Original Research Paper

Qualitative role of heterogeneous catalysts in biodiesel production from *Jatropha curcas* oil

Fatai Alade Aderibigbe 1,*, Sherif Ishola Mustapha 1,2, Tunmise Latifat Adewoye 1, Ishaq Alhassan Mohammed 1, Adebola Bukola Gbadegesin 1, Faith Emmanuel Niyi 1, Opeyemi Idowu Olowu 1, Akinpelumi Gabriel Soretire 1, Harvis Bamidele Saka 1

1Department of Chemical Engineering, Faculty of Engineering and Technology, University of Ilorin, Ilorin, Nigeria.
2Department of Chemical Engineering, Durban University of Technology, South Africa.

**HIGHLIGHTS**

➢ Tri-metallic (Fe-Co-Ni) catalyst was synthesized through two different techniques; green synthesis and wet impregnation.
➢ Impacts of synthesis method and support material on final biodiesel product was scrutinized.
➢ Catalyst support material/synthesis method influenced the yield of the produced biodiesel.
➢ Catalyst support/synthesis method influenced the composition and properties of the resultant biodiesel.
➢ Green-synthesized Fe-Co-Ni-MgO catalyst led to highest biodiesel yield of 97.9%.

**GRAPHICAL ABSTRACT**

Biodiesel properties are in general attributed to the composition and properties of the oil feedstock used, overlooking the possible impacts of the catalyst preparation details. In light of that, the impacts of different catalyst preparation techniques alongside those of different support materials on the yield, composition, and fuel properties of biodiesels produced from the same oil feedstock were investigated. More specifically, tri-metallic (Fe-Co-Ni) catalyst was synthesized through two different techniques (green synthesis and wet impregnation) using MgO or ZnO as support material. The generated catalyst pairs, i.e., Fe-Co-Ni-MgO and Fe-Co-Ni-ZnO prepared by wet impregnation and Fe-Co-Ni-MgO and Fe-Co-Ni-ZnO prepared by green synthesis (using leaf extracts) were used in the transesterification process of *Jatropha curcas* oil. Detailed morphological properties, composition, thermal stability, crystalline nature, and functional groups characterization of the catalysts were also carried out. Using Box-Behnken Design response surface methodology, it was found that the green-synthesized Fe-Co-Ni-MgO catalyst resulted in the highest biodiesel yield of 97.9%. More importantly, the fatty acid methyl ester (FAME) profiles of the biodiesels produced using the four catalysts as well as their respective fuel properties were different in spite of using the same oil feedstock.

© 2020 BRTeam. All rights reserved.

**ARTICLE INFO**

**ABSTRACT**

Biodiesel properties are in general attributed to the composition and properties of the oil feedstock used, overlooking the possible impacts of the catalyst preparation details. In light of that, the impacts of different catalyst preparation techniques alongside those of different support materials on the yield, composition, and fuel properties of biodiesels produced from the same oil feedstock were investigated. More specifically, tri-metallic (Fe-Co-Ni) catalyst was synthesized through two different techniques (green synthesis and wet impregnation) using MgO or ZnO as support material. The generated catalyst pairs, i.e., Fe-Co-Ni-MgO and Fe-Co-Ni-ZnO prepared by wet impregnation and Fe-Co-Ni-MgO and Fe-Co-Ni-ZnO prepared by green synthesis (using leaf extracts) were used in the transesterification process of *Jatropha curcas* oil. Detailed morphological properties, composition, thermal stability, crystalline nature, and functional groups characterization of the catalysts were also carried out. Using Box-Behnken Design response surface methodology, it was found that the green-synthesized Fe-Co-Ni-MgO catalyst resulted in the highest biodiesel yield of 97.9%. More importantly, the fatty acid methyl ester (FAME) profiles of the biodiesels produced using the four catalysts as well as their respective fuel properties were different in spite of using the same oil feedstock.

© 2020 BRTeam. All rights reserved.

Please cite this article as: Aderibigbe F.A., Mustapha S.I., Adewoye T.L., Mohammed I.A., Gbadegesin A.B., Niyi F.E., Olowu O.I., Soretire A.G., Saka H.B. Qualitative role of heterogeneous catalysts in biodiesel production from *Jatropha curcas* oil. Biofuel Research Journal 26 (2020) 1159-1169. DOI: 10.18331/BRJ2020.7.2.4
1. Introduction

There have been several literature reports on the influences that biodiesel chemical structure such as its degree of unsaturation could have on engine performance, combustion, and emissions characteristics (Lapuerta et al., 2009; Benjumea et al., 2010; Sokoto et al., 2011; Altun, 2014; Yang et al., 2016; Hellier et al., 2017; Fohsany et al., 2019). For instance, the work of Benjumea et al. (2010) has shown that a higher degree of unsaturation of biodiesel fuels causes a more retarded start of combustion, while Gopinath et al. (2010) showed that biodiesels having more unsaturated fatty acids emit more oxides of nitrogen and exhibit lower thermal efficiency compared to biodiesels having more saturated acids.

Overall, biodiesel properties depend on the properties of the various individual fatty esters constituting the fuel which are in turn determined by the structure and features of their fatty acid and alcohol moieties (Refaat, 2009). Exactly for this reason, factors such as molecular structure and composition of the oil feedstocks and alcohols are principally considered to optimize the performance of the final biodiesel fuel (Refaat, 2009). Extensive studies on various oils have considered the use of different catalysts to obtain biodiesels of specific fatty acid methyl ester (FAME) profiles and qualities (Omotoso et al., 2011; Sharmula et al., 2016; Gupta and Agarwal, 2016; Cruz-Ortiz and Ríos-González, 2017). Commonly, these studies conclude that the oils used are responsible for the chemical structures and properties of the produced biodiesel. However, there seem to be some ambiguities as the possible involvement of catalyst type and synthesis route in determining FAME profiles is not generally monitored nor reported on in these studies. Consequently, from most of the previous investigations, it is difficult to infer the exact role of catalysts and their selectivity towards the formation of particular methyl ester molecules.

