KINETIC MODELING STUDIES OF HETEROGENEOUSLY CATALYZED TRANSESTERIFICATION OF NON-EDIBLE OIL

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Abstract-The analytical process characterizing the experimental changes of reversible reaction of neem oil utilizing activated catalyst (CaO) derived from waste of animal bone as heterogeneous catalyst was used to determine the optimum reaction time and temperature. The standard reactants used for transesterification includes: heterogeneous and homogeneous catalysts. Though, similar synergists are hard to regain and advance to subsequent effluent remedy, raise in the value of methyl ester synthesis. Alkaline reactants increases the peroxide values resulting to soap deposit/ use of synergists. Furthermore, is delicate to aqua absorption. Acid catalysts are utilized for oils with high free fatty acids. However, dissimilar reactants might ameliorate mixture techniques and extinguishing added distillation value integrated with similarity. For this reason, utilization of dissimilar reaction is an alternate form of similar response presently been considered. The variables that effect the yield of methyl ester via reversible reaction of liquid edibles include: methanol to oil molar ratio, reaction temperature, reaction time, and catalyst concentration. The different means carried out in synthesis of biodiesel from liquid edibles and tallow fats viz: dilution, micro-emulsification, pyrolysis and transesterification process/technique (Demirbas et al., 2009; Aderemi et al., 2010; Leng et al., 1999; Jabalu et al., 2009). Amidst these means, reversible reaction is the crucial and best means to make the refinier and eco-friendly secure fuel (Younis et al., 2009; Atlana et al., 2004). Methyl ester is produced through a chemical reaction known as reversible reaction of distinct liquid edible/non-edible oil or tallow fat with a short chain alcohol, in which one mole of glyceride mixes with three moles of alcohol in the proximity of adequate volume of reactant to form mono methyl ester and glycerol. Solid waste based catalyst was used to generate value efficient synergist and petroleum fuel. In this research, catalyst grain volume, methanol to oil molar ratio, effects of temperature and revolution momentum were analyzed to ascertain the highest processes. The increase in rate of a chemical reaction of catalyst was also examined. The appropriate reaction rate model (kinetic study) was also performed and the rate of chemical reaction/coefficient (k) and energy of activation (Ea) at different temperatures was investigated.

Keywords: Biodiesel, Catalyst, Transesterification, Neem oil, and Kinetics.

I. INTRODUCTION
The rapid decrease of the global hydro-carbon substitute/ increased ecological interests have established substantial expect for ecologically friendly sustainable reserves of energy (Ashish et al., 2010). There is an increasing global interest for environmental natural resources conservation. The prospect of establishing an alternate renewable energy sources to reestablish the long-established hydrocarbons has received tremendous concern in the past couple of years (Vinceote et al., 1998). Biodiesel fuel is well-chosen as a feasible alternate and prospective petroleum for diesel engine because of the forecast scarcity of non-renewable fuels and rise in the cost of the fuel. It is biodegradable, renewable, harmless, ecologically-friendly, high cetane number , better lubrication, high flash point, and has complete affinity interest with physical and chemical attributes with that of standard petroleum diesel (Sanjay, 2013; Demirba 2003; Kayu et al., 2009; Hetxi et al., 2009). Methyl ester is a combination of mono alkyl esters obtained from plants or animals and therefore termed as renewable energy (Lin et al., 2006).

II. MATERIALS AND METHODS
Neemseed oil compositions as shown in table 1.0 was achieved from National Research Institute for Chemical Technology (NARICT), Zaria, Nigeria. Waste of animal bones was sourced from a local market in Kubwa, Abuja. Methanol and other chemicals/reagents were acquired from Zaria, Nigeria. All reagents were of analytical grades and were utilized as received without any additional refining.

