



Synthesis and characterization of anthill-eggshell-Ni-Co mixed oxides composite catalyst for biodiesel production from waste frying oil

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Abstract: This study was conducted to develop a new composite heterogeneous catalyst, anthill-eggshell-Ni-Co mixed oxides (AENiCo), for biodiesel production via transesterification of waste frying oil. The catalyst was synthesized using a co-precipitation method and was characterized by Brunauer-Emmett-Teller (BET) surface area analysis, Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray fluorescence (XRF). The effects of parameters affecting the catalytic reaction, reaction temperature (40–80 °C), reaction time (1–5 h), catalyst loading (1–9 wt%), and methanol-to-oil ratio (3:1–15:1) were investigated. The stability of the spent catalyst was also investigated during reuse. The data obtained showed that the maximum biodiesel yield of 90.23% could be obtained at a reaction temperature of 70 °C, reaction time of 2 h, with a catalyst loading of 3 wt% and methanol-to-oil ratio of 12:1. The stability study showed that the AENiCo catalyst could be reused for up to four cycles. © 2018 Society of Chemical Industry and John Wiley & Sons, Ltd

Keywords: Biodiesel; catalyst; characterization; transesterification; waste frying oil.

Introduction

Research has shown that the sustainability of biodiesel production relies solely on feedstock and catalysts and this is due to the fact that biodiesel is commonly produced via transesterification of plant oil or animal fat with alcohol in the presence of a catalyst. In biodiesel production, three forms of catalyst, namely

homogeneous, enzyme and heterogeneous, can be used. However, disadvantages associated with homogeneous catalysts (wastewater generation and inability to reuse the catalyst) and enzymes (exorbitant cost and easy deactivation) have motivated the search for alternative catalysts.^{1,2} Reusability and easy separation from product mixtures gives heterogeneous catalysts an edge over the others. Their application in the field of renewable energy to



synthesize renewable and biodegradable fuel has become an area of research interest and much effort is needed to discover effective solid catalysts that can be synthesized easily from waste/abandoned materials.

A large number of heterogeneous catalysts for biodiesel production has been extensively investigated and reported in the literature.^{2,3} The reported solid catalysts include pure metal oxide,⁴ mixed metal oxide,⁵ sulfated metal oxide,⁶ biomass-derived catalyst,⁷ naturally occurring material,⁸ domestic waste,⁹ and industrial waste.¹⁰ There is an increasing interest in deriving heterogeneous catalysts from natural and waste materials for biodiesel production. However, anthills have not been explored as catalysts to transesterify vegetable oil to fatty acid methyl esters (FAME). This also includes their 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 (composite) form to synthesize fatty acid methyl esters.

An anthill is a pile of earth, sand, pine needles, or clay, or a composite of various materials that build up at the entrances of the subterranean dwellings of ant colonies.¹¹ In most places, several hundreds of these wonderful ant-created features persist for many years. Each anthill is formed as a result of many lifetimes' labor by thousands of tiny yellow meadow ants (*Lasius flavus*).¹² According to Akinwekomi *et al.*¹³ an anthill is a form of fire clay that is made up of silica (SiO₂), alumina (Al₂O₃), iron oxide (Fe₃O₄), and many other metal oxides. Numerous researchers have used silica and alumina as catalyst supports for heterogeneous catalyzed transesterification. Umdu *et al.*¹⁴ employed Al₂O₃-supported CaO and MgO as heterogeneous catalysts. Calcium oxide supported on mesoporous SiO₂ was used as a heterogeneous catalyst by Albuquerque *et al.*¹⁵ for transesterification of soybean oil. Liu *et al.*¹⁶ synthesized a Fe₃O₄-supported CaO magnetic base catalyst using the precipitation method. In this study, however, anthill is chosen because it can serve as cheap source of catalyst supports.

Chicken eggshell is a component in domestic or agricultural waste. A typical eggshell contains more than 90% calcium carbonate (CaCO₃).¹⁷ Eggs are consumable products in every household because of their richness in amino acids, vitamins, and minerals.¹⁷ In Nigeria, the Poultry Association of Nigeria (PAN) and Nutrition Society of Nigeria have been increasing awareness of the importance of egg consumption, thus making their consumption common. Due to the high proportion of CaCO₃ in dry eggshell and its availability in large quantities, it is therefore possible to synthesize CaO-based catalysts from it. Several researchers have conducted successful experiments on the

use of CaO catalysts derived from waste chicken eggshells for transesterification of vegetable oils.^{17–20}

In the present work, a composite catalyst from locally sourced anthills and waste chicken eggshells modified with mixed metal (Ni, Co) oxides was developed. The prepared catalyst was characterized using various techniques in order to evaluate its properties and was used as a catalyst for the production of FAME from waste frying oil (WFO). The influences of various parameters such as reaction temperature, reaction time, methanol/WFO molar ratio, and catalyst loading on catalytic reaction were investigated. Moreover, the stability of the spent catalyst was investigated during reuse.

