

KINETIC STUDY OF TRANSESTERIFICATION OF WASTE FRYING OIL TO BIODIESEL USING AN THILL-EGGSHELL-Ni-Co MIXED OXIDE COMPOSITE CATALYST

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Abstract

In this present study, the transesterification of waste frying oil with methanol over anthill-eggshell-Ni-Co mixed oxide catalyst was investigated. The composite catalyst was prepared via co-precipitation method and characterized by Brunauer-Emmett-Teller (BET), basicity, X-ray diffraction (XRD) and Fourier transform infrared (FTIR) techniques prior to its activity study. The effects of reaction temperature and reaction time on the catalytic reaction were investigated. The reaction order, activation energy and reaction mechanism based on Eley-Rideal principle were evaluated. From the BET analysis, it was revealed that calcination process has a positive effect on the textural properties of the catalyst. The high basicity exhibited by the catalyst implied that Lewis base sites are active centers for the catalytic reaction. From the XRD analysis, the active phases in the catalyst were determined to be calcium oxide (CaO), silica (SiO₂), nickel oxide (NiO) and cobalt oxide (CoO). From the FTIR studies, the peak changes of the spectra obtained before and after calcination process corresponded to temperature effect. The obtained results showed that both reaction temperature and reaction time had significant influence on transesterification reaction. The reaction was first order with respect to triglyceride and second order with respect to methanol. The activation energy and collision factor were 23.99 kJ/mol and $1.62 \times 10^6 \text{ M}^{-1} \text{ min}^{-1}$ respectively. The reaction mechanism agreed reasonably well with Eley-Rideal kinetic.

Keywords: Biodiesel; composite catalyst; kinetics; transesterification; waste frying oil.

1. Introduction

The global realization of the finite nature of fossil hydrocarbon and the deleterious effect arising from its consumption has triggered a worldwide search for alternative fuels. The utilization of diesel fuel from petroleum source continues to rise due to increase in population, energy consumption and rapid industrialization [1]. These have triggered a worldwide search for alternative fuels which include biodiesel, bio-alcohol, biogases and other biomass sources. Among the aforementioned renewable fuels, biodiesel has received considerable attention mainly because it provides a solution to problems associated with fossil fuel which include its depletion and environmental degradation [2]. Besides, it could be obtained from biomass [3]. Generally, biodiesel is prepared from plant oils or animal fat [4]. Biodiesel is an alternative and biogenic fuel which comprises of different esters of fatty acid and has been attracted worldwide because of the problems associated with the petroleum derived fuel [5].

There are four major techniques, which are usually used for biodiesel synthesis. They include pyrolysis (thermal cracking), micro-emulsification, blending, and transesterification or esterification. Transesterification is a commonly used method whereby triglyceride contained in the vegetable oil or animal fat reacts with primary alcohol (methanol, ethanol, and propanol) to produce alkyl esters and glycerol in the presence of catalyst [7-8]. The required catalyst can either be homogeneous, enzyme or heterogeneous. However, homogeneous catalyzed trans-

esterification process has some disadvantages, which include the formation of the unwanted product, corrosion problems, generation of wastewater, and difficult to recycle [3]. Although, enzymatic transesterification has the advantage to provide high yields, but cannot be employed industrially as a result of the exorbitant cost of the enzyme. Another problem is that of deactivation usually caused by impurities present in reaction feed. Therefore, heterogeneous catalysts are very important for biodiesel production as they possess many advantages over homogeneous catalysts and enzymes [5]. They are noncorrosive, environmentally benign and do not form soaps through free fatty acid neutralization or saponification of triglyceride. Besides, product purity and regeneration of the catalyst are achievable in heterogeneous catalysis [9-10].

Many types of heterogeneous catalysts for biodiesel production have been reported ranging from the use of strong acid catalysts to strong base catalysts [11]. Findings have proven that rare earth metals are the most suitable heterogeneous catalyst in biodiesel production [12], but unfortunately, these catalysts are expensive, and their preparation is quite complex. Therefore, to make biodiesel production sustainable, the use of low cost solid heterogeneous catalysts from waste and naturally occurring materials is suggested [13]. These are being investigated to replace the homogeneous catalysts and enzymes, and this research constitutes part of that investigation. These low cost materials include chicken eggshell [14], ostrich eggshell [15], quail eggshell [16], waste shells of mollusk [17], waste animal bone [18], solid waste coral fragment [19], alum [20], montmorillonite clay [21], modified- peanut husk ash [22], just to mention, but few.

