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Synthesis and characterization of zinc oxide nanoparticles (ZnO-NPs) for biodiesel production using waste frying oil (WFO)

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In this research, zinc oxide nanoparticles (ZnO-NPs) were synthesized by simple solution-based approach using zinc nitrate [Zn(NO3)2.6H2O] and sodium hydroxide (NaOH) as precursor. The Synthesized ZnO-NPs were characterized by XRF, XRD and TGA methods. XRD method confirmed the formation of nanosized zinc oxide particles in the size range of 13–47 nm. XRF and TGA were used to determine the elemental composition and thermal stability of ZnO-NPs, respectively. The ZnO-NPs were used as catalyst in the production of biodiesel from waste frying oil (WFO) via transesterification method. The transesterification process yielded 97.8 % (w/w) WFO biodiesel. The results of the fuel properties revealed that, all the parameters tested are within the ASTM limits, indicating that the biodiesel produced could be used as an alternative diesel fuel.

Keywords: Nanomaterials, nanoparticles, zinc oxide, zinc nitrate, sodium hydroxide.

1. Introduction

Over the past decade, variety of nanomaterials such as nanoparticles, nanofibers, nanotubes, nanowires, nanocapsules, nanocomposites, nanoflowers and nanofluids and quantum dots have attracted the attention of many researchers due to their wide range of application especially in areas of applied sciences and engineering.[1] In nanotechnology, nanomaterials are particles having nanoscale dimension and differ in chemical and physical properties from those of the bulk materials.[2,3] They have found numerous applications such as in catalysis, adsorption, energy storage, water purification and also in medicine.[4]

Nanoparticles are substances with a dimension of less than 100nm that behave as a whole unit in terms of its transport and properties. Nanoparticles play an important role in the field of chemistry because of their unique features such as their surface to mass ratio, which is much larger than that of other materials allowing catalytic promotion of reactions as well as their ability to absorb and carry other compounds.[5]

Recently, zinc oxide nanoparticle has promoted itself as an interesting metal oxide material because of its unique physical and chemical properties such as high chemical and mechanical stability, broad range of radiation absorption, high catalytic activity, good electrical conductivity, non-toxic and environmentally friendly nature etc.[6] Because of its distinct properties its widely used as biosensor, solar cells, chemical sensor, gas sensor, photo detectors, catalysts, active fillers for rubber and plastics, optical material, additive in treatment of water and waste water etc.[3,7,8]

Different researchers have employed different methods in the synthesis of zinc oxide nanoparticles which include Sol–gel, spray pyrolysis, solution based, micro emulsion techniques, thermal evaporation, ultrasonic atomization, chemical vapor deposition, mechanical milling, microwave and hydrothermal methods.[7-9] Among the above methods, solution-based approach is simplest. This is because, the morphology of nanoparticles can be controlled by optimizing various reaction conditions such as pH, concentration of precursors, temperature and reaction time.[6,8,9]

The utilization of nanomaterials as catalysts for biofuels production has been of recent interest because of their unique features such as high selectivity, high activity, long lifetime as well as large surface to mass ratio, which is much larger than that of bulk materials allowing catalytic promotion of reactions as well as their ability to adsorb and carry other compounds. Therefore, this research focuses on biodiesel was production and characterization from waste frying oil (WFO) by transesterification method using zinc oxide nanoparticles (ZnO-NPs) as catalyst. The ZnO-NPs was synthesized by solution-based approach and was characterized using different instrumental methods.

2. Materials and Methods

2.1 Synthesis and Characterization of ZnO-NPs

The ZnO-NPs was synthesized by direct precipitation method using zinc nitrate [$Zn(NO_3)_2.6H_2O$] and sodium hydroxide (NaOH) as precursor. In this method, aqueous solution of 0.4 M NaOH was slowly added to aqueous solution of 0.2 M $Zn(NO_3)_2.6H_2O$ at room temperature under vigorous stirring until white suspended precipitate was formed. The white precipitate was filtered and centrifuged at 5000rpm for 20 min. It was then washed three times with distilled water and lastly with absolute alcohol. The white product obtained was dried, crushed into uniform sized particles and calcined in a muffled furnace at 450 °C for 3hrs.[6,9] The resulted ZnO-NPs was characterized using X-ray florescence (XRF), X-ray diffraction (XRD), and Thermogravimetric analysis (TGA) methods.