Materials and methods

Materials

The anthill used is situated behind the works and maintenance department of Afe Babalola University (ABUAD), Ado-Ekiti, Nigeria. Waste chicken eggshell and WFO were collected from the postgraduate student cafeteria, ABUAD, Ado-Ekiti, Nigeria. The specific gravity, free fatty acid (FFA), acid value and saponification value of WFO are 0.91 g m⁻³, 0.64 wt%, 1.28 mg KOH g⁻¹ and 181.6 mg KOH g⁻¹, respectively. As the FFA content of WFO is less than 2 wt%, a single-step transesterification process could be used. The synthesis-grade methanol (CH₃OH, JHD, AR China), nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O, BDH, England), cobalt nitrates hexahydrate (Co(NO₃)₂·6H₂O, BDH, England), heptane (solvent), and propylene acetate (internal standard) were all purchased from Nizo Chemical Enterprise, Akure, Nigeria. The distilled water that was used was prepared in the laboratory.

Preparation of catalyst

The harvested anthill in lump form was manually pulverized by mortar and pestle. The crushed anthill was then sieved through sieve mesh of 0.3 mm to obtain particles with a size less than 0.3 mm. The fine anthill powder was dried in an oven at 105 °C for 4 h to remove moisture content. The dried anthill powder was then kept in a sealed plastic container. The chicken eggshell was thoroughly washed to remove white membrane and impurities from it and then it was heated up at 110 °C in an oven overnight in order to remove the water. The dried eggshell was ground with the aid of a mechanical grinder, and sieved to the required particles size. The eggshell powder that was obtained was kept in a covered plastic container.

The anthill-eggshell-Ni-Co (AENiCo) mixed oxides composite catalyst was prepared using a co-precipitation



method with anthill powder, eggshell powder, nickel nitrate, cobalt nitrate, and $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{CO}_3$. The technique reported by Sirichai *et al.*²¹ was adopted in this current study. Typically, 50 g of constituents of AENiCo catalyst in a mixing proportion of 4.3%, 8.6%, 17.4%, and 69.7% for nickel nitrate, cobalt nitrate, anthill powder, and eggshell powder respectively were dissolved in 100 mL of deionized water under continuous stirring for 5 h at 80 °C. The pH of the resulting slurry was adjusted by adding $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{CO}_3$ and then aged in a fume hood at 80 °C for 2 h with stirring. The solution was then filtered with filter paper and the residue collected was dried in an oven at 110 °C for 12 h. Thereafter, the raw catalyst, henceforth referred to as AENiCo, was calcined at 1000 °C for 4 h.

Characterization of catalyst

The textural features of the prepared catalyst were determined by the Brunauer–Emmett–Teller (BET) technique using a Quantachrome instrument (Autosorb-1 Model No. 11.03, Florida, USA), which was based on the nitrogen adsorption/desorption principle acquired at 77 K and 60/60 s (ads/des) equilibrium time. Scanning electron microscope (SEM-JEOL-JSM 7600F) was used to determine the external morphology, crystalline structure, and orientation of the catalyst sample. The functional groups on the catalyst surface were determined by Fourier transform infrared radiation (FTIR, IR Affinity-1S Shimadzu, Japan) spectroscopy. X-ray diffraction (XRD) was used to confirm the structural characteristics and unique fingerprints of the catalyst sample, which was conducted on a model GBC Emma XRD analyzer. $\text{CuK}\alpha$ radiation (1.54051 \AA) was employed to generate diffraction patterns at ambient temperature in the scanning angle 2θ of 5–70°. The catalyst crystallite size was determined using Scherrer's expression, which is given in Eqn (1). X-ray fluorescence (XRF) was carried out using a Varian 102WXRF analyzer to determine the chemical compositions of the prepared catalyst.

$$d = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

where d is the crystallite size of the active phase (nm), λ is the x-ray wavelength, θ is the angle of diffraction and β is the full width at half maximum of the peak.

Transesterification reaction study

The conversion of WFO into biodiesel using AENiCo catalyst 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

to monitor the temperature of the reaction mixture, and was placed on a temperature- and speed-controlled orbital shaker with constant maximum agitation rate to prevent diffusion limitation. For each run, 50 mL of WFO was weighed out and poured into the reaction container. The appropriate quantity of methanol based on the ratio of WFO to methanol was weighed out and poured into a beaker. The required amount in mass of the catalyst was then activated by shaking the methanol-catalyst mixture and this was then added to the preheated WFO at 60 °C in the batch reactor, while the condenser was immediately fitted with the reactor and the stirring speed knob was tuned to the maximum allowable speed. The stirring speed was kept constant for all experiments. The reactions were performed under different conditions, considering catalyst weight (1–9 wt%), temperature of reaction (40–80 °C), period of reaction (1–5 h), and molar ratio of methanol to WFO (3:1–15:1), while keeping stirring rate constant.

After the reaction was completed, the catalyst was separated from the product mixtures (biodiesel and glycerol) by cloth filtration. The biodiesel collected from the product mixture was stored in a sample bottle for methyl ester characterization. A gas chromatography–mass spectrometry (Varian 4000 GC/MS/MS system) equipped with flame ionization detection (FID) and an Agilent J&W capillary column (60 mm × 0.320 mm × 1.8 μm) with helium as the carrier gas was used to determine the composition of the methyl esters in the biodiesel samples.

