Kinetic Study of Waste-derived Solid Hydroxy Sodalite Catalyst during Transesterification of Animal Fat Oil to Biodiesel in a Batch Reactor

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Abstract
Kinetic studies of heterogeneous catalytic reactions form a crucial step necessary for the understanding of catalytic behaviour of a catalyst towards designing, controlling and optimizing a reactor. This study reports kinetics of waste animal fat oil (AFO) transesterification to biodiesel using waste-derived heterogeneous catalyst, hydroxy sodalite (HSOD) in a batch reactor. The catalyst was synthesized from coal fly ash and waste industrial brine via hydrothermal treatment. At a temperature range of 49 - 62 °C and a time range of 30 -120 minutes, the transesterification of animal fat oil to biodiesel was conducted at a fixed methanol/oil mass proportion 9:1, percent mass weight of catalyst 3 (based on the AFO) and stirring intensity of 300-500 rpm. Experimental findings reveal that reaction rate, which is first-order, was anticipated to increase with increasing temperature, resulted in an activation energy and a pre-exponential factor of 58554.65 J mol⁻¹ and 2.83 min⁻¹, respectively. The value of the activation energy suggests that the reaction is endothermic and a minimum energy of 58.55 kJ is required to achieve an effective collision at a frequency of 2.83 min⁻¹. The highest biodiesel yield was 90 % at 62 °C and this corresponds to a highest AFO conversion of 93 % at a reaction time of 120 minutes.

Keywords: Waste-derived solid hydroxy sodalite; Transesterification; Biodiesel; Animal fat oil.

1. Introduction
The heavy pollution caused by fossil fuels and their depletion coupled with the enormous demand of energy in the industries, has shifted attention to biodiesel as an alternative renewable energy source [1]. Biodiesel has low toxicity, low emission profiles and higher biodegradability in natural conditions in contrast with fossil fuels. This makes biodiesel a better fuel alternative [2-4]. Biodiesel could be produced from vegetable and animal fat oil feedstocks. However, vegetable oil feedstock competes with the food chain to increase the cost of biodiesel production [5, 6]. On the other hand, animal fat oil (AFO) is a fat oil waste generated from abattoirs around the world. Particularly, this waste is in abundance in South Africa. Over 604 functional and accessible abattoirs have been reported in South Africa [7] which provide sustainable animal fat waste feedstock. This waste is a source of environmental pollution due to its disposal into the open landfills. Due to the high raw material costs in biodiesel production [8], beneficiation of the AFO waste into biodiesel could reduce the production costs significantly and also protect...
the environment from pollution. AFO consists of triglycerides of three long-chain fatty acids. These triglycerides have high viscosity and therefore cannot be used in common diesel engines as fuel. To reduce the viscosity of these long-chain fatty acids, transesterification reaction is used to convert them into alkyl esters known as biodiesel.

The transesterification of oils to biodiesel is carried out in the presence of catalysts to increase the rate of reaction and yield of biodiesel [9,10]. The types of catalysts used in the reaction include but not limited to basic and acidic catalysts [11-13]. The alkaline catalysts have lower corrosive effect compared to the acid catalysts. Therefore, base catalysts such as alkaline metal alkoxides, hydroxides and potassium or sodium carbonates are preferred in transesterification processes [14] for homogeneous catalysis reactions. These advantages of the latter make basic catalysis the main route of biodiesel production. This is because it requires low amount of catalyst, low temperatures and shorter reaction time to accomplish the process. The main drawback of the base catalyzed homogeneous transesterification reaction is the presence of high free fatty acids (FFAs) in the animal fat oil and or other triglyceride feedstocks used [5]. The FFAs react with the alkaline catalyst to form soap which makes it difficult to separate biodiesel from the reaction product mixture. There is also the problematic large quantity of wash water spillage and glycerol separation during product recovery stage [4].

To counteract the effect of the high FFA content of AFO or other similar feedstock on biodiesel yield, an esterification reaction is performed to reduce the FFA content and allow the transesterification reaction to occur [15]. The esterification step increases the number of process units which increases the biodiesel production costs because of the pre-treatment step that is involved [16,17]. Previous studies have reported biodiesel production using different heterogeneous catalysts. For example, Jatropha curcas oil transesterification to biodiesel using heterogeneous calcium oxide (CaO) catalyst, has been reported [18]. The heterogeneous catalysis of producing biodiesel are widely reported [19-21]. Currently, the use of sodalite in biodiesel production has not been widely published in the literature. Recently, [22] studied the reaction parameters of biodiesel production by transesterifying animal fat oil using hydroxy sodalite as a heterogeneous catalyst. This was synthesized from pure chemical precursors. It was observed that the catalyst demonstrated good catalytic performance at 60 °C after a 24 h time. This resulted in a biodiesel yield of 78.3 %. Similarly, [23] produced biodiesel using sodalite as a heterogeneous catalyst. The catalyst was derived from coal fly ash (CFA) for the transesterification of Soy oil to biodiesel. At a temperature of 65 °C and a reaction time of 2 h, the maximum conversion of 95.5 % Soy oil was achieved. Meanwhile, no study on the heterogeneous catalytic transesterification of CFA and waste industrial brine (WIB) derived sodalite catalyst for biodiesel production has been reported.