Table 1. Physicochemical Characteristics of Neemseed oil

| Properties             | Values          |
|------------------------|-----------------|
| Specific gravity       | 0.948           |
| Kinematic viscosity    | 30.6cst         |
| Acid value(mg KOH/g oil)| 0.28            |
| Iodine value(g I2/100g oil)| 73.47           |
| Moisture (%)           | 0.001           |
| Saponification value(mg/g oil) | 212.3          |
| Refractive index at 250C| 1.476           |
| Peroxide value(mg/kg)  | 40.0            |
| PH value               | 3.39            |
| Ester value(mg/g)      | 211.7           |
| Boiling point          | 52°C            |
| Free fatty acid        | 0.140           |
| Cloud point            | 13              |
| Pour point             | 3               |
| Oxidation stability 10°C| 5.0 hours       |
A. Preparation of Catalyst

The catalyst (waste animal bones) from goats was sourced from a municipal market in Kubwa, Abuja. The sourced waste bones was immersed in a steaming water for several hours (6-8 hours) at about 75°C to remove tissues and fats in the bone and then rinsed with distilled water for 3-4 times to remove dust and contaminants. The waste bones were dehydrated in the desiccating furnace at 110°C for 4hr to remove water and mist before being crushed into smaller particles of 2mm grain volume. The powdered catalyst was sieved using varying mesh size to get particle of steady size of mesh. The sieved catalyst was kept in a mass transfer process prior to further usage.

B. Catalyst Activation

Sample of the crushed catalyst was impregnated with concentrated phosphoric acid (H3PO4) at different ratios of raw material to acid (1:1, 1:2, 1:3, 1:4, and 1:1.5) on weight basis. The impregnated samples were dried in an oven at 100°C for 12hr. After the activation, and slow cooling in air at room temperature, the slurry was washed with distilled water several times until PH 6-7 filtered to be free from any acid and then dried at a temperature of 110°C for 24hr and finally ground into a fine powder, sieved and stored in desiccators for further usage.

C. Catalyst Characterization

Fourier Transform Infrared (FTIR)

The catalyst was examined using spectrophotometer with ranges 560-4000cm⁻¹ after 16 investigation using a design of 8 cm³. KBr was utilized as the grounding phenomenal in the investigation to remove signal noise. FTIR spectra were recorded using FTIR spectrophotometer.

Thermal Gravimetric Analysis/Differential Thermal Analysis (TGA/DTA)

Thermal gravimetric analysis (TGA) was carried out using a Perkin Elmer Pyris diamond thermogravimetric/differential thermal analyzer (TGDTA).

D. Reaction Procedure

Reversible process was carried out in a 500 mL round bottom flask as a reactor. The reactor was fitted with a reflux condenser (to minimize alcohol loss), a mechanical stirrer, and a thermometer. 30ml (28.44g) of refined neem oil was transesterified into a flat bottom flask placed on a hot magnetic stirrer. 1.4g (4wt% based on weight of oil) of catalyst partially dissolved in 11 ml of alcohol was added to the oil using molar ratio of 8:1. The response decanter was heated on a stirrer at a temperature of 45°C and constant speed of 400rpm at various times (0.5, 1, 2, 3, 4, and 5 hours). At a defined time (1-2 hours), the sample was taken out, cooled and the biodiesel was separated from the by-product by sediment settlement under ambient temperature. The test was replicated for temperatures of 50°C and 55°C Experimental processes were determined Kubwa, Abuja.

Kinetics of Transesterification

Below equations represents a reversible response being driven by excess alcohol and a catalyst.

\[
\begin{align*}
TG + A &\rightarrow DG + BD \\
DG + A &\rightarrow MG + BD \\
MG + A &\rightarrow G + BD
\end{align*}
\]

The total transesterification of neem oil with methanol is presented as (4)

\[
TG + 3A \overset{k_3}{\rightarrow} 3BD + GL
\]

Where \( k_1, k_2 \) and \( k_3 \) are rate constants for forward reactions; \( k_s \) and \( k_4 \) are reaction rates for reverse reactions (backward reaction rate). The minimum value of \( k \) is the rate determining step of the reaction. Where TG, Triglyceride, DG, Diglyceride, MG, Monoglyceride, G, Glycerol, BD, fatty acid methyl ester and A... concentration of alcohol.