The biodiesel yield (Y) was evaluated using the mathematical expression given in Eqn (2):

$$\text{Biodiesel yield, } Y\% = \frac{W_i A_b}{W_b A_i} \times 100\% \quad (2)$$

where W_i and W_b are the weights of the internal standard and the biodiesel sample, respectively. A_i and A_b are the peak areas of the internal standard and biodiesel sample, respectively.

Catalyst stability and reusability studies

After the end of the reaction process, the spent catalyst was collected and washed with 20 mL of methanol to dispose of glycerol that was attached to the catalyst surface, and dried in an oven at 90 °C for 12 h. It was thereafter employed for the next reaction. The same procedure was repeated for the subsequent cycles. The volume of WFO required for each reaction cycle was calculated based on Eqn (3), which connects catalyst dosage and amount of WFO used. The required volume of methanol used for each cycle was calculated using the established optimum methanol/oil molar ratio of 12:1. The



functional groups present on the surface of the regenerated reused catalyst were identified by FTIR analysis:

$$\frac{M_{OI}}{M_{CI}} = \frac{M_{OF}}{M_{CF}} \quad (3)$$

where M_{OI} is the initial mass of oil used (g), M_{OF} is the final mass of oil used (g), M_{CI} is the initial mass of catalyst used (g), and M_{CF} is the final mass of catalyst used (g).

Results and discussion

Characterization of catalysts

Determination of textural properties

The textural properties of the synthesized catalyst samples, which include surface area, total pore volume, and average pore diameter, were determined. The surface areas of the catalysts were determined using the Brunauer–Emmett–Teller (BET) model. Pore volume and average pore diameter were calculated using the Dubinin–Radushkevich (DR) model. The results of the analyses are presented in Table 1. The result revealed that the textural properties of the calcined AENiCo catalyst improved after calcination and this is attributed to complete removal of adsorbed gases and organic matter, thus exposing its active sites. A similar observation was reported by Tan *et al.*⁷ This is corroborated by SEM, FTIR, and XRD analyses. The large BET surface area and expanded pore volume of calcined AENiCo indicated that the catalyst external surface is dominated by active molecular sites and, therefore, can promote adsorption of methanol.⁸

SEM analysis

The SEM images of raw and calcined AENiCo catalysts are presented in Fig. 1. The SEM image of raw catalyst in Figure 1(a) indicates that it has a regular and defined shape with small cavities on its surface. Figure 1(b) shows the SEM image of calcined AENiCo, which was thermally treated at calcination temperature of 1000 °C for 4 h. Various wide pores were clearly seen on the calcined AENiCo catalyst. This indicates that the adsorbed gases and the moisture content that filled up the pores for methanol adsorption

were completely removed during calcination at higher temperature. This is corroborated by XRD and XRF analyses and is considered to be the reason why AENiCo catalyst exhibited better performance during the reaction.

FTIR analysis

This characterization technique is employed to identify those functional groups on the surfaces of raw (A), calcined (B), and reused (C) AENiCo catalysts. As shown in Fig. 2, the major absorption peaks in raw catalyst appeared at 3423.76, 1797.72, 1421.58, 1384.94, 875.71, and 713.69 cm^{-1} , while those of calcined AENiCo occurred at 3643.65, 3433.41, 1626.05, 1463.66, 1417.73, 999.16, 914.29, and 420.48 cm^{-1} . The sharp absorption band between 3700 and 3325 cm^{-1} can be attributed to the O—H stretching vibration from absorbed moisture. More so, absorption bands at around 1421.58, 875.71, and 713.69 cm^{-1} for the raw catalyst are assigned to C—O asymmetric stretching, out-of-plane bend, and in-plane bend vibration modes of CO_3^{2-} from CaCO_3 contained in chicken eggshell.²² However, the appearance of a band around 1800 cm^{-1} is a result of the C=O functional group contained in aldehydes.¹⁹ The appearance of a band at 1626.05 cm^{-1} , as can be seen in Fig. 2, is attributed to alkenyl C=C stretching vibrations. Bands at 1469.45 and 1463.66 cm^{-1} are attributed to CH_3 antisym deformation and CH_2 scissors vibration, respectively. The observed band at 1417.73 cm^{-1} corresponds to a vinyl C—H in-plane bend. The observed trough between approximately 1000 and 900 cm^{-1} is due to the presence of a silicate ion or C—H out of plane bend of alkenes. Absorption bands less than 500 cm^{-1} are due to CaO vibration.⁷ For reused catalyst (C), sharp absorption peaks at 2922.25 and 2852.81 cm^{-1} are due to C—H stretching vibrations of methyl and methylene groups, respectively. These functional groups are often found in an oily based material.²³ Those absorption bands that are less than 500 cm^{-1} in the FTIR spectrum of reused catalyst (C) are weak compared to the band at 428.21 cm^{-1} in the FTIR spectrum of the calcined AENiCo catalyst (B) as shown in Fig. 2, which is broad and strong. This result implies that there is a reduction in CaO contained in the AENiCo catalyst after use.