The CFA and WIB are abundant waste materials in South Africa. They are beneficiated by using them as feedstock for catalysts synthesis and the synthesized catalyst is employed in biodiesel production. In this case, catalyst and biodiesel costs are reduced, while the environment is equally protected against pollution. To the best of our knowledge, no kinetic studies on the CFA and WIB derived sodalite (waste-derived HSOD) catalyst for animal fat oil transesterification to biodiesel has been reported in the literature. The kinetic study of the waste-derived HSOD could pave the way to understanding the catalytic behaviour during design, control and reactor process optimization for commercial production of biodiesel. The HSOD is immiscible with the
triglycerides and alcohols during transesterification reactions, which makes separation of product mixture simple and cheap [5]. The motivation for this work was therefore based on beneficiation of wastes; where CFA and WIB were used as feedstock for catalyst synthesis and then used to convert another waste (AFO) into biodiesel. Consequently, this article presents the kinetics of waste-derived solid HSOD catalyst during transesterification of AFO to biodiesel in a batch reactor.

2. Materials and Methods

2.1. Materials

Animal fat oil was obtained from Wits University cafeteria. The physical properties using analytical techniques were determined prior to transesterification (Table 2). Methanol, sodium hydroxide, standard biodiesel (F.A.M.E. Mix GLC-100) and hexane were bought from Sigma-Aldrich, South Africa and are of high analytical grade. Deionized water was prepared, and waste coal fly ash (CFA) and waste industrial brine (WIB) obtained from coal power and minefields plants in Mpumalanga, South Africa.

2.2. Characterization of animal fat oil

2.2.1. Determination of free fatty acid (FFA) and acid value (AV)

The FFA content prior to transesterification should be known to avoid its undesirable low biodiesel yield and quality [24]. FFA estimation gave a value representing the amount of alkali added to the AFO to become a neutral solution. The waste animal fat oil used in this study was found to be of high free fatty acid (FFA) content (Table 2). Hence, it is known that higher free fatty acid content of oils/fats cause side reaction producing soap and subsequently low yield of biodiesel. To a considerable extent, a low yield of biodiesel will result if FFA of oils/fats is above 3 wt % [25]. The heterogeneous catalyst (HSOD) used in this work was employed to overcome the drawback of high FFA content in the feedstock. The percent FFA and acid values (AVs) in the animal fat oil were calculated according to the following equation:

\[
\% \text{FFA} = \frac{(V - b)(N)(28.2)}{W} \times \frac{100}{1}
\]  

(1)

where \(V\) is the titrant value in mL; \(b\) is the volume of blank sample in mL; \(N\) is the normality and \(W\) the weight of sample of animal fat oil.

\[
\text{AV} = \frac{(ml \ of \ KOH)(N)(56)}{W}
\]  

(2)

where \(N\) is the normality of KOH and \(W\) is the weight of sample of animal fat oil.

2.2.2. Saponification value (SV)

One of the major side reactions occurring during production of biodiesel is saponification. This reaction can occur when fats or oils are hydrolyzed in the presence of a base resulting in a
glycerol and a salt. The value which represents the milligram of potassium hydroxide used for the neutralization reaction with the fat when one gram of fat reacted is the saponification number. Saponification value of the fat was determined by reacting an accurately measured amount of fat sample and potassium hydroxide solution. After removal of the soap by decanting, the remaining sample was evaluated according to the following equation:

$$SV = \frac{[(a - b)(Molarity\ of\ acid)(56.1)]}{w}$$

where \( a \) is the volume of acid used, \( b \) represents blank volume of acid used \( w \) is the mass of fat.