Although there is an increasing interest in deriving solid catalysts from naturally occurring and waste materials, but locally sourced anthill has not been explored as a catalyst to transesterify vegetable oil to fatty acid methyl esters. This also includes its modification by any of the metal oxides. Moreover, previous research has not provided detailed work on the catalytic performance of two or more of these materials in a combined form (composite) to synthesize fatty acid methyl esters. Furthermore, to the best of our knowledge no literature on the kinetic studies for the transesterification of waste frying oil over mixed metal oxides promoted anthill-eggshell is reported. It has been widely reported that transesterification reaction occurs much faster when uses basic catalyst compared to acidic [23]. Thus, the technique involving the use of the heterogeneous base catalyst in converting waste oil to biodiesel is adopted for this present study.

This research work, however, considers the development of anthill-eggshell-Ni-Co mixed oxides (AENiCo) composite catalyst for biodiesel production from waste frying oil. Waste frying oil is selected for this study because it offers advantages which include a reduction in environmental pollution and the production cost [24]. Following this, the prepared catalyst was characterized to gather information about its properties. The effects of reaction temperature and time on the catalytic reaction process were investigated. Moreover, kinetic of transesterification of waste frying oil (WFO) over AENiCo catalyst was studied in details and all the parameters contained in derived models were evaluated.

2. Materials and methods

2.1. Materials

Chicken eggshells and waste frying oil (WFO) were collected from students' Cafeteria 1, Afe Babalola University, Ado-Ekiti, Nigeria. The specific gravity, acid value, free fatty acid and saponification value of the oil are 0.9147, 3.824 mg KOH/g, 1.412 wt% and 183.1 mg KOH/g, respectively. The anthill employed in this study is situated in Ado-Ekiti, Nigeria on an elevation of 1165 ft above sea level, having latitude (N007°36.409') and longitude (E005°18.627') with height and base of 2.59 m and 4.60 m. The anthill was sprayed with insecticide before it was harvested. Cobalt nitrate hexahydrate [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] and nickel nitrate hexahydrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] used as precursors in this current study were procured from Topjay Chemical Enterprise, Ado-Ekiti, Nigeria. The methanol (JHD, AR China) used was of analytical-grade and was used as received.

2.2. Preparation and characterization of AENiCo composite catalyst

The procedure employed in preparing AENiCo catalyst was referred to our previous study [25]. The nickel nitrate hexahydrate, cobalt nitrate hexahydrate, anthill powder and eggshell powder were mixed in the proportion of 4.3, 8.6, 17.4 and 69.7%, respectively. The rationale behind this adopted mixing proportion was based on preliminary studies. The mixtures were dissolved in 150 mL of deionized water under continuous stirring for 5 h at 80°C. The pH of the resulting slurry was adjusted to 8.0 by adding 0.1 M Na₂CO₃ and then age in a fume hood at 80°C for 2 h with stirring. The solution was then filtered with filter paper and residue collected was dried in an oven at 110°C for 12 h. Thereafter, the raw catalyst was calcined at 1000°C for 4 h. The basicity of the calcined catalysts was determined by colorimetric titration method reported by Abdoulmoumine [27]. The physical properties of the catalysts were obtained by BET method using a Quantachrome Instrument (Nova station-A model No: 11.03). The catalyst samples were degassed at 200°C for 5 h before taking adsorption data. The functional groups present on the catalyst surface were examined by Fourier transform infrared (FTIR) spectrophotometer (IR Affinity-1S, Shimadzu, Japan). The crystalline phases in the as-synthesized catalyst were identified using a GBC eMMA XRD analyzer. A Cu- α radiation (1.54051 Å) was employed to generate diffraction patterns at ambient temperature in the scanning angle 2θ of 5-70°

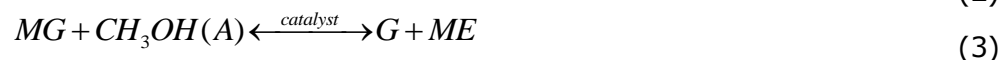
2.3. Transesterification reaction process

The activity of the as-synthesized AENiCo catalyst was tested by subjecting it to transesterification reaction. The reaction was conducted in a batch reactor made up of a 250 mL one way round bottom flask. The inlet mouth of the flask was connected with a condenser, while a thermometer was inserted through the side neck of the flask in order to monitor the temperature of the reaction mixture and was placed on temperature and speed controlled orbital shaker. The WFO was reacted with methanol under the operating conditions; different reaction temperature of 60, 70 and 80°C, the reaction time of 2 h, catalyst loading of 3 wt% and methanol to oil ratio of 12:1 [25]. The stirring speed was kept constant for all experiments.