XRD analysis

X-ray diffraction analysis was carried out to evaluate the catalyst structure and also to identify the phases that constitute the catalyst. However, Fig. 3 displays the X-ray diffraction profile against the angle of diffraction (2θ) of the calcined AENiCo catalyst. It is evident that CaO is the main phase in the calcined AENiCo catalyst in the sense that the majority of the peaks were characteristics

Table 1. Physical properties of raw and calcined AENiCo catalysts.

Sample	BET surface area ($\text{m}^2 \text{g}^{-1}$)	Total pore volume ($\text{cm}^3 \text{g}^{-1}$)	Average pore diameter (\AA)
Raw	55.95	0.0265	24.22
Calcined	411.10	0.151	32.11

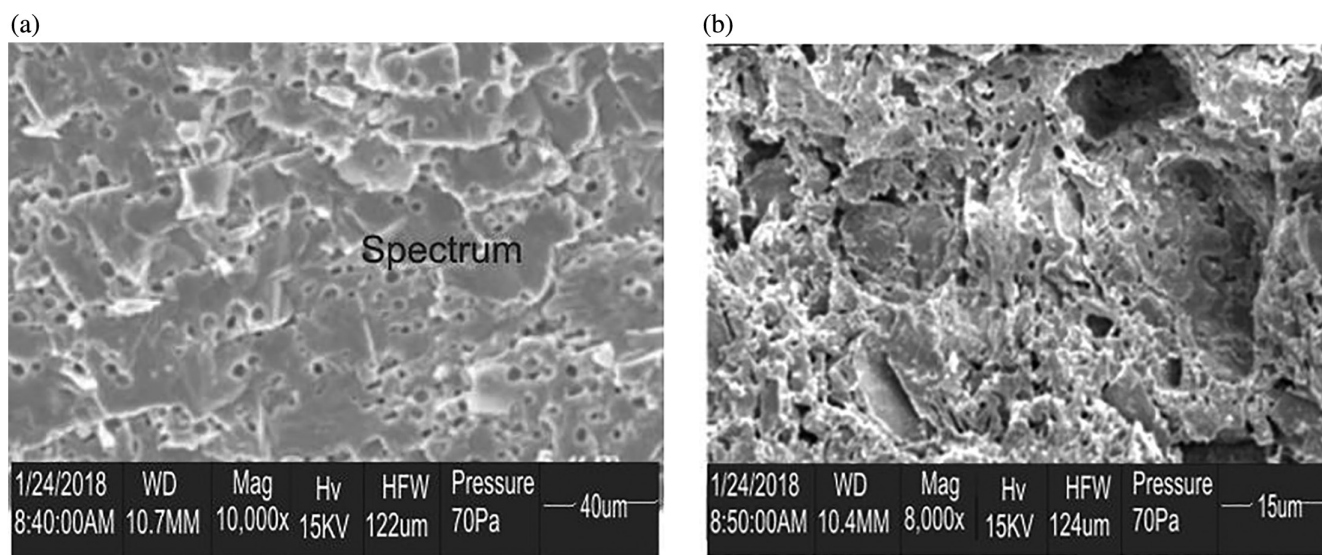


Figure 1. SEM image (a) raw; (b) calcined AENiCo catalyst.

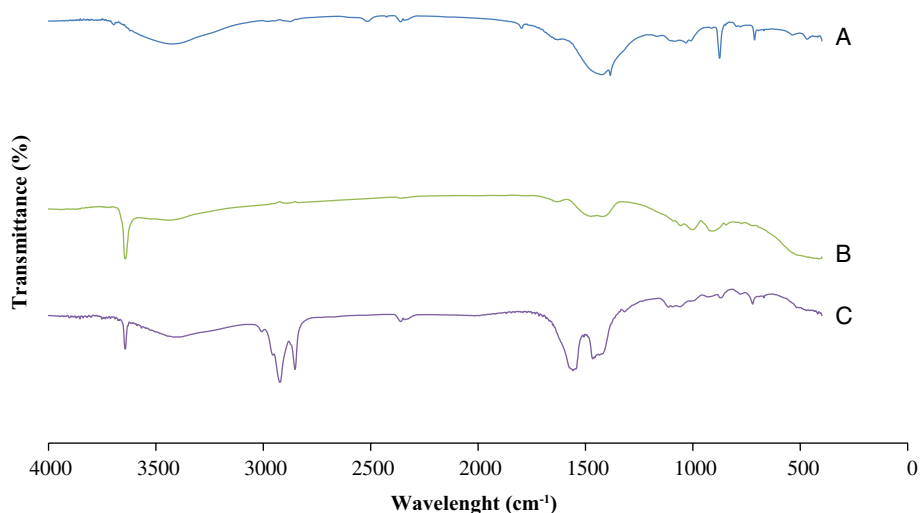


Figure 2. FTIR spectra of raw (A), calcined (B) and reused (C) AENiCo catalysts.

of CaO. The peaks obtained in the catalyst were compared to the Joint Committee on Powder Diffraction Standards (JCPDS) file. No traces of calcium carbonate (CaCO_3) were detected in the catalyst sample. This indicates that complete decomposition occurred during the calcination process, as revealed by SEM, FTIR, and XRF analyses.