B. Characterization of Catalyst

Fourier Transform Infrared

Figure revealed the FTIR spectral of acid activated catalyst. The characteristic PO₄³⁻ absorbed bands of the acid activated waste bones were observed with the broad bands at 3281.4 to 2281.2 cm⁻¹, attributable to adsorbed water. The sharp peaks at 1505.8 to 723.1 cm⁻¹, indicate the vibration peaks of PO₄³⁻. The presence of weak sharp transmittance band at 3261.4 to 3112.3, could be as a result of activation with high H₃PO₄ concentration. This peak may be ascribed to isolated O-H bands.

Beyond 400°C and 450°C no important weight loss was detected. Almost stable curve was noticed within this temperature range denote stage attribute due to completion disintegration and possibly, separation of attached liquids and gases.

In the DTA curve, it showed two endothermic peaks at temperatures between 100 to 150°C and 300 to 350°C. The low endothermic peak at temperature between 100 to 150°C was due to removal of vapor from the surface of the catalyst (Abdel et al., 1981; Figueredo et al., 2005). Why a peak at temperature between 300 to 350°C can be attributed to the elimination of water resulting from loss of hydroxyl group and degradation of organic substances.
Fig. 2. TGA/DTA thermogram of acid activated catalyst.

C. Investigation of Reversible Reaction Results

Transesterification of neem oil using heterogeneous-catalyzed process was carried out at different response temperatures (45, 50 and 55°C). The optimum response states were: methanol to oil ratio (8:1), catalyst concentration (4 wt%), reaction time (4 hour) and stirring momentum (400 rpm). Model concentrations descriptions of TG-triglyceride, DG-diglyceride, MG-monoglyceride, ME-methanol, FAME-methyl ester, and GL-glycerol for the determined response states and temperatures response of: 45°C, 50°C and 55°C in figures 3-5, showed differences in absorption of triglycerides/production of esters and glycerol/incomplete mixtures like glycerides and monoglycerides at all specified period throughout the reaction.

The investigations of figures 3, 4 and 5, showed that the triglyceride concentration gradually diminishes, till it reached point near zero(0) at the climax of the reaction. At same time, FAME absorption rises swiftly throughout the first 3hrs of the response attaining the highest and remained steady. Though, the concentration of glyceride-GL gradually speeds up and its use was not finished/concluded during the reaction period. After 4hrs, infinitesimal modifications in the absorption of all part were determined. The explication for this occurrence are in two states. Foremost, the modification in absorption declines as the reaction reaches stability. Furthermore, fatty acid methyl ester and glycerin are incompatible with each other at a high rise stimulating momentum of 400 rpm (Vicente et al., 2005).

Table 2.0: Concentration-time results at 45°C

| S/N | Time(H) | C_TG | C_DG | C_MG | C_METH | C_FAME | C_GL |
|-----|---------|------|------|------|--------|--------|------|
| 1   | 0       | 6.82 | 0    | 0    | 4.20   | 0      | 0    |
| 2   | 1       | 5.52 | 3.66 | 3.97 | 3.80   | 9.06   | 2.15 |
| 3   | 2       | 4.29 | 3.10 | 3.10 | 2.77   | 10.73  | 3.45 |
| 4   | 3       | 2.25 | 1.50 | 1.03 | 2.30   | 12.05  | 4.48 |
| 5   | 4       | 2.25 | 1.50 | 1.03 | 2.30   | 12.05  | 4.48 |
| 6   | 5       | 2.25 | 1.50 | 1.03 | 2.30   | 12.05  | 4.48 |

Figure 3.0. Result of Response Time on Concentration at 45°C

Table 3.0. Concentration-time results at 50°C

| S/N | Time(H) | C_TG | C_DG | C_MG | C_METH | C_FAME | C_GL |
|-----|---------|------|------|------|--------|--------|------|
| 1   | 0       | 6.82 | 0    | 0    | 4.20   | 0      | 0    |
| 2   | 1       | 6.63 | 3.66 | 3.55 | 2.65   | 7.74   | 3.16 |
| 3   | 2       | 3.59 | 2.97 | 1.05 | 2.40   | 10.73  | 4.90 |
| 4   | 3       | 2.10 | 1.26 | 0.995| 2.26   | 24.48  | 6.36 |
| 5   | 4       | 2.10 | 1.26 | 0.995| 2.26   | 24.48  | 6.36 |
| 6   | 5       | 2.25 | 1.26 | 0.995| 2.26   | 24.48  | 6.36 |
In the study of temperature dependence on rate constants (energy of activation and pre-exponential factor), Arrhenius equation was utilized. The temperature dependent terms for the rate determining step (RDS) were calculated from kinetics experiments.