After the completion of the transesterification reaction, the resulting mixture comprising of unreacted methanol, crude methyl ester (biodiesel), glycerol, and used catalyst was left for 2 h to settle, after which, it was poured into the separating funnel without catalyst. After settling in the separating funnel, the two layers of liquid were observed, the top layer is methyl ester (biodiesel), while the bottom liquid layer is glycerol. The synthesized biodiesel was characterized by FTIR analysis, and its physicochemical and fuel properties were determined in order to ascertain its quality.

2.4. Kinetics of waste frying oil transesterification

The transesterification kinetics of waste frying oil (WFO) on AENiCo catalyst was studied at 60°C, 70°C, and 80°C. In the reaction process, three consecutive reactions were involved as illustrated in Eqs. 1-3. The first reaction is the one between triglycerides (TG) molecules present in WFO and excess methanol (A) which gave diglyceride (DG) (intermediate) and methyl ester (ME). The diglyceride (DG) then reacted with part of the remaining methanol leading to the formation of another intermediate (monoglyceride [MG]) and more methyl ester (ME). The monoglyceride then also combined with remaining methanol to give more methyl ester (ME) and glycerol (G).



(a) Equations (1) - (3) are transesterification reaction steps (b) Equation (4) is the overall transesterification with methanol.

The reaction order, activation energy, and mechanism were determined as explained in details below.

2.4.1. Determination of reaction order and activation energy

The method adopted to investigate the reaction order of WFO conversion was previously documented by Singh *et al.* [26] and Abdoulmoumine [27]. As widely reported in the literature, the transesterification reaction is a reversible type. Thus, the rate expression for the overall reaction equation presented in Eq. (4) could be written as:

$$\frac{-dC_{TG}}{dt} = kC_{TG}^n C_A^m \quad (5)$$

$$C_{TG} = C_{TG_0} (1 - X) \quad (6)$$

$$C_A = C_{TG_0} (\theta - 3X) \quad (7)$$

$$\theta = \frac{C_{A_0}}{C_{TG_0}} \quad (8)$$

Bringing Eqs. (5), (6), (7) and (8) together and also express left hand side of the Eq. (5) in term of fractional conversion (X) to obtain Eq. (9)

$$\frac{dX}{dt} = kC_{TG_0}^{(n+m-1)} (1 - X)^n (\theta - 3X)^m \quad (9)$$

where X = fractional conversion; t = reaction time (min); C_{TG} = concentration of triglyceride (M); C_A = concentration of methanol (M); C_{A_0} = initial concentration of methanol (M); C_{TG_0} = initial concentration of triglyceride (M); θ = molar ratio of methanol to triglyceride; n and m represent the reaction order with respect to triglyceride and methanol; k = reaction rate constant ($\text{mol}^{-1} \cdot \text{min}^{-1} \cdot \text{g}^{-1} \cdot \text{cat}$).

In most of the researches conducted on transesterification kinetics of vegetable oils, the overall reaction order was obtained to be equal to or less than three [26-29]. This implies that the reaction order of triglyceride and methanol could be zero, first or second. In this study, Eq. (9) was solved by integration by partial fraction coupled with excel solver and it was assumed that the reaction order of triglyceride (n) and methanol (m) was either zero, first or second order. Meanwhile, the activation energy and collision factor were both determined using Arrhenius expression given in Eq. (10). Eq. (10) was linearized to obtain Eq. (11) and a plot of $\ln k$ against $1/T$ yields slope equal to $-E/R$ and $\ln k_0$ as intercept.

$$k = k_0 \exp\left(-\frac{E}{RT}\right) \quad (10)$$

$$\ln k = \ln k_0 - (E/R) \frac{1}{T} \quad (11)$$

where: k ($\text{mol}^{-1} \cdot \text{min}^{-1} \cdot \text{g}^{-1} \cdot \text{cat}$), is the reaction rate constant of the rate determining step; k_0 ($\text{M}^{-1} \cdot \text{min}^{-1}$), is the collision factor; E (kJ/mol) is the activation energy; R ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) is the gas constant and T (K) is the reaction temperature.