As can be seen in Fig. 3, the peak represented at 2-theta equal to 32.3° , 37.45° , 54.0° , 64.3° , and 67.55° were attributed to the presence of CaO, while peaks detected at 2-theta equal to 18.1° , 34.1° , 47.25° and 50.6° were due to the presence of $\text{Ca}(\text{OH})_2$. The intense peaks at 18.1° and 34.1° for $\text{Ca}(\text{OH})_2$ are an indication of exposure to moisture.⁷ The XRD results implied that, due to the hygroscopic nature of CaO, the AENiCo catalyst contains a mixture of CaO and $\text{Ca}(\text{OH})_2$,

and other components. The XRD patterns in Fig. 3 displayed peaks at 2θ equal to 19.95° and 26.7° , which were characteristic of SiO_2 . Furthermore, also in Fig. 3, the peaks for the AENiCo catalyst appeared at 2θ equal to 26.7° and 37.45° , and could also be attributed to NiO. Cobalt oxide was observed at 2θ , which was equal to 42.95° . The average crystallite size of the AENiCo catalyst was determined as 16.67 nm by the Scherrer equation; thus the catalyst exhibited nanoparticle character, with an average crystallite size less than 30 nm.²⁴

XRF analysis

The compositional analysis was conducted on raw anthill, natural eggshell, and calcined AENiCo samples using XRF

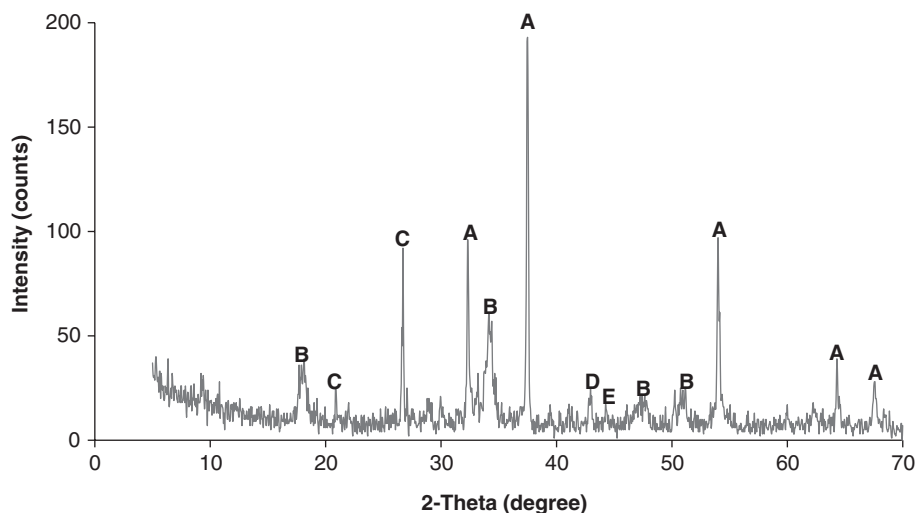


Figure 3. X-ray diffraction spectra of the calcined AENiCo catalysts. The crystalline phases are also correspondingly labeled as: (A) CaO, (B) Ca(OH)₂, (C) SiO₂, (D) CoO, (E) NiO.

and ignition-loss methods. The result obtained is presented in Table 2 and revealed that the anthill contains mainly silica (SiO₂), alumina (Al₂O₃), zirconia (ZrO₂), and ferric oxide (Fe₂O₃). From the result obtained, the anthill could be classified as siliceous fire clay.¹³ However, the presence of ZrO₂ in the anthill sample is a good discovery as it is absent in natural clay. As Table 2 also shows, it could be deduced from the XRF analysis that the CaO detected by the XRF analyzer implied that raw eggshell contains a large percentage of CaCO₃ and the domination of CaO in the calcined AENiCo was attributed to the liberation of CO₂ at an elevated calcination temperature. This observation is in agreement with the findings reported by Eletta *et al.*²⁵ The SiO₂ detected in AENiCo confirmed the presence of anthill. The increase in NiO and CoO content in the AENiCo catalyst as compared with eggshell and anthill, in which they have a lower percentage, was attributed to the loading of nickel and cobalt nitrates onto mixed anthill-eggshell. Generally, this observation is in agreement with the XRD analysis. Meanwhile, the high Loss on ignition (LOI) obtained for the three samples was as a result of the removal of moisture, organic matter, and some adsorbed gases during the ignition process.

Effect of individual process parameters on FAME yield

Effect of reaction temperature

The effect of reaction temperature on the FAME yield during the methanolysis of WFO was studied at various temperatures ranging from 40 °C to 80 °C using calcined AENiCo as catalyst for 2 h with catalyst loading of 3 wt% and methanol/WFO molar ratio of 12:1. As shown in Fig. 4,

Table 2. Chemical composition analysis of raw anthill, natural eggshell and synthesized AENiCo catalyst by XRF and LOI methods.