It should also be noted that the quantitative role of catalysts (i.e., impact on yield) has been the focus of many past studies and been properly addressed (Kaisan et al., 2016; Sharma et al., 2018). While the qualitative impacts of catalysts in influencing the type of methyl esters (saturated/unsaturated) were largely ignored possibly due to the fact that oil feedstock and its fatty acid profile is regarded as the most important parameter.

Currently, the state-of-art in rational design of catalysts involves the development of predictive models using different computational methods and their validation with experiments (synthesis, characterization, and performance tests). Machine learning algorithms are particularly useful as they can find complex correlations from large data sets. Catalysts exhibit complex structure–property–activity relationship, thus an efficient means of discovering improved catalysts is with the rational design of catalysts since physical insights are combined with data to construct predictive models, which lead to design principles for identifying promising candidate catalysts. Systematic experiments are then performed for validating the activity of a predicted catalyst, providing further physical insights while assisting with refining the predictive models and design principles (Tsai, 2017). Existing computational heterogeneous catalysis tools include predictive modeling, density functional theory (DFT), scaling correlations (adsorption scaling relations and transition state theory (TST)), microkinetic modeling, and volcano relations (descriptor-based models). A good review of the general optimization framework for rational design of catalysts can be found in Wang and Hu (2016) and Tsai (2017).

Yet, the future of heterogeneous catalysis is faced with our limited understanding of catalysts’ behavior under dynamic reaction conditions (Kalz et al., 2017). The structure of catalysts is very dynamic and in-depth studies of catalysts and catalytic reactors under such transient conditions have only started recently. For instance, the generation of corresponding pool of candidate complexes such as Cu/Ni/Ca/AlO (Kaisan et al., 2016; Sharma et al., 2018). While the qualitative impact of catalyst type and synthesis route in determining FAME profiles is not generally monitored nor reported on in these studies.

2. Materials and Methods

2.1. Materials

Analytical grade chemicals (Sigma-Aldrich) were used in this study. The J. curcas oil was used obtained from the University of Ilorin J. curcas plantation. Other materials used were Amaranthus spinosus leaves, Citrus aurantifolia leaves, phenolphthalein (indicator), distilled water, de-ionized water and paper foil.

2.2. Methodology

2.2.1. Determination of acid value and free fatty acid of Jatropha Curcas oil

To determine the acid value, 25 mL of ethanol was added to diethyl ether (25 mL) and the mixture was then mixed with 0.1M NaOH. A few drops of phenolphthalein solution serving as the indicator was also added. About 10 g of J. curcas oil was dissolved in the mixture followed by titration against 0.1M NaOH until a pink color was obtained. The acid values and the percentage of free fatty acid (FFA%) were measured according to standard methods (Gurdy et al., 2010), using Equations 1 and 2:

\[ \text{Acid value} = \frac{m_{\text{ROH}}}{\theta} \times C \times 56.11 \] \[ \text{(Eq. 1)} \]

\[ \text{Free fatty acid (\%)} = \frac{\left(V_a - V_b\right)}{W} \times C \times 28.246 \] \[ \text{(Eq. 2)} \]

where \(V_a\) is the consumed volume of titrate for biodiesel sample (mL); \(V_b\) denotes the consumed volume of titrate for the blank (mL); \(C\) stands for the exact concentration of standardized alcoholic potassium hydroxide solution (mole/L), and \(W\) is the mass of biodiesel sample used (g).

2.2.2. Preparation of catalysts

Tri-metallic catalyst of iron, cobalt, and nickel supported on magnesium oxide was prepared by the wet impregnation technique (Fe-Co-Ni/MgO) and a green synthesis route using a plant extract (Fe-Co-Ni-MgO). Moreover, tri-metallic catalyst of iron, cobalt, and nickel supported on zinc oxide was prepared by the wet impregnation technique (Fe-Co-Ni/ZnO) and the green synthesis route (Fe-Co-Ni-ZnO).

References (Mentioned in the text)
(a) Wet impregnation synthesis of Fe-Co-Ni/MgO and Fe-Co-Ni/ZnO catalysts

The Fe-Co-Ni/MgO or Fe-Co-Ni/ZnO catalyst was prepared by dissolving equimolar quantities of the nitrate salts of Fe, Co, and Ni (1:1:1) in deionized water followed by mixing with 16 g of MgO or ZnO. The mixture was allowed to stand for 60 min, and followed by drying at 120°C for 8 h. It was subsequently screened with a 150 μm sieve, and was calcined at 500°C for 3 h.

(b) Green synthesis of Fe-Co-Ni-MgO catalyst

First, unripe leaves of A. spinosus were collected and washed thoroughly with distilled water. The fresh leaves were chopped into small pieces and were subsequently reduced to a paste using a mortar and pestle. The fine paste was used in the preparation of the leaf extract. Distilled water (100 mL) was added to 20 g of the paste which was transferred carefully into a 250 mL Erlenmeyer flask and was magnetically stirred at 100°C for 30 min. The extract obtained was filtered and the clear extract was stored for use in the synthesis of colloidal MgO particles. The extract was characterized using Fourier-transform infrared spectroscopy (FTIR) spectroscopy to check for the various functional groups present.

An equimolar solution of iron, cobalt, and nickel nitrates (1:1:1) was prepared, stirred at 50°C for 30 min using a magnetic stirrer, dried at 120°C for about 2 h, and finally calcined at 500°C for 3 h. The sample was stored for future use to provide the Fe, Co, and Ni active metals of the catalyst.

A 1 M solution of Mg(NO₃)₂·6H₂O was prepared as the source for magnesium oxide nanoparticles, stirred at 50°C for about 10 min using a magnetic stirrer to allow for the proper mixing of the solution. Then, 50 mL of the prepared leaf extract solution was added to the solution while continuously stirred magnetically. The color of the mixture was found to be greenish at first but after being stirred continuously for about 20 min, a marked reduction in the intensity of the color was noticed. The UV-Vis spectrum of the mixture was then recorded to confirm the formation of the MgO nanoparticles (Fig. S1).