2.2.3. Iodine value of animal fat oil

Animal fat oil (AFO) can be described in terms of the degree of fat unsaturation in the carbon chain. The melting point of solid AFO and its oxidative stability are connected to (IV) of the oil [26]. Therefore, this evaluation is important to clarify AFO’s chemical behaviour. The reaction of a sample of the fatty acid with iodine broke the unsaturated carbon bonds of the fat at the site C=C double bond. The reacted iodine monochloride produced a di-iodate single bond with a carbon bonding to iodine. To quantify iodine amount, KI was added to the reaction product mixture. After reaction, 0.1 M sodium thiosulphate (Na₂S₂O₃) was titrated against the unreacted iodine in the presence of starch solution as an indicator. The indicator turns the liberated iodine purple colour confirming endpoint. The iodine value of the oil was determined according to the equation below:

$$IV = \frac{[(B - S)(N\ of\ Na₂S₂O₃)(0.127)]}{W}$$

Where \( B \) is the volume of \( Na₂S₂O₃ \) blank and \( S \) is the volume at the end of titration, \( W \) is the weight of sample.

Average molecular weight (AMW) of the AFO was calculated from the saponification value of the sample as follows:

$$AMW = \frac{168300}{SV}$$

where \( SV \) is the saponification value (M\(_{KOH}\)M\(^{-1}\)Oil, mg g\(^{-1}\)).

2.3. Catalyst preparation and characterization

The waste-derived hydroxy sodalite (HSOD) catalyst used in this study was produced through a two-step hydrothermal method, namely the ageing and hydrothermal treatments, from waste industrial brine and coal fly ash [16,27,28]. The mass ratio of 1:1 of sodium hydroxide (NaOH) pellets and magnetically treated powder samples of waste coal fly ash (CFA) obtained, was combined in a 100 mL of waste industrial brine (WIB) sample. In a 47 °C polytetrafluoroethylene (PTFE) Thermotech beaker condition, CFA and NaOH were mixed in the WIB with magnetic stirring set at a speed of 300-500 rpm for 48 h ageing step to form a slurry. A Teflon-lined autoclave filled with the slurry was subjected to a hydrothermal treatment
in an oven at 140 °C for 48 h reaction time. The resulting mixture was severally washed using distilled water to attain a pH of 7. The resulting product was set to dry at a temperature of 90 °C overnight in an oven. The dried solid sample was ground into powder for a calcination process in a muffle furnace programmed for 2 h at 200 °C prior to characterization and transesterification. X-ray diffractometer (XRD) which operated with Cu Kα radiation was used to check the purity and crystallinity. The elemental composition and surface structure of the solid catalyst was verified using SEM-EDX while the functional group was obtained using FT-IR coupled with an attenuated total reflectance (ATR). The textural properties of the waste-derived catalyst (HSOD) was determined at 77K using Tri-Star 3000 Micromeritic BET-N2 adsorption-desorption analyzer.

2.4. Transesterification reaction

AFO was melted by mild heating at a temperature of 55 °C. It was then filtered to remove solid impurities (suspended particles and solid residues). About 6 g of AFO was measured into the batch reactor containing a small stirring magnetic rod. The setup was placed on a stirring magnetic hot plate. The 3-necked glass reactor was equipped with a reflux condenser clamped to a rigid support as schematically shown in Figure 1.

![Figure 1: Process flow diagram for transesterification experiment](image)

The experimental set-up was equipped with a condenser connected to a water circulating cooling system to ensure effective cooling and a stable vaporizing methanol reflux ratio in the liquid reaction mixture. A thermometer dipped inside the liquid product recorded the temperature of reaction. The setup was half-immersed in an oil heating bath for uniform heating and placed on a digital stirring magnetic hotplate set at a temperature of 104 °C. This was to remove inherent moisture and volatile substances in the AFO that may cause saponification. A known amount of methanol (alcohol) and the waste-derived hydroxy sodalite (solid base heterogeneous) catalyst were measured, mixed and transferred into the reactor using a glass funnel. Time of reaction was recorded and the corresponding temperature set at 60 °C throughout the experimental process. However, the operating conditions of the reacting system is presented in Table 1.
Table 1: Transesterification of AFO to biodiesel process condition

| Variables                  | Operating Condition |
|----------------------------|---------------------|
| Catalyst (Wt. %)           | 3                   |
| Stirring intensity (rpm)   | 500                 |
| Methanol-to-AFO ratio      | 9:1                 |
| Reaction temperature (OC)  | 49 - 62             |
| Reaction time (min)        | 120                 |

AFO: Animal Fat Oil; rpm: revolution per minute

Meanwhile, the reaction product mixture was evaporated to remove methanol in an evaporator maintained at slightly above room temperature. The catalyst, glycerol and biodiesel were then separated by centrifugation and micro filtration.