2.2 Transesterification of the Waste Frying Oil (WFO)

The transesterification reaction was carried out in a three-neck round bottom flask (250 cm^3) equipped with reflux condenser, temperature controller and magnetic stirrer. Suspended solution of methanol (5.64 g) and the ZnO-NPs (2.5 g) catalyst was added to the warmed waste frying oil (50 g) in the reactor. The reactor was then placed on the water bath at 60 °C and the reaction conditions were maintained with constant stirring. After the reaction was completed, the catalyst was removed from reaction mixture by centrifugation. The content was transferred into a separatory funnel and allowed to settle for 24 hrs. This permit the glycerol to settle down since it is denser than the biodiesel. The glycerol was removed from the separatory funnel.[10,11] The biodiesel produced was washed three times with warm distilled water (50 ºC) to remove any residual glycerol and methanol. It was then dried with anhydrous sodium sulphate and filtered before characterization.[12,13] The whole procedure was repeated seven times while varying the reaction time by 10 minutes. The percentage biodiesel yield for different reaction time was calculated using equation below.[13]

$$\%\text{Biodiesel Yield} = \frac{\text{Weight of Biodiesel}}{\text{Weight of WFO}} \times 100\%$$

2.3 Determination Fuel Properties of the Biodiesel

The fuel properties of the biodiesel were determined according to ASTM D methods for biodiesel fuel.

3. Results and Discussion

The following reactions are proposed to take place in the synthesis of ZnO-NPs:

$$Zn(NO_3)_2.6H_2O + 2NaOH \longrightarrow Zn(OH)_2 + 2NaNO_3 + 6H_2O$$

$$Zn(OH)_2 \xrightarrow[-\,H_2O]{heat} ZnO$$

The zinc nitrate hexahydrate reacts with sodium hydroxide (precipitating agent) in molar ratio of 1:2 to give precipitate of zinc hydroxide, sodium nitrate and water. Filtration, multiple washing and drying of the zinc hydroxide precipitate separates the sodium nitrate and water from the mixture. Further drying and calcination of the zinc hydroxide precipitate at 450 °C resulted in the formation of zinc oxide nanoparticles (ZnO-NPs).

Figure 1 illustrates the elemental analysis of the synthesized ZnO-NPs with 94 % zinc oxide concentration. The result also confirms the presence of impurities associated with the ZnO-NPs.

X-ray Diffraction studies were carried out using X-ray diffractometer with Cu kα radiation in the range of 15–75° to determine the crystal structure and phase of the synthesized ZnO-NPs. The XRD diffractogram of the synthesized ZnO-NPs is shown in figure 2. The XRD pattern showed peaks at values of 31.94° (100), 34.58° (002), 36.38° (101), 47.66° (102), 56.56° (110), 62.45° (103), 66.45° (200), 67.59° (112), 69.24° (201) and 72.19° (202) which are typical for the ZnO-NPs structure. The average particle size of the synthesized ZnO-NPs was 25.03nm according to Scherrer's equation. Other details regarding the XRD of the synthesized ZnO-NPs are given in table 1. While the variation of particle sizes of the synthesized ZnO-NPS particles (nm) determined by the XRD data are shown in figure 3. Both results from table 1 and figure 3 confirm that the particles size of the synthesized ZnO-NPs falls within the nano range.

Figure 4 showed the TGA curve of the ZnO-NPs with three distinct changes in weight during the thermal analysis. At the onset of the analysis, there was a mild weight loss from a temperature of 70.30°C to 540.74°C. The percentage weigh loss recorded in this stage was 1.47%. This weight loss is associated with dehydration and volatilization of low molecular weight organic substances adhered to the ZnO-NPs. The second stage showed a moderate weight loss from a temperature of 540.74°C to 764.11°C. The percentage weight loss recorded in this stage was 7.81% and this is attributed to the decomposition of $NaNO_3$ to Na_2O. The third stage showed severe and rapid weight loss from a temperature of 764.11°C to 882.41°C. This percentage weight loss recorded in this stage was be 27.47% which could be attributed to the loss of inorganic impurities. Then the curve stabilized which indicate the end of thermal decomposition.

Biodiesel production was successful via transesterification method using ZnO-NPs as a catalyst. Figure 5 showed the Percentage conversion of oil to biodiesel with time. It is clear from the figure that conversion rate of oil into biodiesel increases with reaction time. After 50 minutes, a yield of 96.1 % of biodiesel was observed, and after 60 minutes, the percentage conversion was almost the same. The biodiesel yield obtained using ZnO-NPs in this research is higher than those reported by many other researchers that used larger size zinc oxide as catalyst for transesterification of oil to biodiesel.[14,16]

Table 2 showed the fuel properties of the produced biodiesel in comparison with those of ASTM D6751 standard for biodiesel. From the results, it is clear that all the fuel properties tested are within the ASTM limits, indicating that the biodiesel produced could be used as an alternative diesel fuel.