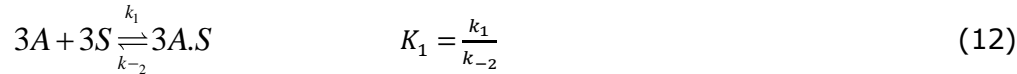
2.4.2. Investigation of the reaction mechanism

In order to develop a kinetic model able to represent adsorption, desorption and surface reaction steps (mass transfer phenomena), the following probable assumptions are made:

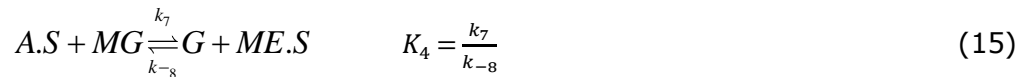
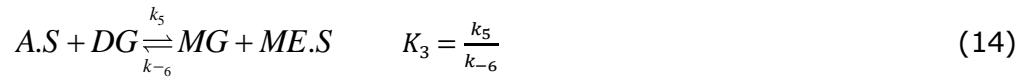
- (1) The catalyst behaviour is a single site, Eley-Rideal (ER), that is, only methanol is adsorbed on the catalyst surface.
- (2) The reaction takes place at the active site of the catalyst.
- (3) The surface reaction step is the rate-controlling step (RCS), and the adsorption and desorption are quasi-equilibrated steps, which are used to eliminate the intermediates (DG and MG) that could not be taken into account.
- (4) The rate of reaction is not influenced by internal and external diffusion.

However, the following mechanistic scheme can then be written for the overall transesterification reaction (Eq. 4).

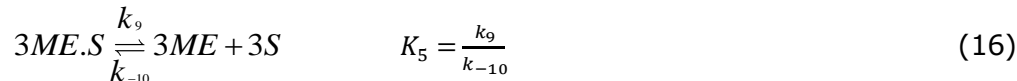
Adsorption step:



Surface reaction step:



Desorption step:



The total concentration of catalyst active sites is:

$$C_T = C_S + C_{A.S} + C_{ME.S} \quad (17)$$

Thus, based on those aforementioned assumptions and reaction mechanisms, the global/overall rate equation was derived and given in Eq. (18).

$$R = \frac{C_T k_3 K_1 \left(C_{TG} C_A - \frac{C_{ME}^3 C_G}{K K_1^2 K_2^2 C_A^2} \right)}{1 + K_1 C_A + \frac{C_{ME}}{K_5}} \quad (18)$$

where A.S = adsorbed methanol on catalyst surface, S = vacant site, ME.S = methyl esters on catalyst surface, C_T = total concentration of catalyst active sites (M); $C_{A.S}$ = concentration of adsorbed methanol on catalyst surface (M); $C_{ME.S}$ = concentration of adsorbed methyl ester on catalyst surface (M); K_i = equilibrium rate constant; k_i = forward reaction rate constant, $\text{mol}^{-1} \text{min}^{-1} \text{g}^{-1} \text{cat}$ and k_{-i} = backward reaction rate constant, $\text{mol}^{-1} \text{min}^{-1} \text{g}^{-1} \text{cat}$.

3. Results and discussions

3.1. Catalyst characterization

The textural properties and basic sites of raw and calcined AENiCo catalysts are presented in Table 1. The result revealed that the surface area of calcined catalyst was higher than that of the raw. This implies that calcination process has a positive effect on performance of the composite catalyst [15]. According to Olutoye and Hameed [21], calcination of solid catalyst at an elevated temperature eliminates adsorbed gases, moisture content and volatile components, thus opening up the surface of the catalyst

Table 1. Summary of the textural properties and basic sites of raw and calcined AENiCo catalyst

Sample	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore diameter (\AA)	Basic sites (mmol/g cat)
Raw	8.12	0.0228	12.40	2.40
Calcined	424.9	0.1119	17.72	12.80

In addition, as can be seen in Table 1, the total pore volume and average pore diameter of the calcined AENiCo catalyst were determined to be $0.1119 \text{ cm}^3/\text{g}$ and 17.72 \AA respectively and found to be higher than those values obtained in the case of raw. Therefore, these results imply that external surface of the calcined catalyst is largely dominated by active sites and it has a tendency to eliminate the mass transfer limitation [15]. This explains the reason why calcined catalyst exhibited better performance in the transesterification reaction.