Finally, the resulting product mixture was analyzed using the Fourier transform infrared technique on a Perkin Elmer 100 FT-IR Spectrometer coupled with diamond attenuated total reflectance (ATR). This method was used to obtain the band vibration characteristics or the functional groups of the AFO and AFO BioD product within the range 4000-400 cm\(^{-1}\). The animal fat oil biodiesel (AFO_BioD) was qualitatively and quantitatively determined using a gas chromatography-mass spectrometer (GC-MS-QP2010 Ultra/SE Shimadzu Corporation, Japan). The GC-MS was operated with helium as a carrier gas and the flow rate was set at 1.5 mL min\(^{-1}\). The column with 30 m x 0.32 mm x 0.25 µm dimension operated at a temperature in the range of 120 – 300 °C at a rate of 10 °C min\(^{-1}\) while the detector to the GC-MS was flame ionization (FID). 250 °C was set as the operating temperature for the injector and the detector interface, respectively. 1.0µL was the injection volume for the samples and the mode of injection was splitless. Scanning rate of the MS was from 35-550 m/z.

The percent yield in AFO_BioD and conversion products were calculated using Eqn (6) and Eqn (7), respectively, [29]:

\[
\% \text{ Yield of } AFO_{\text{BioD}} = \frac{\text{Mass of } AFO_{\text{BioD}}}{\text{Mass of } AFO_{\text{used}}} \times 100 \%
\]

\[
\% \text{ Conversion of } AFO = \left(1 - \frac{AFO_{\text{final}}}{AFO_{\text{initial}}}\right) \times 100 \%
\]

2.5. Kinetic model development

The development of kinetic model for AFO transesterification catalyzed by waste derived HSOD with methanol was guided by Equation (8) [30,31]:

\[
TG + 3M \leftrightarrow 3F + G
\]

TG is the animal fat oil, M denotes methanol, F Fatty Acid Methyl Ester (FAME) and G glycerol.

Assumptions: reaction was regarded as irreversible, methanol was in excess of AFO, and reaction order was assumed pseudo-first order

Chemisorption of AFO molecules follows the first-order adsorption isotherm [32]. Thus,
\[-r_{AFO} = -\frac{dC_{AFO}}{dt} = K_s \theta_M C_{AFO,s}\]  

(9)

Where the concentration of the AFO in the main stream of the liquid is \(C_{AFO}\). \(K_s\) denotes associated rate constant on the surface and if \(\theta_M\) denotes fraction of space filled by methanol at the reactive site, then, rate of adsorption-desorption becomes:

\[-r_{ads\text{-}des} = K_{ads} (1 - \sum \theta) C_{AFO} - K_{des} C_{AFO,s} = -r_{AFO} = -\frac{dC_{AFO}}{dt} = K_s \theta_M C_{AFO,s}\]  

(10)

Equation (10) is an expression for adsorption-desorption rate of AFO, the associated rate constants are \(K_{ads}\) and \(K_{des}\) while \(\sum \theta\) denotes total occupied space of all species present [33].

\[
(1 - \sum \theta) = \frac{1}{1 + K_M C_M + K_{AFO} C_{AFO} + K_P C_p + K_{GL} C_{GL}}
\]  

(11)

For components \(i\), the equilibrium constant for the adsorption-desorption is denoted by \(K_i\) and \(C_i\) the concentration.

\[
C_{AFO,s} = \frac{K_{ads}(1 - \sum \theta)}{K_{des} - K_s \theta_M} \cdot C_{AFO}
\]  

(12)

Rearrange equation (10) to yield non-measurable \(C_{AFO,s}\), in terms of the measurable \(C_{AFO}\), we obtain equation (12).

Substitute equation (12) into (9), results in equation (13):

\[
-r_{AFO} = -\frac{dC_{AFO}}{dt} = (K_s \theta_M) \frac{K_{ads}(1 - \sum \theta)}{K_{des} + K_s \theta_M} \cdot C_{AFO}
\]  

(13)

Introducing equation (12) as:

\[
K_{eff} = (K_s \theta_M) \frac{K_{ads}(1 - \sum \theta)}{K_{des} + K_s \theta_M}
\]  

(14)

And rewriting equation (13) as

\[
-r_{AFO} = \frac{dC_{AFO}}{dt} = K_{eff} C_{AFO}
\]  

(14b)

\(K_{eff}\) elucidates adsorption-desorption rates and that of the chemical reactions on the catalyst interface. It can be stated thus: For a single stage reactor, concentration \(C_{AFO}\) may be written as a conversion of AFO \(x_{AFO}\) and thus:

\[
C_{AFO} = C_{AFO}(1 - \sum x_{AFO})
\]  

(15)
Thus, \( C_{AFO} \) is the initial concentration of AFO.