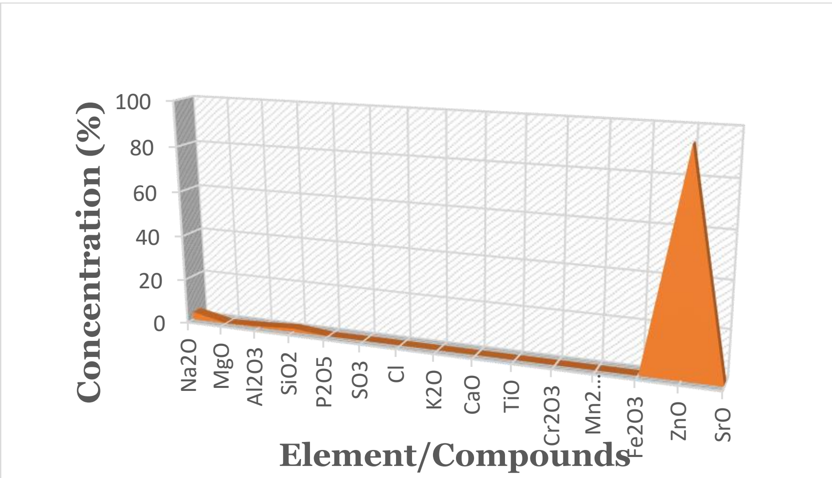

Figure 1: XRF results of the synthesized ZnO-NPs

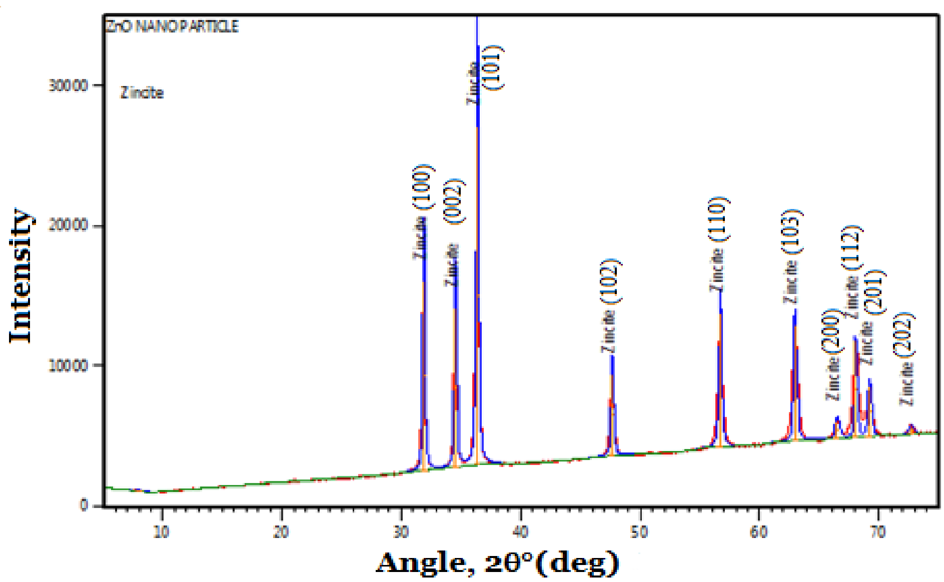

Figure 2: XRD Spectrum of the synthesized ZnO-NPs

Table 1: Different angles and their corresponding FWHM, size of synthesized ZnO-NPs from X-ray Diffraction

Angle, 2θ°(deg)	FWHM (Å)	Size (nm)
31.9356	0.1219	13.4
34.5832	0.0925	18.2
36.3771	0.0936	18.4
47.6556	0.1056	19.5
56.5596	0.1216	20.7
62.3537	0.1311	22.8
66.4518	0.1325	26.2
67.5903	0.1250	29.1
69.2370	0.1096	35.7
72.1852	0.0979	46.3