Finally, the Fe-Ni-Co-MgO catalyst was prepared by adding 3 g of the calcined sample to the mixture containing the MgO nanoparticles and stirred magnetically at 50°C for about 20 min to increase the homogeneity of the sample. This mixture was then dried at 120°C for 2 h and was subsequently calcined at 500°C for 3 h. The calcined material was recovered and stored for use in the biodiesel production process.

(c) Green synthesis of Fe-Co-Ni-ZnO catalyst

The Fe-Co-Ni-ZnO catalyst was prepared by hybridization in which the Fe, Ni, and Co were obtained by direct dissolution and mixing of their nitrate salts in deionized water, while ZnO was derived from the reduction of nitrate salt. The sources of iron, cobalt, and nickel metals in the catalyst were the mixed nitrates of iron, cobalt, and nickel (1:1:1) in deionized water. The mixture was dried for 3 h and calcined at 500°C for 3 h resulting in a fine black powder.

The Fe-Ni-Co-ZnO catalyst was finally prepared by mixing the calcined material (fine black powder) with the deep yellow colored paste obtained from zinc nitrate, and was stirred at 50°C for 30 min. The mixture was then calcined at 500°C for 2 h.

2.2.3. Characterization of catalysts

The four synthesized catalysts: (a) Fe-Co-Ni/MgO, (b) Fe-Co-Ni/ZnO, (c) Fe-Co-Ni/ZnO, and (d) Fe-Co-Ni-ZnO were characterized for their crystalline nature, morphological properties, elemental compositions, functional groups, and thermal stability using X-ray powder diffraction (XRD), scanning electron microscope with an energy dispersive X-ray spectrometer (SEM-EDS), FTIR, and thermal gravimetric analysis (TGA), respectively. The XRD analysis was performed on a Bruker AXS D8 Advance (USA) with Cu-Kα radiation. A portion of the crystals were sprinkled on a de-greased glass slide, and diffractionograms were recorded between diffraction angles of 15° and 80°. The SEM morphology results of the synthesized catalysts were acquired using a high-resolution Zeiss Auriga (USA). A crystal sample (1 mg) was sprinkled on a carbon adhesive tape and sputter coated with Au-Pd using a Quorum T150T for 5 min prior to the analysis. The microscope was operated with an electron high tension at 5 kV for imaging. In the FTIR analysis, infrared light in the range 500–4000 cm⁻¹ was used to scan the sample. The sample was prepared using a standard potassium bromide (KBr) and was then placed on a crystal in the Nicolet iS5 spectrometer. In the TGA procedure, small quantity of the sample was placed on the sample pan and the TGA-DSC analysis was performed using a TGA SDT Q600 instrument (TA Instruments). The programmed heating range was from room temperature (30°C) to 800°C at the rate of 10°C·min⁻¹ under nitrogen atmosphere.

2.2.4. Optimization of biodiesel production

The catalysts (Fe-Co-Ni/MgO, Fe-Co-Ni/ZnO, Fe-Co-Ni-MgO, and Fe-Co-Ni-ZnO) as prepared were employed in producing biodiesel using J. curcas oil and methanol. From several experimental runs conducted (Table 1), optimal conditions for biodiesel yield were identified for each of the catalysts used. Optimization of biodiesel production was performed using Box-Behnken Design (BBD), a response surface methodology by varying the reaction temperature, reaction time, methanol to oil molar ratio, and catalyst concentration.

Table 1. Design of experiment for biodiesel production.

<table>
<thead>
<tr>
<th>Factors</th>
<th>Temperature (°C)</th>
<th>MeOH/Oil molar ratio (w/w)</th>
<th>Catalyst concentration (% w/w of oil)</th>
<th>Reaction time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Level 1</td>
<td>50</td>
<td>10.1</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>Level 2</td>
<td>55</td>
<td>15.1</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>Level 3</td>
<td>60</td>
<td>20.1</td>
<td>15</td>
<td>3</td>
</tr>
</tbody>
</table>

Experiments were carried out in 20 mL test tubes placed in a water bath shaker with a constant temperature. In a typical run, 1 g of J. curcas oil was measured into the test tube. Then, 2 mL of hexane was added to the oil to serve as a co-solvent and enhance the miscibility of oil with methanol and to speed up the rate of transesterification. Known amounts of catalyst (5%, 10%, or 15% w/w of oil) and methanol (methanol to oil ratio; 10:1, 15:1, or 20:1) were added to the mixture and stirred vigorously using a constant agitation speed, while maintained at a certain temperature (50, 55, or 60°C) and for a certain reaction duration (1, 2, or 3 h). Upon the completion of reaction time, 5 mL of n-hexane and 5 mL of distilled water were added to the products (biodiesel and glycerol), giving rise to two distinct phases which were separated from each other using a separating funnel. The catalyst and glycerol were dispersed in the water phase (the lower phase) while the biodiesel was dispersed in the n-hexane phase (the upper phase). Biodiesel was recovered from the mixture with n-hexane by heating until n-hexane was evaporated. The catalyst was then regenerated by filtering the products in the water phase, followed by drying. The yield of biodiesel was calculated using Equation 3:

\[ \text{Yield(%) } = \frac{\text{Weight of biodiesel}}{\text{Weight of oil}} \times 100 \]  

(Eq. 3)
2.2.5. Properties of biodiesel

The quality of the produced biodiesel was investigated by determining its physicochemical properties such as flash point, density, and viscosity. It was also characterized by using Gas Chromatography-Mass Spectroscopy (GC-MS) to investigate functional groups present, as well as the geometry and spatial isomerism of the produced biodiesel. An Agilent 7890A gas chromatograph (USA) hypenated to a 5975C mass spectrophotometer with triple axis detector equipped with an auto-injector (10 µL syringe) was used. Helium was used as carrier gas. All chromatographic separation was performed on a capillary column having the following specifications: length: 30 m, internal diameter 0.2 µm, thickness; 250 µm, and treated with phenyl methyl silox. Other GC-MS conditions included ion-source temperature: 250 °C, interface temperature: 300 °C, pressure: 0.1171 MPa, out time: 1.8 mm, 1µl injector in split mode with the split ratio of 1:50 and with an injection temperature of 300 °C. The column temperature was set at 35 °C for 5 min and was elevated to 150 °C at the rate of 4 °C/min, the temperature was the raised again to 250 °C at the rate of 20 °C/min and held for 5 min. The total elution was 47.5 min. MS solution software provided by the manufacturer was used to control the system and to acquire data. Identification of the compounds was carried out by comparing the mass spectra obtained with those of the standard mass spectra from the NIST library (NIST1).