Equation 14b can be rewritten as:

\[
\frac{dX_{AFO}}{dt} = K_{eff}(1 - x_{AFO})
\]  

(16)

Integrating equation (16) results in equation (17) for heterogeneous regimes [34, 35]:

\[-ln(1 - x_{AFO}) = K_{eff} \cdot t + C\]

(17)

C is the integration constant.

A plot of \(-ln(1 - x_{AFO})\) against \(t\) yields a straight-line graph with a slope equal to \(K_{eff}\). \(K_{eff}\) designates effective reaction constant for adsorption-desorption.

Arrhenius law can be used to explain the rate constant of a chemical reaction:

\[K = A_o e^{\frac{-E_a}{RT}}\]

(18)

From Eqn (18) the pre-exponential factor of Arrhenius Equation is \(A_o\), whereas \(E_a\) denotes activation energy, \(T\) and \(R\) are the absolute temperature and universal gas constant, respectively. Linearization of Eqn (18) leads to Eqn (19)

\[lnK = lnA_o - \frac{E_a}{R}T\]

(19)

Using equation 17, substitute, \((ln K_{eff})\) into equation 20,

\[lnK_{eff} = -\frac{E_a}{RT} + lnA_o\]

(20)

where \(lnK_{eff}\) is the effective reaction rate constant.

A plot of \(lnK_{eff}\) and \(\frac{1}{T}\) yields a straight-line graph with slope \((-\frac{E_a}{R})\). Activation energy of the reaction can be evaluated.

3. Results and Discussion

3.1. Characterization of the animal fat oil and the catalyst

The characterization results of the animal fat oil are summarized in Table 2. The FFA content obtained from the AFO was around 24.69 %, but this value is higher than the standard value of FFA required for transesterification reaction. The implication is that there is a tendency of soap formation if the AFO is used for biodiesel production without pre-treatment or esterification. Normally, an FFA content greater than 1% will cause saponification which reduces catalyst efficiency. The viscosity increases and separation of glycerol from product difficult [36,37].
reported a high acid value of 17 mg-KOH g\(^{-1}\) during the transesterification of jatropha oil, while [39] suggested that FFA value less than 1 mg-KOH g\(^{-1}\) was suitable for transesterification reaction.

Table 2: Physical and Chemical properties of waste animal fat oil

| Property                        | Value       | [40] | [41] | This study                      |
|---------------------------------|-------------|------|------|--------------------------------|
| Density (g cm\(^{-3}\))         | 0.917       | 0.929| 0.787|
| Kinematic viscosity (mm\(^2\)s\(^{-1}\)) | -           | 46.37| 84.14|
| Saponification value (mg KOH g\(^{-1}\)) | -           | -    | 179.53 (old stock), 187.97 (fresh stock) |
| Acidity value (mg KOH g\(^{-1}\)) | 6.40 ± 1.42 | 1.07 | 24.69|
| Free fatty acid (%)             | -           | -    | 12.42|
| Iodine value (g Meq Kg\(^{-1}\)) | -           | 45.3 (gI 100g\(^{-1}\) fat) | 5.08|
| Peroxide value (Meq Kg\(^{-1}\)) | -           | -    | 14.33|
| Average molecular weight (calculated) (g mol\(^{-1}\)) | 834.8 | 846.4 | 937.45 (old stock), 895.36 (fresh stock) |

This shows that the free fatty acid value of 24.69 mg-KOH g\(^{-1}\) obtained in this study is higher than the prescribed value for transesterification reaction. Pre-treatment of the animal fat oil to reduce the FFA content by esterification is normally done industrially, but this increases the costs of biodiesel production. To overcome the drawback of high FFA content and AV of the AFO, a heterogeneous waste-derived HSOD catalyst calcined at 200 °C for 2 h to improve its catalytic activity was used.

3.2. Characterization of the catalyst
3.2.1. Morphology and surface chemistry

Figure 2 represents the SEM image and the spectrum of the waste-derived hydroxy sodalite catalyst used in this study. From the micrograph, the structural morphology indicates round balls of thread-like framework of sodalite [42]. The spectrum typically shows the main elemental constituent of the sample namely Na, Al, O and Si. It can be seen that there is, however, carbon in the spectral menu. However, Carbon was detected as a contaminant from the sample preparation stage most probably due to the carbon tape used to secure the powder sample on the stud. The calculated Si/Al ratio is 1.16 and this is consistent with the literature [22, 42,43]. The characteristic transmittance bands in this spectrum including 954 cm\(^{-1}\) is associated with the framework modes of T-O-T; T = Si or Al, sodalite. This is assignable to the
asymmetric vibration of the stretch [44]. The T-O-T; T= Si or Al, stretch at 665-736 cm\(^{-1}\) bending is symmetric and typical vibrations to the framework of sodalite in the fingerprint region of the spectrum.