The high activity of calcined catalyst was also attributed to the large number of basic sites 12.80 mmol/g.cat , which exceeds that of raw catalyst. The increase in basic strength of the composite catalyst is partly attributed to the presence of oxides of calcium, nickel, and cobalt as revealed by XRD analysis (Fig. 1) [21]. According to Di Serio *et al.* [30], the high biodiesel

yield could be achieved in short period of time when stearate metal oxides are used as heterogeneous catalysts in the transesterification reaction. However, those stearate metals in their oxides form possess Lewis acidity (electron acceptor), and negative oxygen ions are thus Lewis bases (proton acceptor) [2, 31]. Therefore, the high basicity exhibited by calcined AENiCo catalyst implied that Lewis base sites are active centers for transesterification reaction.

Figure 1 shows the XRD spectrum of calcined sample of AENiCo catalyst. The main peaks observed at $2\theta = 32.34^\circ$, 54.05° , 64.33° and 67.69° were attributed to CaO, while the peak at $2\theta = 34.35^\circ$ was a characteristic of $\text{Ca}(\text{OH})_2$ and its appearance is as a result of hydroscopic nature of CaO, which may have reacted with atmospheric moisture [15]. More so, the XRD patterns in spectrum shown in Figure 1 displayed peaks at $2\theta = 20.80^\circ$ and 26.70° , which were attributed to SiO_2 . According to Hassani *et al.* [32], the two observed peaks indicate crystal phases. The peak occurred at $2\theta = 37.52^\circ$ was a characteristic of NiO, while peak at $2\theta = 42.97^\circ$ was for CoO. However, it could be noted that the calcined AENiCo catalyst is made up of CaO, $\text{Ca}(\text{OH})_2$, SiO_2 , NiO and CoO..