3. Results and Discussion

3.1. Leaf extracts and formation of colloidal nanoparticles

3.1.1. Amaranthus spinosus extract and colloidal MgO

The FTIR spectrum of A. spinosus leaf extract is presented in Figure S2, showing characteristic bands for several functional groups. The spectrum analysis confirmed the presence of amaranthine and phenolic compounds, functional groups in the leaf extract. The absorption band at 3445.91 cm⁻¹ implies the presence of strong OH as well as NH stretching of phenol and amine group. The presence of carboxyl functional group around 1631.66 cm⁻¹, C–O group around 1159.89 cm⁻¹, and >C=O at about 1064.91 cm⁻¹ are also observed. The result obtained agrees in part with the previous works by Das et al. (2012) and Muthukumar and Matheswaran (2015) who also observed hydroxyl, aromatic amines, aliphatic amines, carbonyl, –C=H, and C=C (benzene) functional groups.

Being effective reducing and capping agents, the presence of these groups in the leaf extract assisted with the formation of nanoparticles from the precursor solution. Presented in the Figure S1 is the UV-Vis spectrum of the colloidal MgO nanoparticles that were formed by using the green synthesis route.

The solution containing the MgO nanoparticles was analyzed using a UV-Vis spectrophotometer to confirm the formation of the particles. The resulting absorbance peak at 330 nm confirmed the successful formation of the MgO nanoparticles.

3.1.2. Extract of Citrus aurantifolia and colloidal ZnO

Figure S3 shows the FTIR spectrum of C. aurantifolia leaf extract. The band at 570.98 cm⁻¹ is associated to the CH₃ group deformation. The C–O of aliphatic acid groups are attributed to the peak from 1216.89 cm⁻¹. The medium strong band at 1641.16 cm⁻¹ is assigned to the deformation C=OH of carboxyl. The intense absorption peak around 3493.40 cm⁻¹ indicates the presence of free and intermolecular bonded hydroxyl groups. The OH stretching vibrations occur within a broad range of frequencies indicating the presence of “free” hydroxyl groups and bonded OH groups of carboxylic acids (Andronie et al., 2017). The presence of these compounds suggests that the leaf extract is a suitable reducing agent that could effectively precipitate out the zinc oxide from the zinc nitrate precursor.

3.2. Characterization of catalysts

3.2.1. Crystalline nature of the catalysts

The XRD patterns of the catalysts prepared by the green synthesis and wet impregnation methods were acquired and are presented in Figures 1a-d. All catalyst samples were shown to be crystalline, forming complex metal oxides of the metals involved. The identified peaks of MgO and ZnO shown in Figures 1b and 1d reveal that the nitrate salts of magnesium and zinc which were used as starting materials during the green synthesis method were adversely reduced to their respective oxides by the leaf extracts of A. spinosus and C. aurantifolia, respectively. In Figure 1a, the MgO is seen to exhibit four peaks at 20 angles of 37.0°, 42.8°, 62.3°, and 78.5° mainly due to MgO – periclase (JCPDS card No.00-045-0946).

In the XRD pattern of green synthesized Fe-Co-Ni-MgO shown in Figure 1b, the peaks at 35.5°, 44.0°, 43.0°, 62.3°, and 78.6° represent majorly MgFe₂O₄ phase – magnesioferrite (JCPDS card No.00-036-0398). Some other peaks representing MgO – periclase (JCPDS card No. 00-045-0946) were also observed.

The XRD analysis of the wet impregnation-prepared Fe-Co-Ni/ZnO catalyst is presented in Figure 1c. The major peaks at 31.7°, 34.5°, 36.2°, 47.5°, 56.8°, 62.9°, 66.3°, 67.9°, 69.1°, 72.5°, and 76.9° indicate the presence of ZnO – zincite (JCPDS card No. 00-036-1451). At 43.3°, a small peak confirms the presence of NiO (JCPDS card No.00-047-1049). The sharpest peak occurring at 36.2° denotes the ZnO present in the nanocatalyst which is highly crystalline. In Figure 1d, the XRD pattern of the green synthesized Fe-Co-Ni-ZnO is presented. In addition to the highly crystalline nature, very similar result was obtained compared to the XRD pattern of Fe-Co-Ni/ZnO catalyst prepared by wet impregnation method (Fig. 1c).

Moreover, major peaks at 20 angles of 31.8, 34.4, 36.3, 47.5, 56.6, 62.9, 67.9, and 72.5° were identified, showing the presence of ZnO – zincite (JCPDS card No. 00-036-1451). The peak at 34.4° indicates the presence of NiO. The peaks corresponding to individual metallic particles (Fe, Co, or Ni) were not detected possibly due to their low concentrations in the mixture.

3.2.2. Morphological characteristics of the catalysts

Despite similar starting materials used as precursors in their preparation, the four catalysts exhibited distinct morphologies due to their different methods of synthesis.

(a) The SEM analysis of Fe-Co-Ni/MgO catalyst

High resolution SEM images of the Fe-Co-Ni/MgO catalyst are shown in Figures 2a-d. The SEM was used to investigate the morphological characteristics of the catalyst and the extent of deposition of the active metals on the support. As shown in Figure 2a, the SEM result at 100 nm scale depicts clustered solid catalyst material that is crystalline, in which particles are near-spherical in geometry. Agglomerates seen in the SEM image could have formed from the drying process during sample preparation. The material is observed to exhibit micro-porous structure (Figs. 2c and d); lower magnification images at 1µm and 10µm. Homogeneous appearance of the material’s surface is indicative that Fe, Co and Ni nanoparticles were properly dispersed on the MgO support material.

