows linear independent relation with fractional conversion. Reaction time (t) exhibited same uniformity as conversion increases.

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 (29) recalling;

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

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

\[t = \frac{1}{-2K_1 C_{AO}} \ln(2) \quad (45)\]

Upon further substitution of the parameters K1 and C_{AO} values gives t = 69.87 ≈ 70min.

3) Kinetic Reaction Rates versus and Reaction Time

Kinetic rates and time show linear independency as in Fig. 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 VI.

4) Fractional Volume change Versus Conversion

Alkali catalyzed transesterification of PKO and methanol reaction process demonstrated exothermic status with fractional volume change or voidage ε = -0.5 as in (34). Fractional volume change increases with decrease in fractional conversion as show in Fig. 12.

Interestingly, fractional volume change (1+ εn 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 VII as well.

VII. 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**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
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</thead>
<tbody>
<tr>
<td>PKO</td>
<td>Palm Kernel Oil</td>
<td>N/A</td>
</tr>
<tr>
<td>TG</td>
<td>Triglyceride</td>
<td>N/A</td>
</tr>
<tr>
<td>MG</td>
<td>Monoglyceride</td>
<td>N/A</td>
</tr>
<tr>
<td>E</td>
<td>Ethyl ester</td>
<td>N/A</td>
</tr>
<tr>
<td>DG</td>
<td>Diglyceride</td>
<td>N/A</td>
</tr>
<tr>
<td>(K_s, K_a, K_r)</td>
<td>2nd Order Reaction Rate</td>
<td>Vol/mols.m (\min)</td>
</tr>
<tr>
<td>(n_{PA}, n_{DA})</td>
<td>Matrix Components</td>
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</tr>
<tr>
<td>A</td>
<td>PKO</td>
<td>N/A</td>
</tr>
<tr>
<td>B</td>
<td>NaOH</td>
<td>N/A</td>
</tr>
<tr>
<td>R</td>
<td>Glycerol</td>
<td>N/A</td>
</tr>
<tr>
<td>S</td>
<td>Methyl ester</td>
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</tr>
<tr>
<td>(C_{PA})</td>
<td>Concentration</td>
<td>mols/m(^3)</td>
</tr>
<tr>
<td>(C_{DA})</td>
<td>Concentration</td>
<td>mols/m(^3)</td>
</tr>
<tr>
<td>(C_{RO})</td>
<td>Concentration</td>
<td>mols/m(^3)</td>
</tr>
<tr>
<td>(\alpha)</td>
<td>Fractional volume Change</td>
<td>N/A</td>
</tr>
<tr>
<td>(X_{eq})</td>
<td>Equilibrium conversion</td>
<td>N/A</td>
</tr>
<tr>
<td>NW(_1), NW(_2), NW(_3), NW(_4)</td>
<td>Molar Mass Mols/g</td>
<td></td>
</tr>
</tbody>
</table>

**REFERENCES**