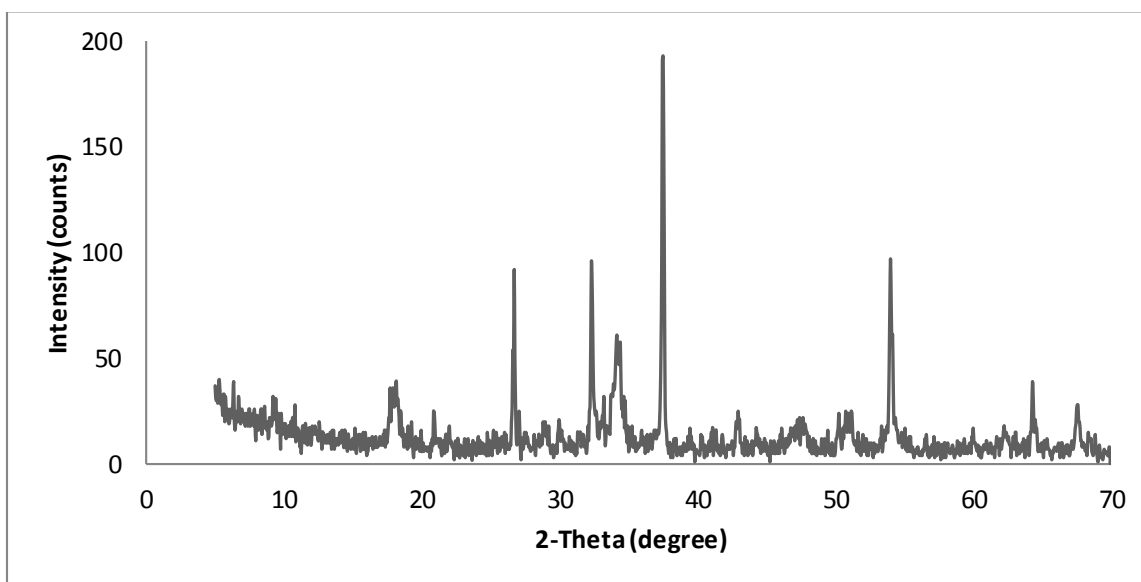


Figure 1. X-ray diffraction spectrum of the calcined AENiCo catalyst

The FTIR spectra of raw and calcined AENiCo catalysts presented in Figure 2 revealed that some peaks were shifted, changed or vanished after calcination process. However, in the raw AENiCo catalyst the absorption band occurred around 3689 cm^{-1} was attributed to O-H stretching vibration mode. The appearance of band at 2517 cm^{-1} was assigned to C-H symmetric stretching bond, while peaks around 1406 cm^{-1} , 874 cm^{-1} and 712 cm^{-1} were due to the symmetric stretch, out-of-plane bend and in-plane bend of C-O vibration modes, respectively [14]. These peaks confirmed the presence of CaCO_3 , which was decomposed into CaO upon calcination [15]. This is corroborated by XRD analysis. The observed peak around 1089 cm^{-1} could be attributed to the Si-O-Si stretching [21]. As well the band at 538 cm^{-1} was due to Al-OH stretching. For calcined catalyst, the peaks around 1647 cm^{-1} and 1001 cm^{-1} were due to C=O and C-O stretching respectively. Appearance of peak at 1055 cm^{-1} could be attributed to Al-Al-OH vibration of anthill clay [33]. The wide absorption band at 428 cm^{-1} was due to CaO vibration formed as a result of complete decomposition of CaCO_3 in eggshell [34]. Moreover, there was a new peak form around 3641 cm^{-1} which could be attributed to O-H stretching vibration and this peak is usually assigned to hydroxyl bond in calcium hydroxide, $\text{Ca}(\text{OH})_2$ [15]. However, formation of $\text{Ca}(\text{OH})_2$ was as result of adsorption of atmospheric moisture onto calcined catalyst surface during analysis. This is corroborated by XRD analysis and is attributed to why calcined AENiCo exhibited high basicity. A similar observation was reported by Margaretha *et al.* [35] in the production of biodiesel using CaO based catalyst derived from *Pomacea sp.* shell.

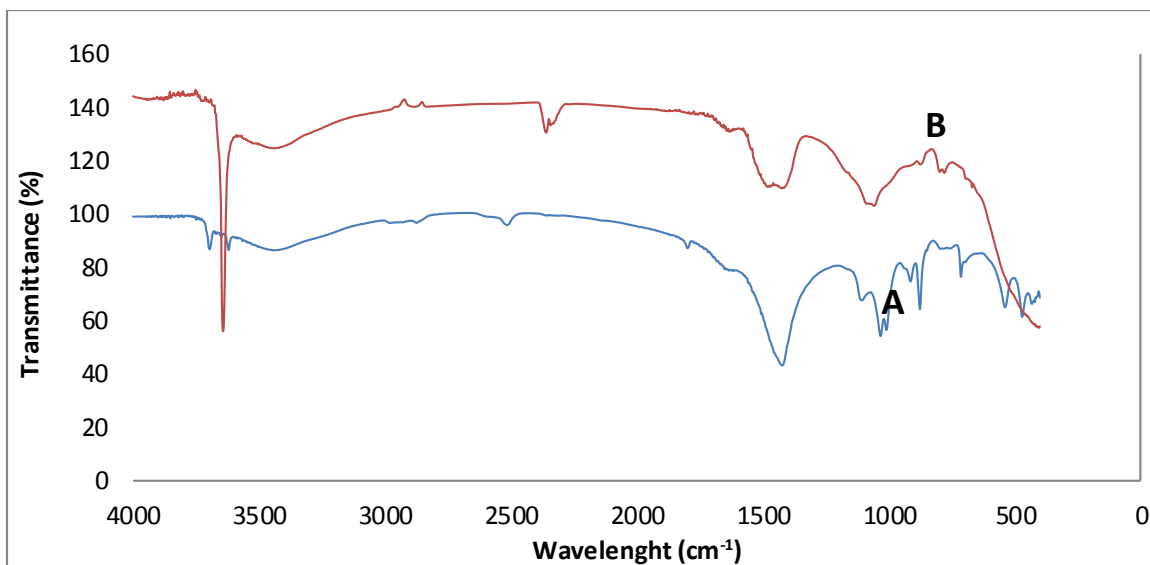


Fig. 2. FTIR spectra of A- raw and B-calcined AENiCo catalysts

3.2. Kinetics of waste frying oil transesterification

The influence of the reaction temperature on the transesterification of WFO to biodiesel using AENiCo catalyst is shown in Figure 3.