(b) The SEM analysis of Fe-Co-Ni/MgO catalyst

Figures 3a-d present the SEM results of the green-synthesized Fe-Co-Ni-MgO catalyst, showing a regular structure which is well defined with smaller nanosized particles dispersed over its surface (Figs. 3a and b). The regular structure is presumably that of MgO caused by combined chemical effect and thermal treatment. While Figures 3a and 3b show clearly the deposition of smaller crystals of Fe, Co, and Ni onto the larger MgO particles. These images (Figs. 3a and b) also suggest that the larger tetrahedron particles be in the order of microns. An approximate estimation of the size of the nanoparticles dispersed on the surfaces is in the sub-100 nm range. In Figure 3d which depicts the catalyst material in clusters, the catalyst is shown to be porous and should therefore have abundant active reaction sites.

(c) The SEM analysis of Fe-Co-Ni/ZnO catalyst

Presented in Figures 4a-d are the SEM images of the Fe-Co-Ni/ZnO catalyst synthesized by wet impregnation. The small nanoparticles of Fe,
Co, and Ni, and the ZnO support material can be observed. The SEM images shown in Figures 4a and 4b represent three dimensional particles of near-spherical shape that are highly crystalline. The high crystallinity is in agreement with the XRD result presented earlier in Figure 1. The deposition of iron, cobalt, and nickel nanoparticles on the zinc oxide support is clearly seen as represented by particles in the sub-20 nm size range. In Figures 4c and 4d, small micro-pores could be identified. It was also revealed that there was an even dispersion/distribution of the metals onto the ZnO support material.

(d) The SEM analysis of Fe-Co-Ni-ZnO catalyst

In the catalysts prepared by the wet impregnation method, phase distinction between the deposited active components and the support...
material could be observed (Figs. 2 and 4). In contrast, the catalysts prepared by the green synthesis method appeared bespoke (Figs. 3 and 5). The Fe-Co-Ni-ZnO catalyst synthesized by the green synthesis route, as shown in Figures 5a-d, exhibited regular near-spherical structures with a narrow particle size distribution (Figs. 5a and 5b), which are characteristics of bespoke green nanomaterials. All the nanoparticles were within the sub-10 nm particle size range, with some agglomerated to form bigger particle clusters (Fig. 5b). Similar to the morphology difference observed between the Fe-Co-Ni/MgO and Fe-Co-Ni-MgO catalysts prepared by the wet impregnation and green synthesis methods, the Fe-Co-Ni-ZnO catalyst obtained through the green synthesis route also showed a morphology that was different from its wet impregnation counterpart. Moreover, the solid catalyst material was highly crystalline (Figs. 5c and 5d), which was also evident from the related XRD results (Fig. 1d). Micropores could also be identified in the catalyst composite.

In the EDS qualitative and quantitative elemental analyses of all the four catalysts, metallic Fe, Co, Ni, Mg, and Zn were found. Based on the EDS results, the presence of the Fe, Co, Ni, Mg, and Zn metals around the line energy position of oxygen indicate the formation of complex oxides of these metals with oxygen. The EDS elemental analysis also showed that carbon is present in all the samples because carbon was used as the coating material during the EDS analysis. Carbon is the recommended coating material as it does not interfere with the characteristics X-ray peaks from elements in samples. The EDS results are presented in Figure S4.

In the qualitative EDS result of the Fe-Co-Ni/MgO catalyst presented in Figure S4a, the elemental composition in the catalyst was found as (in atomic %): C (12.71), O(46.64), Mg(35.45), Fe(1.55), Co(1.05), and Ni (2.61).

The EDS of the green synthesized Fe-Co-Ni-MgO catalyst (Fig. S4b) presented atomic % elemental composition of C(17.74), O(36.54), Mg(33.11), Cl(4.56), Fe(0.24), Co(3.15), Ni(0.49), and Na(6.17). Obviously, Mg, O, Fe, Co, and Ni were introduced by the precursor salts, while Cl and K were from the leaf extract. In this case, carbon could be from the plant extract or coating material used during sample preparation for the EDS analysis.

The Fe-Co-Ni/ZnO catalyst prepared by wet impregnation presented EDS elemental composition of C(29.22), O(28.17), Na(6.53), Fe(3.62), Co(1.4), Ni(2.85), and Zn(28.4) (in atomic %). Again, carbon was introduced from the coating material during the EDS sample preparation stage, and Na was an impurity. The presence of oxygen is indicative of formation of complex oxides of the Fe, Co, Ni, and Zn metals. These components are were found in the qualitative EDS result shown in Figure S4c.

In Figure S4d, the qualitative EDS result of the green-synthesized Fe-Co-Ni/ZnO catalyst is presented. Its atomic % elemental composition was found to be C(19.65), O(45.76), Cl(0.46), Fe(6.27), Co(8.58), Ni(12.41), and Zn(16.64). The composition of Fe-Co-Ni-ZnO significantly differed from that of Fe-Co-Ni/ZnO, thus implying potentially different catalytic activity. Based on the EDS results, oxides of Fe, Co, Ni, and Zn might have been formed. Carbon could be from the leaf extract or EDS coating material as mentioned earlier. The metals Fe, Co, and Ni are from the salt precursor while K might have been introduced by the leaf extract.

3.2.4. Thermal stability

The thermal behavior of the prepared catalysts was investigated using the TGA/DSC analyses over a temperature range of up to 900°C at the rate of 10°C min⁻¹ under nitrogen atmosphere. Accordingly, the catalysts prepared by the wet impregnation technique were found to be more thermally stable than their equivalent ones prepared by the green synthesis method. Figure 6a reveals that the Fe-Co-Ni/MgO catalyst was thermally stable, losing only about 6 wt% of its original weight by rising the temperature up to 900°C. A two-step thermal degradation and weight loss was first observed; at 100–200°C, and 220–320°C. The first weight loss could represent the loss of absorbed moisture while the second might be ascribed to the elimination of the crystal water. But a weight gain regime was also observed which occurred at above 550°C. The initiation of a third weight loss regime above 300°C could be attributed to the decomposition of magnesium oxide while the subsequent weight gain could be indicative of phase transformation, involving the formation of new compound(s) – Mg(OH)₂.