At close to 3600 cm\(^{-1}\), no apparent broadband were observed. This suggests that the catalyst calcination process efficiently removed moisture from the matrix. Presence of moisture after calcination may be by adsorption as reported elsewhere [42].

![Figure 2: SEM image with the EDX spectrum (left) and the FTIR spectrum of the waste-derived HSOD (right)](image)

3.2.2. Textural Property of the Catalyst

From the analysis, the specific surface area, pore volume and the pore size of the waste-derived HSOD catalyst are, respectively, 33.05 m\(^2\)g\(^{-1}\), 0.13 cm\(^3\)g\(^{-1}\) and 16.23 nm. In comparison with previous studies, the waste-derived HSOD displays higher specific surface area and pore volume than the reference non-waste-derived HSOD used in a similar application by [22,42]. However, in a related synthesis, [45] obtained the specific surface area of solid hydroxy sodalite catalyst produced from fine fractions of sandy loam soil to be 31.70 m\(^2\)g\(^{-1}\). Similarly, a surface area of 9.70 m\(^2\) g\(^{-1}\) was obtained in a hydrothermal sol-gel process [23].

3.3. FT-IR Analysis of AFO and AFO biodiesel

The biodiesel produced from the AFO (AFO_BioD) and AFO were characterized using an FT-IR technique to determine the functional groups. The essence was to qualitatively confirm whether biodiesel was formed during the waste-derived HSOD catalyzed AFO transesterification reactions. Figure 3 shows the FT-IR spectra of the animal fat oil AFO, and the produced (AFO_BioD). The AFO_BioD and the AFO (Figure 4) do not show peaks at the regions around 3400 cm\(^{-1}\). This signified an absence of moisture in both samples as this is the region of O-H bonds associated with water molecules. This shows that the AFO pre-treatment (moisture removal) was successful. The C=O stretching vibration of the carbonyl group at 1743 cm\(^{-1}\) shows strong peak in the AFO.
Figure 3: FT-IR spectrum of AFO and AFO_BioD.

At 1120-1090 cm⁻¹ span stretching vibrations of C-O [46]. In addition, the peak at 1742 cm⁻¹ confirmed the asymmetric stretching vibration of C-O in the esters, and the peaks present in the range of 1300-1000 cm⁻¹ conform to the symmetric vibrations of the C-O stretch in the fingerprint region of the spectrum. The peak characterized by O-CH₃ vibrations at 1200 cm⁻¹ is prominent and sharp in the AFO_BioD spectra [16]. The attachment of the alkyl group of the alcohol to the fatty acid group is confirmed; it also indicates the presence of a tertiary alcohol in the AFO_BioD spectra which assigns the fatty acid methyl ester, alcohol group. The presence of a small peak at approximately 1600 cm⁻¹ in AFO_BioD spectra as against the AFO spectrum implies the presence of an ester carbonyl (C=O) group stretching vibration [47]. From Figure 3 (spectrum (a)), a magnified spectral band (spectrum (b)) shows the chemical transformation of the AFO transesterification to AFO_BioD. At 1450-1000 cm⁻¹ of spectrum (b), it is evidenced that the symmetric vibration band which is prominent in the AFO_BioD did not show markedly in the AFO spectrum in the juxtaposed diagram. The results of the FT-IR of the AFO and AFO_BioD reveal that biodiesel was successfully synthesized from the AFO.

3.4. AFO_BioD Production

3.4.1. Effect of reaction temperature and time on AFO_BioD yield and AFO conversion

Figure 4 shows that as the temperature of the reaction increases the yield of biodiesel increases. Normally, the increase in temperature increases the average kinetic energy of molecules/atoms/radicals. This is due to increased number of collisions of molecules at the walls of the containing vessels per unit time. The increase in reaction time from 5 to 120 minutes considerably improved the yield of AFO_BioD production at the transesterification operating temperatures of 49-62 °C. The maximum AFO_BioD yield obtained at a temperature of 62 °C after 120 minutes, was about 93 %. Haas et al. [48], reported that at a free fatty acid level above
3%, yield of biodiesel would drastically fall during transesterification reaction with base catalysts. In this study, heterogeneous base catalyst was used which exhibited a very high FFA tolerance. In addition to the high tolerance of the waste-derived HSOD, the AFO employed for the biodiesel production was pre-treated (moisture removal) hence, leading to zero saponification and a high amount of produced (93%) biodiesel.