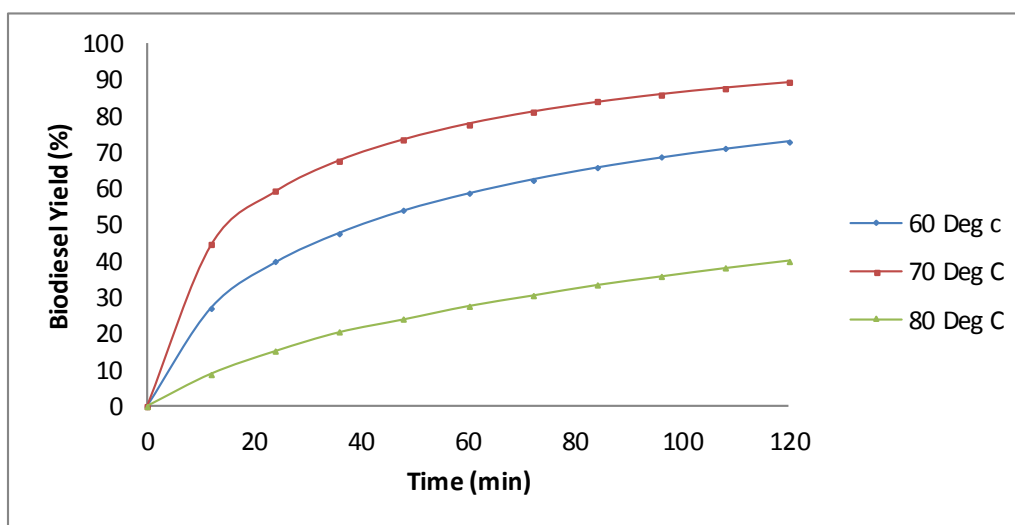


Figure 3. Effect of time and temperature on the biodiesel yield

It can be observed that considering reaction temperature from 60°C to 70°C, the biodiesel yield (%) increased with increased temperature and remained constant after the reaction attained equilibrium. As reflected in literature, higher reaction temperature enhances mass transfer of reactants and dispersion of the catalyst particles [15]. High temperature also favours high reaction rate, which eventually results to high conversion to biodiesel [36]. Meanwhile, at lower reaction temperature, there would be poor interaction between methanol and catalyst particles, thus leading to slower reaction rate [37]. Relatively, either high reaction temperature or reaction time is needed to achieve a maximum yield of biodiesel in most of the heterogeneous catalyzed transesterification reactions [37]. This is attributed to why maximum biodiesel yield of 89.22% was attained at reaction temperature of 70°C. However, with reaction temperature above 70°C, that is 80°C, lower yield was recorded. This is due to liquid

methanol in the reaction medium that had been totally gasified, therefore favouring the formation of glycerol over biodiesel [15].

3.2.1. Determination of reaction order and activation energy

In an attempt to determine the order of the overall reaction with respect to triglyceride and methanol (n and m) at temperatures 60, 70 and 80°C, eight cases were examined. The best overall reaction order was chosen based on the values of correlation coefficient (R^2). The closer the R^2 value to unity, the more accurate the order for the overall reaction could give the best fit with the experimental results [27]. The R^2 values for all the three temperatures considered were highest when reaction is first order with respect to triglyceride and a second order with respect to methanol. The values of R^2 were obtained to be 0.835, 0.914 and 0.948 for 60°C, 70°C and 80°C respectively. Thus, a third overall order ($n = 1$ and $m = 2$) indicates better agreement with the experimental data. This confirms that rate of reaction is sensitive to change in temperature. As reported by Nouredini and Zhu [38], transesterification process being a multiple and reversible reaction often exhibits an optimal temperature with respect to the biodiesel yield. Thus, these findings show that an optimal reaction temperature favours reaction rate.

The activation energy (E) and collision factor (k_o) were determined from the plot of $\ln k$ against $1/T$ (the plot is not given) to be 23.99 kJ/mol and $1.62 \times 10^6 \text{ M}^{-1}\text{min}^{-1}$ respectively.

3.2.2. Reaction mechanism

In order to evaluate the kinetic parameters contained in overall reaction rate expression (Eq. 18), it was assumed that the concentration of glycerol was extremely low and eliminated. The reduced model derived based on Eley-Rideal kinetic was solved by using least mean square analysis. The estimated kinetic parameters are presented in Table 2.

Table 2. Estimated kinetic parameters based on Eley-Rideal principle

Reaction temperature	$\beta \times 10^{-5}$	K_1	$K_5 \times 10^{-6} (\text{mol}^{-1})$
60°C	8.35	5.19	1.12
70°C	14.03	5.60	3.84
80°C	2.23	3.10	0.96

where β is $C_T K_5$

Based on the results obtained, it could be concluded that the transesterification of waste frying oil over AENiCo composite catalyst obeyed Eley-Rideal mechanism. The result obtained herein is in trend with the work reported by Abdoulmoumine [27].