In the TGA/DSC curves of Fe-Co-Ni/MgO (Fig. 6b), there are several regimes of weight loss which is typical of a mixture of many components exhibiting their individual thermal degradation. As one would expect, the leaf extract contained several phytochemicals and must have presumably introduced these to the catalyst material, possibly by forming complexes with the Fe, Co, Ni, and Mg metal cations or their oxides. Throughout the heating up to 800°C, this catalyst lost about 12 wt% of its initial weight. Of these, about 7 wt% was lost below 220°C which could be attributed to several volatile compounds from the green source. Apart from the weight loss prior to 220°C, a weight loss was observed at 300–550°C, and another at 720–820°C. Some decomposition also occurred in this material thereby changing its thermal degradation behavior; the latter two regimes could be attributed to the degradation of individual components which could be complex compounds that had formed. Agglomeration and grain growth forming large crystalline structures with sizes in microns was also observed in the high resolution TEM images of this sample (Fig. 3).
Overall, given their total weight loss percentages at above 800°C, Fe-Co-Ni/MgO could be regarded as more thermally stable compared with Fe-Co-Ni-MgO.

Similarly, the spectra of Fe-Co-Ni/ZnO and Fe-Co-Ni-ZnO presented in Figures S7 and S8 were observed to share bands, stretches, and vibrations at the same wavelengths. In Figure S7, the absorption band at 3474.41 cm⁻¹ represents the presence of –OH hydroxyl groups. The 1615.83 cm⁻¹ absorption band reveals the presence of C=O functional group stretching deformation and that at 992.08 cm⁻¹ suggests the presence of C-O-stretching deformation. The presence of C–H functional group deforming vibration is represented by the peaks at 1492.35 cm⁻¹ and 881.27 cm⁻¹, while the presence of C–N stretching vibration is indicated by the band recorded at 1356.20 cm⁻¹.

The FTIR spectrum of the green-synthesized Fe-Co-Ni-ZnO shown in Figure S8 reveals the presence of aromatics and alkanes/alkyl groups. The absorption bands at 1587.34 cm⁻¹ and 1558.84 cm⁻¹ indicate the presence of C=C functional groups. The absorption bands at 1482.85 cm⁻¹, 1448.02 cm⁻¹, and 1381.53 cm⁻¹ represent the presence of C–H deforming vibration. Generally, despite the observed similarities in their functional groups, the participation of each pair of the four catalysts in the transesterification reaction may not present similar activities because of the influences of the other structural factors of the catalytic materials.

3.3. Optimization of biodiesel production

The performance of the four synthesized catalysts in the transesterification reaction was investigated by varying reaction parameters in a Box–Behnken Design (BBD) of experiment as tabulated in Table 1. Each experiment had 27 experimental runs and the optimum value was identified in each case. The summary of the BBD experimental results is presented in Table 2.

The ANOVA for these experiments was used to generate regression models which are represented in Equations 4-7. The regression models show how the four reaction parameters; i.e., MeOH:oil ratio, temperature, time, and catalyst concentration, influenced biodiesel yield when each catalyst was employed.

\[
Y_{Fe-Co-Ni/MgO} = -2268.82 + 42.84A + 72.20B + 602.8C - 6.92D - 0.348AB - 1.855AC - 0.307AD + 0.245BD - 0.87CD - 0.545A^2 - 0.623B^2 - 0.85C^2
\]  
\[\text{(Eq. 4)}\]

\[
Y_{Fe-Co-Ni/ZnO} = -2894.69 + 18.25A + 100.10B + 26.96C - 6.90D - 0.21AB - 1.08AC - 0.413AD + 0.28BD - 1.585CD - 0.88B^2
\]  
\[\text{(Eq. 5)}\]

\[
Y_{Fe-Co-Ni/ZnO} = -1622.69 + 17.44A + 61.02B - 75.63C - 4.16D - 0.39AB + 1.45AC + 0.478AD - 0.98BC + 1.455CD - 0.13A^2 - 0.52B^2 + 0.95C^2 - 0.26D^2
\]  
\[\text{(Eq. 6)}\]
where A is MeOH:oil molar ratio, B stands for temperature (°C), C is time (h), and D denotes catalyst concentration. The model equations were reliable, showing significant (<0.05) model p-values of 0.0456, 0.0094, 0.0367, and 0.0390 in Equations 4, 5, 6, and 7, respectively. The highest biodiesel yield of 97.9% was obtained with the green-synthesized Fe-Co-Ni-MgO catalyst. It was also observed that both catalysts based on MgO support exhibited relatively higher catalytic performance compared to their ZnO-based counterparts.

3.4. Physicochemical properties and FAME profiles

The FAME profiles of the J. curcas oil-based biodiesel products and their physicochemical properties were investigated in order to establish the effect of catalyst type on the quality/composition of the produced biodiesel. A summary of the FAME profiles of biodiesel products produced by various catalysts are presented in Table 3. As shown in Table 3, the biodiesel samples showed a total saturated fatty acid of 2.94–21.73% and total unsaturated fatty acid of 78.27–97.06%. The high degree of unsaturation is typical feature of Jatropha biodiesel produced using the four catalysts are presented in Figures S9-12.

The Jatropha biodiesel obtained using the green-synthesized Fe-Co-Ni-MgO contained unsaturated acid of oleic acid (78.27 wt%), and saturated acids of n-hexadecanoic acid (12.14 wt%), octadecanoic acid (6.87 wt%), cyclohexanecarboxylic acid, undecyl ester (2.72 wt%). The total percentage composition of FAMEs was greater than the minimum FAME requirement of 96.5% specified by the ASTM (Fig. 7). Overall, the product produced by Fe-Co-Ni-MgO catalyst consisted of 78.27% unsaturated and 21.73% saturated fatty acids (Fig. 8). Hence, the biodiesel obtained using this green-synthesized catalyst resulted in the highest yield and the lowest degree of unsaturation in spite of the fact that high degree of unsaturation is a general characteristic of Jatropha biodiesels (Mofijur et al., 2017).