Furthermore, the pore volume of the catalyst used for the biodiesel production was small (16.23 nm), but with an enhanced surface area in comparison with the large pore volume of 30.92 nm reported by [22,42]. In this study, the catalyst surface area was enhanced and it assisted the diffusion of the triglycerides and alcohol to the catalyst active sites, thus; resulting to efficient reactions. Figure 5 also presents the conversion of AFO to AFO_BioD at different temperatures ranging from 49 to 62 °C and reaction time 0 to 120 minutes.

Effect of temperature on kinetics and equilibrium of reactions are positive [49]. This is because temperature determines the time rate of the concentration and triglyceride conversion. As can be seen from the time evolution of transesterification reaction, AFO conversion to AFO_BioD increased with the increase in temperatures (49 - 62 °C). This has proven that methyl ester content of biodiesel increased to an optimum as shown in Figure 5.

Figure 4: Biodiesel yield and conversion as a function of reaction temperature and reaction time.

At 0-5 minutes of the reaction, the AFO conversion was 0.70 at 49 °C and 0.73 at 57 °C, while the maximum AFO conversion of 0.83 was obtained at 62 °C. In addition, it was observed that at the 20th minute of AFO conversion, the conversion decreased to 0.43, 0.52, and 0.64 at 49...
°C, and 57 °C and 62 °C, respectively. The AFO conversion decreased with an increase in time, while the corresponding biodiesel increased with an increase in temperature. This can be due to the improved and available specific surface area of waste-derived HSOD for surface reactions, coupled with the elevated percentage FFA content tolerance of the catalyst that resulted in very high AFO conversion at the reference temperature and time.

This observation is in agreement with the findings of [50] that obtained a maximum conversion of 0.99 resulting in a 99.0 % methyl ester content yield from a waste shell’s transformation of Jatropha curcas seed oil to fatty acid methyl ester. Process conditions used by [50] and his co-workers were: temperature of 65 °C, 9:1 methanol/oil molar ratio, reaction time 3 h and catalyst loading 3 wt. % of the oil. A similar result was obtained [51] when frying oil was used in producing biodiesel over a calcined snail shell derived catalyst.

The maximum biodiesel yield of 87.25 % obtained from 0.87 frying oil conversion set at a temperature of 65 °C for 2 h reaction time. Also from waste frying oil, [52] similarly obtained 95.52 % maximum methyl ester content yield from 0.95 frying oil conversion at optimum temperature of 50 °C. Increasing the temperature beyond the temperature of optimum conversion results in diminished viscosity of AFO_BioD products as a result of evaporation [49;50;53-55] with possibility of reversibility [50] of transesterification. This condition also improves the mass transfer limitations [53,55], enhances saponification possibilities [52,56,57], lowers the methyl ester yields content [50,53-55], and thus decreases the catalyst activity [58]. However, the catalyst activity seems to be reduced as the reaction progressed as shown in Figure 4, but at equilibrium, it is expected that the activities of the catalyst may not adversely affect the conversion of the AFO to biodiesel.

3.5. Kinetics of Heterogeneously waste-derived HSOD catalyzed transesterification

3.5.1. Determination of reaction rate constant

This study is typically a heterogeneously catalyzed transesterification (Htr-CT) system requiring a tri-phasic component system occurring at the interface of the waste-derived HSOD. The elementary steps of reaction can consist of the following [59]: Each of these steps has the potentiality of limiting the rate and consequently determine the reaction rate expression. When this happens, the other steps equilibrate with the system [60]. It has been suggested that the rate-limiting step in a solid base catalyzed reaction system of this nature functions in relation to the catalyst’s basicity. It also depends on the pore size and with the property of one or more of the reactants [61,62].

Figure 5 presents -ln [AFO_BioD] as a function of time and temperatures 49, 57 and 62 °C which is equivalent to –ln (1-X_{AFO}) Vs time as expressed in Equation (17).
It can be seen that each plot yielded a straight-line with various rate constants and corresponding coefficients of regression as shown in Table 3. This confirms a first-order kinetic transesterification reactions for this study. Table 3 also shows that rate constant increased as temperature increased which depicts that rate constant of a chemical reaction is temperature-dependent. This is because with the increase in temperature, the kinetic energy of the reacting molecules increases, leading to more collisions and number of successful reactions.