Compound	Chemical composition of sample (wt%)		
	Raw Anthill	Raw Eggshell	Calcined AENiCo
Magnesium oxide (MgO)	—	0.41	0.027
Aluminum oxide (Al ₂ O ₃)	13.64	0.34	2.08
Silicon oxide (SiO ₂)	58.46	0.30	11.04
Phosphorus oxide (P ₂ O ₅)	0.29	0.48	0.51
Trioxosulphate (SO ₃)	0.38	0.57	0.81
Potassium oxide (K ₂ O)	3.17	—	0.11
Calcium oxide (CaO)	0.21	82.81	71.87
Titanium oxide (TiO ₂)	0.38	—	—
Iron (III) oxide (Fe ₂ O ₃)	6.47	0.14	0.45
Molybdenum oxide (MoO ₂)	0.24	0.29	0.083
Tin oxide (SnO ₂)	1.19	—	0.25
Antimony oxide (Sb ₂ O ₃)	1.21	0.29	0.24
Nickel oxide (NiO)	0.059	0.03	5.60
Cobalt oxide (CoO)	—	—	7.06
Copper oxide (CuO)	0.059	—	—
Zirconium oxide (ZrO ₂)	9.85	0.72	0.047
Zinc oxide (ZnO)	0.11	—	0.02
Manganese oxide (MnO ₂)	0.068	—	—
Tungsten oxide (WO ₃)	0.037	—	—
Loss on ignition (LOI)	4.18	13.63	2.24

the FAME yield increases from 42.56% at 40 °C to 89.23% at 70 °C. Meanwhile, with reaction temperature above 70 °C, that is 80 °C, a drop in the FAME yield was recorded. This

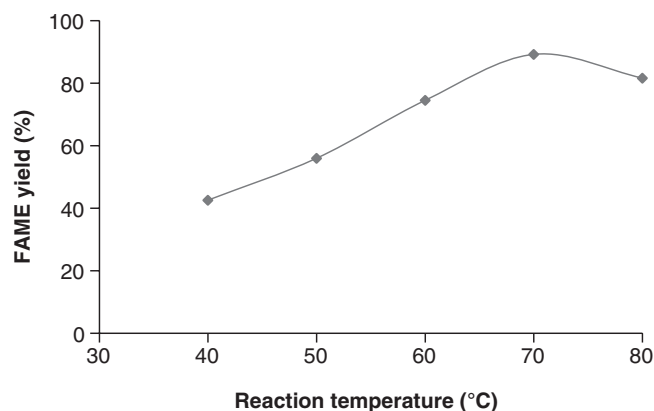


Figure 4. FAME yield at different reaction temperatures, at reaction time = 2 h; catalyst loading = 3 wt% and methanol/WFO molar ratio = 12:1.

finding revealed that the FAME content was dependent on the reaction temperature. Elevated reaction temperatures enhanced the mass transfer of reactants and the dispersion of the catalyst particles.⁸ High reaction temperatures promoted interactions between the catalyst with hydrogen ion from methanol and mixed oxide catalyst with the alkyl group of triglycerides.²⁶ The reduction in the FAME content at temperatures exceeding 70 °C might be due to a reduction in the amount of reactant. Thus, the reaction temperature of 70 °C was considered as optimum and was employed for further investigation in the present research.

Effect of catalyst loading

To investigate the influence of catalyst loading on the yield of FAME, the transesterification of WFO with methanol was carried out using various catalyst loadings ranging from 1.0 to 9.0 wt% at 70 °C reaction temperature, 2 h reaction time, and with a methanol/WFO molar ratio of 12:1. As shown in Fig. 5, the FAME content increases as the catalyst loading increases from 1 to 3 wt%. When the catalyst loading was increased above 3 wt%, the FAME content reduced. However, maximum FAME yield was obtained at a catalyst loading of 3.0 wt%. The result obtained indicates that a catalyst dose of 3 wt% was adequate to provide the required adsorption sites for reactants. Waste frying oil conversions at the catalyst loadings above 3 wt% were low. This is because when the catalyst dose was in excess, mass transfer between catalyst and reactants decreased, thus reducing the interactions between them and, at the same time, reducing the FAME content.²⁶ This finding might be attributed to the formation of soap as a result of an unwanted reaction between triglycerides and the alkali content of the catalyst. The

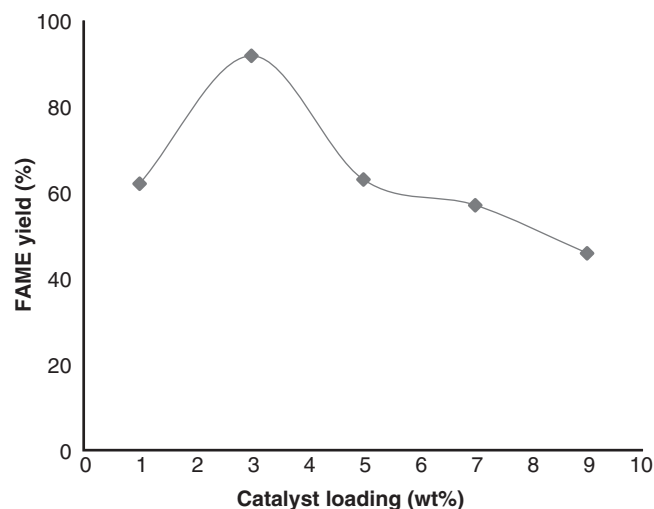


Figure 5. FAME yield at different catalyst loadings, at 70 °C reaction temperature, 2 h reaction time and methanol/WFO molar ratio of 12:1.

optimum catalyst loading obtained was used for further investigation in this same study.