The Jatropha biodiesel produced from the wet impregnation-prepared Fe-Co-Ni/ZnO catalyst consisted of 88.9% unsaturated and 11.1% saturated fatty acids (Fig. 8). This indicates that the catalyst produced a low-grade biodiesel, since the higher the percentage of unsaturated fatty acids in biodiesel, the lower its oxidative and thermal stability would be. In another words, this denotes that the resultant biodiesel would deteriorate faster in high-temperature environments. The biodiesel produced by green-synthesized Fe-Co-Ni/ZnO catalyst contained 8.74 wt% n-hexadecanoic acid, 81.4 wt% oleic acid, 7.71 wt% octadecanoic acid, and 2.51 wt%

Table 3.

Table FAME compositions of the biodiesel products by various catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>RT*</th>
<th>Methyl ester</th>
<th>Molecular formula</th>
<th>Composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-Co-Ni/MgO (Wet Impregnation)</td>
<td>38.737</td>
<td>Oleic acid, 9-Octadecenoic acid, cis-Vaccenic acid</td>
<td>C_{18}H_{34}O_2</td>
<td>97.06</td>
</tr>
<tr>
<td></td>
<td>43.959</td>
<td>Cylohexanecarboxylic acid, pentadecyl ester; Docosanoic acid,4,4-dimethyl-ester; Adipic acid, butyl 2-pentylester</td>
<td>C_{18}H_{34}O_2</td>
<td>2.94</td>
</tr>
<tr>
<td>Fe-Co-Ni-MgO (Green Synthesis)</td>
<td>35.555</td>
<td>n-Hexadecanoic acid</td>
<td>C_{18}H_{34}O_2</td>
<td>12.14</td>
</tr>
<tr>
<td></td>
<td>39.037</td>
<td>AN(^{4}) palmitic acid</td>
<td>C_{18}H_{34}O_2</td>
<td>78.27</td>
</tr>
<tr>
<td></td>
<td>39.276</td>
<td>9-Octadecanoic acid</td>
<td>C_{18}H_{34}O_2</td>
<td>6.87</td>
</tr>
<tr>
<td></td>
<td>43.971</td>
<td>Cylohexanecarboxylic acid, undecyl ester; Cylohexanecarboxylic acid, heptyl ester; Adipic acid, butyl 2-pentylester</td>
<td>C_{18}H_{34}O_2</td>
<td>2.72</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>20.872</td>
<td>Cyclohexasiloxane, dodecamethyl-cyclohexasiloxane, dodecamethyl-5-[4-(Dimethylamino) benzylideneamino]-2-phenyl-2H-benzotriazole</td>
<td>C_{24}H_{34}N_2S</td>
<td>3.32</td>
</tr>
<tr>
<td></td>
<td>25.221</td>
<td>N-benzyl-N-ethyl-p-isopropylbenzamide, pentasiloxane, dodecamethyl-4H-1,2,4-Triazole-3-thiol, 4-allyl-5-(1-naphthylmethyl)-</td>
<td>C_{24}H_{34}NO</td>
<td>8.25</td>
</tr>
<tr>
<td></td>
<td>29.115</td>
<td>Silane,[4-[1,2-bis[(trimethylsilyloxy)ethyl]-1,2-phenylene[</td>
<td>bis[oxyl][bisis[tris[trimethyl-silane,[4-[1,2-bis[(trimethylsilyloxy)ethyl]-1,2-phenylene]bis[oxyl][bisis[tris[</td>
<td>C_{36}H_{80}S</td>
</tr>
<tr>
<td></td>
<td>36.979</td>
<td>13-Hexylcyclooctadec-10-en-2-one</td>
<td>C_{36}H_{64}O</td>
<td>3.01</td>
</tr>
<tr>
<td></td>
<td>37.697</td>
<td>9-octadecenoic acid (Z)-, methyl ester</td>
<td>C_{18}H_{34}O_2</td>
<td>3.06</td>
</tr>
<tr>
<td></td>
<td>38.648</td>
<td>cis-13-octadecenoic acid, cis-vaccenic acid</td>
<td>C_{18}H_{34}O_2</td>
<td>77.59</td>
</tr>
<tr>
<td>Fe-Co-Ni/ZnO (Wet Impregnation)</td>
<td>35.489</td>
<td>n-Hexadecanoic acid</td>
<td>C_{18}H_{34}O_2</td>
<td>8.74</td>
</tr>
<tr>
<td></td>
<td>38.982</td>
<td>Oleic acid</td>
<td>C_{18}H_{34}O_2</td>
<td>81.04</td>
</tr>
<tr>
<td></td>
<td>39.221</td>
<td>9-Octadecanoic acid</td>
<td>C_{18}H_{34}O_2</td>
<td>7.71</td>
</tr>
<tr>
<td></td>
<td>43.960</td>
<td>Cylohexanecarboxylic acid, undecyl ester</td>
<td>C_{18}H_{34}O_2</td>
<td>2.51</td>
</tr>
</tbody>
</table>

RT: Retention time; Sat.: Saturated; Unsat.: Unsaturated; AN: Another name
cyclohexanecarboxylic acid undecyl ester (Fig. 8). The maximum FAME conversion achieved using this catalyst stood at 81.04% (Fig. 7) with oleic acid as the most abundant FAME. Moreover, the FAME profile consisted of 81.04% unsaturated and 18.96% saturated fatty acids. Overall, apart from the major influence of Jatropha oil used as feedstock, the catalysts prepared either by the wet impregnation or green synthesis methods were shown to affect the FAME compositions of the final biodiesel products. It is however interesting to note that the combined influence of MgO as support material and the green synthesis route as catalyst preparation technique (i.e., using green-synthesized Fe-Co-Ni-MgO catalyst) resulted in the most favorable outcomes both quantitatively and qualitatively in comparison with the application of the three catalysts. A comparison of the highest FAME yield obtained in the current study (i.e., for Fe-Co-Ni-MgO) and those reported in the most recent literature is presented in Table 4.

Table 4. Comparison of the FAME yield of Fe-Co-Ni-MgO with the other solid catalysts used for biodiesel production reported in the literature.