Table 3: Rate constants at various reaction temperatures

| Catalyst type | Feedstock | T (K) | K (min⁻¹) | References |
|---------------|-----------|-------|-----------|------------|
| Alkali catalyst | AFW       | 303   | 4.5 x 10⁻¹ |            |
|                |           | 323   | 2.1 x 10⁰  |            |
|                |           | 343   | 1.8 x 10⁰  | [40]       |
| Pure Solid     | AFO       | 313   | 2.0 x 10⁻⁴ |            |
| H-SOD          |           | 323   | 7.0 x 10⁻⁴ |            |
|                |           | 333   | 1.1 x 10⁻³ | [63]       |
| CFA + WIB      | AFO       | 322   | 7.9 x 10⁻¹ |            |
| HSOD           |           | 330   | 12.6 x 10⁻³|            |
|                |           | 335   | 18.6 x 10⁻³| This study |

CFA: Coal fly Ash; AFO: Animal Fat Oil; WIB: Waste Industrial Brine; HSOD: Hydroxy Sodalite; AFW: Animal Fat Waste
Therefore, the reaction rate constant increased with an increase in temperature. Similar rate constant dependence on temperature has been reported in the literature. The rate constants for the transesterification of WCO catalyzed by a non-waste derived solid HSOD catalyst were found to have a minimum and maximum values of 0.0002 min\(^{-1}\) and 0.011 min\(^{-1}\), respectively at temperatures of 40 °C and 60 °C [22]. The enhanced rate constants obtained in this study (Table 2) can be attributed to the enhanced waste-derived HSOD catalyst. This is higher than the results obtained from non-waste-derived HSOD catalyst reported by [40] and [63] due to enhanced textural properties and purity of the catalyst coupled with the catalyst’s tolerance to presence of high free fatty acid of AFO.

### 3.5.2. Rate constant \( K \) for the transesterification reaction

The temperature dependency of the rate can be explained using Arrhenius expression (equation (18)) [64]:

\[
\ln K = \ln A_0 - \frac{E_a}{RT}
\]  

Figure 6 depicts the plot of the reaction rate constant as a function of temperature. From the figure, the pre-exponential factor, \( A_0 \) and the activation energy, \( E_a \), were evaluated and obtained as 2.83 min\(^{-1}\) and 58554.65Jmol\(^{-1}\), respectively. Similar studies had been carried out and reported in the literature. For instance,

![Figure 6: Arrhenius plot of ln (k) versus the inverse of temperature (1/T).](image)

Lukić et al. [65] reported a rate constant of 0.000174 min\(^{-1}\) using a CaO: ZnO to transesterify sunflower oil at 300 rpm reaction mixing speed. Singh and Fernando [66] communicated rate constants of 0.0032 min\(^{-1}\) and 0.0011 min\(^{-1}\) for heterogeneous PbO and MgO catalysts respectively in the transesterification of soybean oil to biodiesel.

### 4. Conclusions

The kinetics of the waste-derived hydroxy sodalite (HSOD) catalyst for the transesterification of AFO to biodiesel was carried out using CFA and WIB as the feedstock for catalyst synthesis. The process conditions employed for the transesterification were; catalyst: 3 wt. %; stirring
intensity: 500 rpm; Methanol-AFO ratio: 9:1; reaction temperature: 49 – 62; reaction time: 120 min. A pseudo-first-order model was assumed but experimental results proved to be a reaction kinetics of first-order. The following conclusions were drawn from the investigation:

- The activation energy and the pre-exponential factor obtained were 58554.65Jmol⁻¹ and 2.83 min⁻¹ respectively. The rate constants were determined at temperatures of 49 °C, 57 °C, and 62 °C and were found as 7.86 x 10⁻³ min⁻¹, 12.55 x 10⁻³ min⁻¹ and 18.59 x 10⁻³ min⁻¹ respectively.
- The optimum yield of biodiesel and triglycerides conversion were 90 % and 93 %, at 62 °C and 120 minutes, respectively.
- The high conversion of AFO and yield of biodiesel were attributed to the enhanced textural properties and purity of the waste-derived HSOD catalyst. Furthermore, the catalyst displayed a stable state of tolerance to the exceedingly high AFO free fatty acid content of 24.69 mg-KOH g⁻¹ due to absence of saponification leading to high catalytic activity and high biodiesel yield.
- The kinetic model which describes the waste-derived HSOD catalyst used for the transesterification of AFO to AFO_BioD can be represented by a reaction rate model.

5. Recommendation
It is recommended that additional parameters such as effect of methanol/AFO molar ratio, catalyst concentration and particle size be studied. This will allow for further understanding of the catalyst activity during the transesterification reaction in a fixed bed reactor (FBR) that will be compared to that of a batch reactor.

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