Effect of reaction time

The influence of reaction time on FAME content during the transesterification of WFO with methanol was studied at different periods ranging from 1 to 5 h using AENiCo as catalyst with a reaction temperature of 70 °C, 3 wt% catalyst loading, and 12:1 methanol/WFO molar ratio. As depicted in Fig. 6, it was observed that the FAME yield increased as the reaction time increased from 1 to 2 h. However, FAME content continued to decrease when the reaction time was increased above the optimum value. The possible cause for the higher yield of biodiesel at lower reaction time might be the high reaction temperature as the reaction rate increases with temperature. In most of the heterogeneous transesterification reactions, high temperature or time is required to achieve high FAME yield.²⁷ The FAME yield also largely depends on the methanol-to-oil molar ratio. According to Yin *et al.*²⁸ the higher methanol/oil molar ratio, the shorter the reaction time for reaching the equilibrium. Since transesterification reaction is reversible, prolonging the reaction time decreases the FAME yield.^{7,29} In the present study, the maximum biodiesel yield was achieved at reaction time of 2 h and it was considered as the optimum value for the subsequent reaction.

Effect of methanol to oil molar ratio

The influence of the molar ratio of methanol to WFO on the FAME content was investigated, while other variables

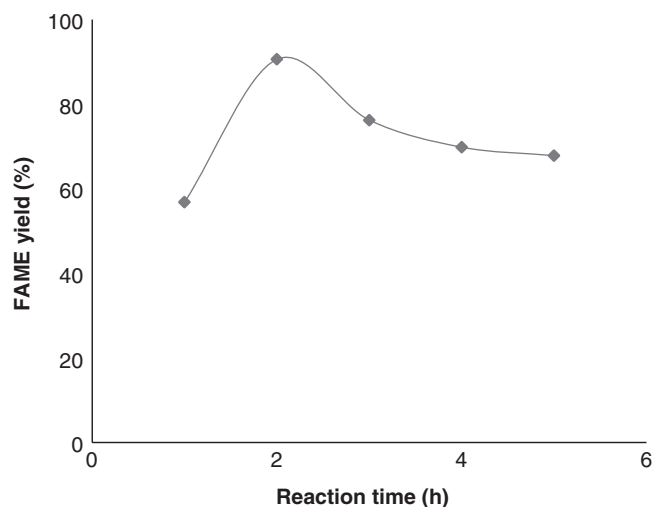


Figure 6. FAME yield at different reaction times, at 70 °C reaction temperature, 3 wt% catalyst loading and methanol/WFO molar ratio of 12:1.

(70 °C reaction temperature, 3 wt% catalyst loading, and 2 h reaction time) were held constant. Figure 7 shows the effect of methanol-to-oil ratio (3:1–15:1) on the yield of FAME. The relationship between methanol/oil ratio and FAME yield was found to be linear to a certain level. The FAME yield increased significantly from 17.51% at ratio of 3:1 to 88.65% at ratio of 12:1. The increase in the yield of biodiesel at higher molar ratio of methanol to oil was due to shifting of the reaction equilibrium to the forward direction, in the sense that the transesterification reaction is reversible.⁷ Besides, at a higher molar ratio the oil mol-

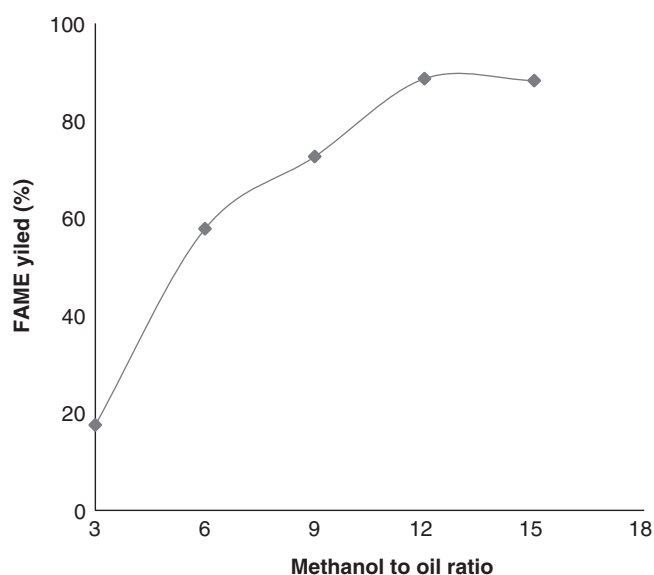


Figure 7. FAME yield at different methanol-to-oil ratios, at 70 °C reaction temperature, catalyst loading of 3 wt% and 2 h reaction time.

ecules interact strongly with excess methanol.²⁶ Too much methanol could hinder the separation of products, thus affecting the final yield of biodiesel. The methanol-to-oil ratio of 12:1 gave the highest FAME yield, so it was chosen as the optimum molar ratio and employed for further investigation in the present study.