<table>
<thead>
<tr>
<th>S/N</th>
<th>Catalyst</th>
<th>Synthesis method</th>
<th>FAME Yield (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Magnetic core-shell SO₄/Mg-Al-Fe₃O₄</td>
<td>Stepwise co-precipitation, encapsulation, and surface functionalization</td>
<td>98.5</td>
<td>Gardy et al. (2019)</td>
</tr>
<tr>
<td>2</td>
<td>Mg/Al/Zn-based hydrotalcite/SBA-15</td>
<td>Rational design using a versatile in situ method including synthesis of macroporous hydrotalcite-derived oxides comprising ordered silica architectures</td>
<td>90</td>
<td>Prabu et al. (2019)</td>
</tr>
<tr>
<td>3</td>
<td>Fe-Co-Ni-MgO</td>
<td>Green synthesis</td>
<td>97.9</td>
<td>Present Study</td>
</tr>
</tbody>
</table>

Table 5. Physicochemical properties of biodiesel produced by the four different catalysts, i.e., (a) Fe-Co-Ni-MgO, (b) Fe-Co-Ni-MgO, (c) Fe-Co-Ni/ZnO, and (d) Fe-Co-Ni-ZnO.

<table>
<thead>
<tr>
<th>Fuel properties</th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
<th>(d)</th>
<th>ASTM standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density at 15 °C (g/cm³)</td>
<td>0.882</td>
<td>0.8673</td>
<td>0.886</td>
<td>0.866</td>
<td>0.860 − 0.900</td>
</tr>
<tr>
<td>Kinematic viscosity at 40 °C (mm²/s)</td>
<td>-</td>
<td>2.31</td>
<td>-</td>
<td>-</td>
<td>1.9 − 6.0</td>
</tr>
<tr>
<td>Flash point (°C)</td>
<td>198</td>
<td>142</td>
<td>209</td>
<td>219</td>
<td>≥130</td>
</tr>
<tr>
<td>Cloud point (°C)</td>
<td>-8</td>
<td>2</td>
<td>10</td>
<td>-2</td>
<td>-3 − 12</td>
</tr>
<tr>
<td>Pour point (°C)</td>
<td>2</td>
<td>-10</td>
<td>-4</td>
<td>-15</td>
<td>-15 − 10</td>
</tr>
<tr>
<td>Fire Point (°C)</td>
<td>193</td>
<td>148</td>
<td>223</td>
<td>230</td>
<td>≥130</td>
</tr>
<tr>
<td>Acid value (mg KOH/g)</td>
<td>0.4039</td>
<td>0.59466</td>
<td>0.5553</td>
<td>0.4544</td>
<td>≤0.80</td>
</tr>
<tr>
<td>FFA concentration (wt%)</td>
<td>0.5428</td>
<td>0.5069</td>
<td>0.4148</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

1 ASTM D1298, 2 ASTM D445, 3 ASTM D92, 4 ASTM D2500, 5 ASTM D97, 6 ASTM D92, 7 ASTM D664

route as catalyst preparation technique (i.e., using green-synthesized Fe-Co-Ni-MgO catalyst) resulted in the most favorable outcomes both quantitatively and qualitatively in comparison with the application of the three catalysts. A comparison of the highest FAME yield obtained in the current study (i.e., for Fe-Co-Ni-MgO) and those reported in the most recent literature is presented in Table 4.

Physicochemical properties of the biodiesel produced by the catalysts vs. the ASTM standard values are tabulated in Table 5 and Figure 9, confirming the acceptable quality of the products while also revealing considerable differences among them depending on the catalyst employed.
4. Conclusions

The effects of green synthesis (using leaf extracts) and wet impregnation methods for the preparation of catalysts along with different support materials, on yield, composition, and properties of Jatropha biodiesel were investigated. As for the catalyst properties, the green-synthesized heterogeneous tri-metallic catalysts appeared more bespoke in morphology, but exhibited lower thermal stability. Irrespective of the method of synthesis, the crystalline phases revealed by the XRD and the FTIR spectra of the catalysts were dependent on the catalyst support material (MgO or ZnO). Moreover, the findings obtained revealed that catalyst type could determine FAME profile of the biodiesel produced from the same oil feedstock. More specifically, the support material used and the method employed for catalyst synthesis influenced the type of methyl esters found in the final biodiesel product. Higher yield was obtained with magnesium oxide as support material than with zinc oxide, and higher yields were obtained with green-synthesized catalysts.
compared with their counterparts synthesized through wet impregnation.

Acknowledgements

The authors wish to acknowledge the Department of Chemical Engineering, University of Ilorin, Nigeria, for permitting the use of laboratory facilities especially the GC-MS equipment.

References


Supplementary Data

Fig. S1. FTIR spectrum of *Amaranthus spinosus* leaf extract.

Fig. S2. UV-Vis spectrum of colloidal MgO nanoparticles.
Fig. S3. FTIR spectrum of Citrus aurantifolia leaf extract.
Fig. S4. The EDS analysis of different catalysts: (a) Fe-Co-Ni/MgO, (b) Fe-Co-Ni-MgO, (c) Fe-Co-Ni/ZnO, and (d) Fe-Co-Ni-ZnO.
Fig. S5. FTIR spectrum of Fe-Co-Ni/MgO catalyst.

Fig. S6. FTIR spectrum of Fe-Ni-Co-MgO catalyst.
Fig. S7. FTIR spectrum of Fe-Co-Ni/ZnO catalyst.

Fig. S8. FTIR spectrum of Fe-Ni-Co-ZnO catalyst.
Fig. S9. FAME profile of the biodiesel produced by Fe-Co-Ni/MgO.

Fig. S10. FAME profile of the biodiesel produced by Fe-Co-Ni-MgO.
Fig. S11. FAME profile of the biodiesel produced by Fe-Co-Ni/ZnO.

Fig. S12. FAME profile of the biodiesel produced by Fe-Co-Ni-ZnO.
Fig. S13. Interactive effects of the transesterification parameters using Fe-Co-Ni/MgO.
Fig. S14. Interactive effects of the transesterification parameters using Fe-Co-Ni-MgO.
Fig. S15. Interactive effects of the transesterification parameters using Fe-Co-Ni/ZnO.
Fig. S16. Interactive effects of the transesterification parameters using Fe-Co-Ni-ZnO.