The mathematical process of equation (11) resulted in equation (12).

\[
k = A e^{-\frac{E_\text{a}}{RT}}
\]

(11)

The plot of Ink versus \((1/T)\) gives slope \(=E_\text{a}/R\) and intercept = InA

\[
\ln k = (E_\text{a}/R) + \ln A
\]

(12)

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

The slopes give the activation energies \((E_\text{a})\) the intercepts and pre-exponential factors. As seen from Table 5.0, the forward reactions for the triglyceride adsorption (TGads) have lower activation energies than their reverse counterparts which theoretically would mean more favourable reverse reactions. The rate constants obtained at different temperature are shown in figures 3, 4 and 5, respectively. It could be observed that concentration decreases as time increases for triglyceride, diglyceride, monoglyceride and methanol showing they were consumed to process methyl ester and glycerin with biodiesel been dominant.

### E. Determination of Kinetic Variables

The energy of activation influences the degree of dependence of rate constants on reaction temperature at a given condition. The energy of activation and frequency factor for the rate determining step (RDS/TG ads.) were estimated from the Arrhenius equation by plotting Ink vs \(1/T\) as shown in figure 4.0.

![Fig. 4 Result of Response Time on Concentration at 50°C](image)

**Table 4.0. Concentration-time results at 55°C**

| SN | Time(H) | C\(_{\text{TG}}\) | C\(_{\text{DG}}\) | C\(_{\text{MG}}\) | C\(_{\text{SHOH}}\) | C\(_{\text{FAME}}\) | C\(_{\text{G}}\) |
|----|---------|----------------|----------------|----------------|----------------|----------------|----------------|
| 1  | 1       | 6.83           | 0              | 0              | 4.20           | 0              | 0              |
| 2  | 1       | 5.52           | 2.79           | 3.33           | 2.45           | 16.93          | 2.78           |
| 3  | 2       | 3.46           | 2.45           | 3.0            | 2.24           | 22.98          | 4.81           |
| 4  | 3       | 1.45           | 1.01           | 0.77           | 2.10           | 31.87          | 5.12           |
| 5  | 4       | 1.45           | 1.01           | 0.77           | 2.10           | 31.87          | 5.12           |
| 6  | 5       | 1.45           | 1.01           | 0.77           | 2.10           | 31.87          | 5.12           |

![Fig.5. Result of Response Time on Concentration at 55°C](image)

**Table 5.0. Data for determination of Arrhenius parameters**

| Temp.(Kelvin) | Rate constant (K) | InK | \(1/T\)(1/K) |
|---------------|-------------------|-----|-------------|
| 318           | 1.96E-5           | -10.83 | 0.00314    |
| 323           | 2.17E-5           | -10.74 | 0.00315    |
| 328           | 5.18E-5           | -9.87  | 0.00305    |

![Fig. 6.0: Arrhenius plots of the Rate Determining Step](image)
IV. CONCLUSION

In this research, kinetics of reversible reaction of neem methyl ester with acid activated catalyst was analysed to determine the reaction order and the rate constant. The reaction orders for triglyceride at temperatures of 45.50 and 55°C were established to be the rate determining step (RDS) of triglyceride adsorption with energy of activation of 90.98kJ/mol and rate constants of 1.96E-5, 2.17E-5 and 5.18E-5 respectively. Activation energy was determined from the plots of log k vs 1/T. The rate constants of the RDS increased when the temperature was increased. This shows that the rate RDS of reversible reaction is desired at greater temperature, which is standard investigation for an endothermic reaction. The high evaluation of coefficient of determination R² showed that the data conformed to Arrhenius equation.

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