Catalyst stability studies

The reusability of the AENiCo catalyst was examined for four reaction cycles under the optimum reaction conditions obtained earlier. As shown in Fig. 8, the FAME yields for first and last reaction cycles were 83.22% and 77.05% respectively. The reduction in activity of the recovered catalyst after each cycle was as a result of deactivation of active centers/basic sites.⁷ Moreover, the observed decline might be attributed to its structural deformation. This is corroborated by the FTIR spectrum of reused catalyst presented in Fig. 1(c). Nevertheless, the AENiCo catalyst showed good performance for conversion of WFO into FAME and also exhibited high stability for the same process with little reduction in catalytic activity during reaction.⁷

Comparison between synthesized catalyst and other catalysts

The FAME yield provided by the AENiCo catalyst was compared with other previously used heterogeneous catalysts for biodiesel production from different varieties of feedstock and at different optimum reaction conditions as can be seen in Table 3. It was revealed that the prepared AENiCo catalyst exhibited better performance as it provided a maximum FAME yield of 90.23% under optimum reaction conditions (70 °C reaction temperature (T), 2 h reaction time (t), 3 wt% catalyst loading (CL) and 12:1 methanol/WFO molar ratio (M/O)), and this indicates that it could be considered as an effective catalyst for biodiesel production from used vegetable oil, mostly when

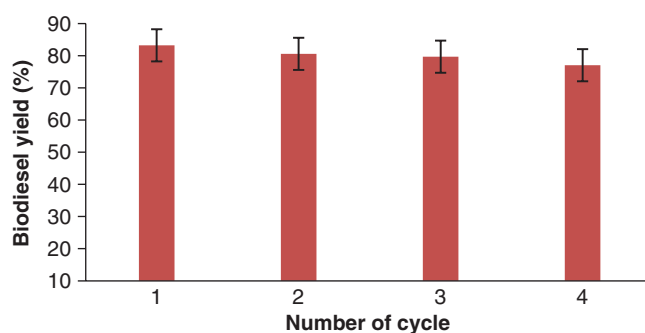


Figure 8. Effect of reusability of AENiCo catalyst on transesterification under optimum reaction conditions.


Table 3. Comparison of FAME yield at optimum condition using different oils and heterogeneous catalysts.

Catalyst	Feedstock	T (°C)	t (h)	M/O	CL (wt%)	Yield (%)	CR	Reference
Zeolite	WCO	70	6	5:1	0.65	46	—	Hassani et al. ³¹
BMK10	WCO	150	5	12:1	3.5	83.38	3	Olutoye et al. ²⁶
KSF clay	JSO	160	6	1:1	4.8	70	5	Calgaroto et al. ³²
K ₂ O/γ-Al ₂ O ₃	RSO	60	1	9:1	4	84.52	—	Hongbin et al. ³³
KOH/JS	WFO	60	2	16:1	—	86.7	5	Buasri et al. ³⁰
SO ₄ ²⁻ /ZrO ₂ /Al ₂ O ₃	Palm oil	127	3	8:1	6	83.3	—	Yee and Lee ²⁷
HPA	WCO	65	14	70:1	10	88.6	4	Talebian-Kiakalaieh et al. ³⁴
AENiCo	WFO	70	2	12:1	3	90.23	4	Current study

WCO, waste cooking oil; JSO, *Jatropha curcas* oil; RSO, rapeseed oil; HPA, heteropoly acid; JS, *Jatropha curcas* fruit shell; CR, catalyst reusability.

compared with KOH-supported *Jatropha curcas* fruit shell (KOH/JS) catalyst (86.7%)³⁰ and barium-modified montmorillonite K10 (BMK10) catalyst (83.38%).²⁶

Conclusion

In the present study, a new heterogeneous catalyst (AENiCo) was successfully developed and used for biodiesel synthesis via transesterification of WFO with methanol. The BET analysis revealed that calcination had a positive effect on prepared catalyst as its textural properties were improved. The XRD analysis showed that phase transformations occurred after calcination of raw catalyst and also identified CaO, SiO₂ and NiO, and CoO phases as active ingredients, support and promoters, respectively. Moreover, the result obtained showed that the synthesized catalyst is a nanomaterial with average crystallite size less than 30 nm. The SEM image of a calcined catalyst sample revealed various cavities on its surface. The maximum FAME yield of 90.23% was obtained under the optimum reaction conditions of 3 wt% catalyst loading, 12:1 methanol/WFO molar ratio, reaction time of 2 h, and 70 °C reaction temperature. The result of reusability study showed that the AENiCo catalyst has good activity and stable when subjected to four successive runs.

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