3.3. Analysis of synthesized biodiesel

3.3.1. FTIR analysis

The functional groups of biodiesel prepared at reaction temperature of 70°C, catalyst loading of 3 wt%, reaction time of 2 h and methanol to WFO ratio of 12:1 was confirmed by FTIR analysis. As shown in Figure 4, the broad absorption band at 3439 cm^{-1} was attributed to O-H stretching vibration. Those sharp peaks around 2926 cm^{-1} and 2854 cm^{-1} were due to C-H stretching vibrations of methylene groups. The strong peak at 1745 cm^{-1} (C=O ester) and at 1165 cm^{-1} (C-O ester) which are obviously present in the spectrum were assigned to carbonyl functional groups. These two functional groups confirm the presence of esters and are only attributed to biodiesel [39]. While the band at 1466 cm^{-1} could be attributed to the CH_3 group in the methyl ester mixtures [40]. As well the peak at 721 cm^{-1} was attributed to C-H_2 methylene rock. The presence of these functional groups confirmed the quality of the synthesized biodiesel and this observation is in trend with the experimental data reported by Yadav *et al.* [41].

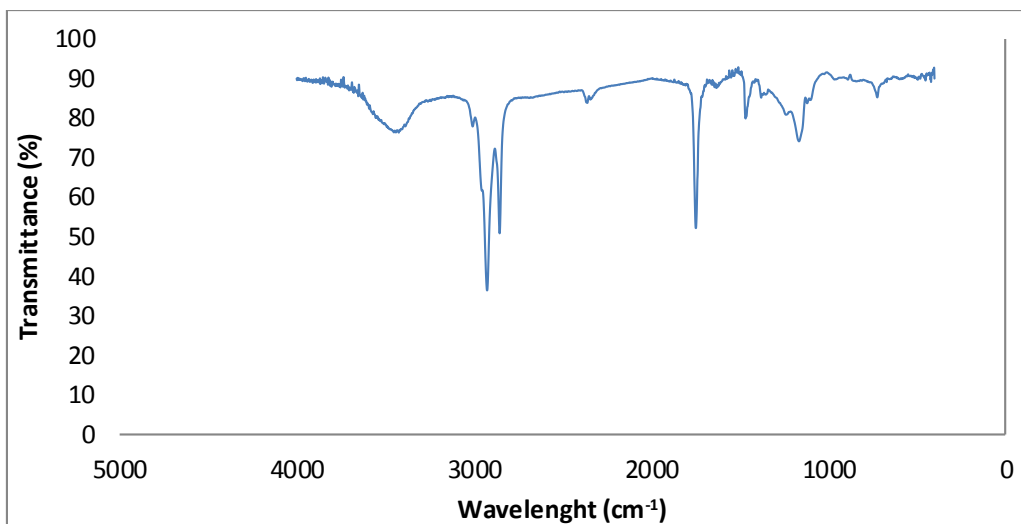


Figure 4. FTIR spectrum of synthesized biodiesel at reaction temperature of 70°C

3.3.2. Determination of physicochemical properties

The biodiesel prepared under the reaction temperature of 70°C, catalyst loading of 3 wt%, the reaction time of 2 h and methanol to WFO molar ratio of 12 was characterized based on its physicochemical and fuel properties. Table 3 shows the properties of the WFO-biodiesel. However, these properties were compared with those of commercial biodiesel [23] and ASTM/EN standard for biodiesel. Some of these properties were found to be comparable and in reasonable agreement with ASTM/EN standard for biodiesel.

Table 3. WFO-biodiesel physicochemical and fuel properties

Parameter	WFO-biodiesel	Commercial biodiesel	Biodiesel standard ASTM/EN
Specific gravity	0.886	0.844	0.86-0.90
Kinematic viscosity at 40°C (mm ² /s)	3.58	-	1.9-6.0
Acid value (mgKOH/g)	0.92	0.34	>0.8
Flash point (°C)	148	70	100-170
Cloud point (°C)	-9	-	-
Pour point (°C)	-12	-10	-15-10
Lower heating value (MJ/kg)	37.49	40.9	40.13

4. Conclusion

The activity of anthill-eggshell-Ni-Co mixed oxide composite catalyst in transesterification of WFO to biodiesel was investigated. The results of BET and basicity analyses revealed that the surface area and basic sites of as-synthesized catalyst increased upon calcination. XRD analysis showed that the calcined AENiCo catalyst contains a mixture of CaO, Ca(OH)₂, SiO₂, NiO and CoO, thus indicating a composite catalyst. Various surface functional groups of the catalyst were identified from the FTIR results. A detail study on the kinetics of WFO transesterification at 60°C, 70°C and 80°C showed that the reaction was first order with respect to triglyceride and second order with respect to methanol. The activation energy and collision factor were found to be 23.99 kJ/mol and 1.62 x 10⁶ M⁻¹ min⁻¹ respectively. After evaluation of model parameters, it was found that the transesterification reaction obeyed Eley-Rideal kinetic.

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