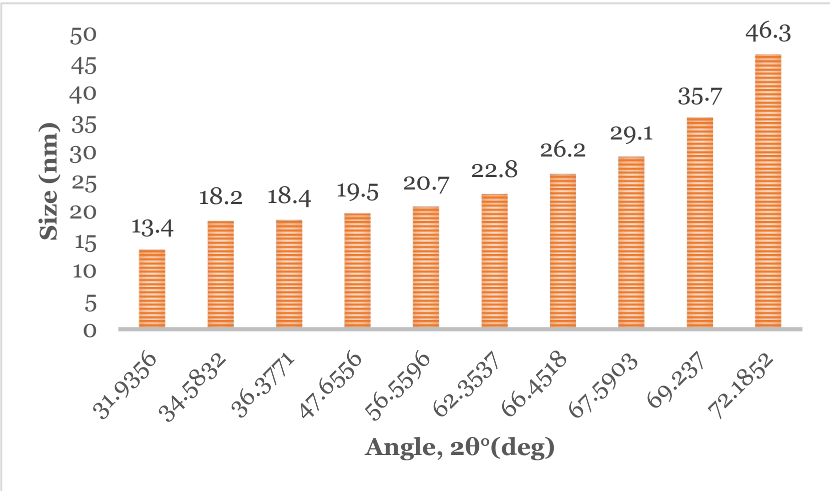

Figure 3: Variation of particle size of the synthesized ZnO-NPs.

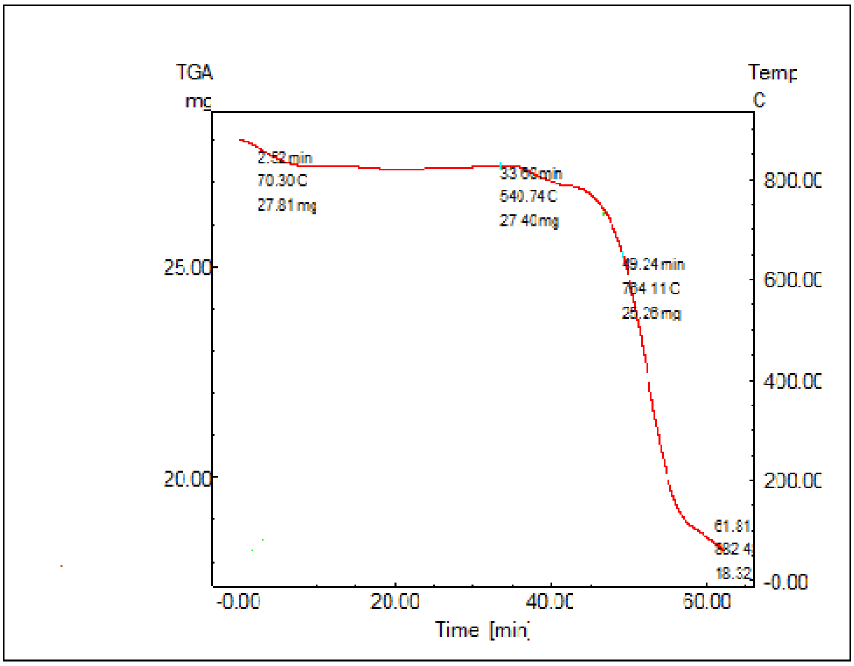

Figure 4: Thermogravimetric analysis of the synthesized ZnO-NPs

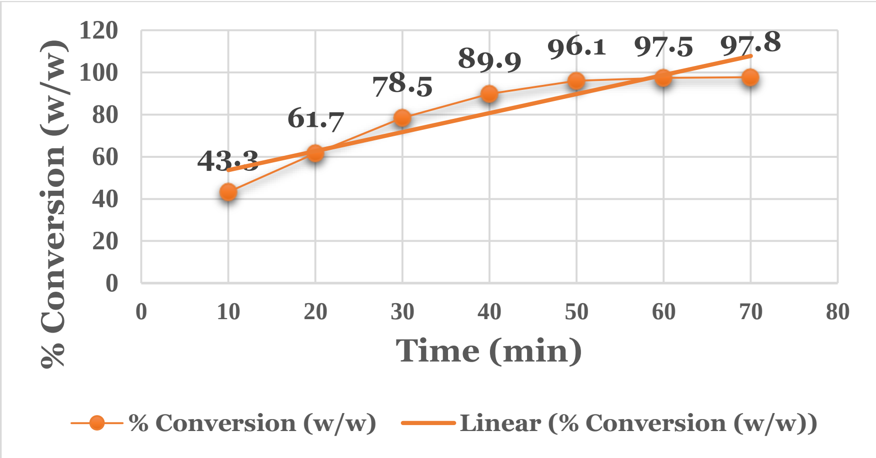

Figure 5: Percentage conversion of oil to biodiesel with time.

Table 2: Fuel Properties of the produced Biodiesel

Properties	Unit	Biodiesel ASTM D6751	WFO Biodiesel
Specific Gravity	-	0.86 to 0.90	0.88±0.003
API Gravity	-	-	29.30±0.90
Diesel Index	-	-	30.27±0.77
Cetane Number	-	47 min	51.86±0.20
Saponification Value	mgKOH/g	-	22.50±1.90
Higher Heating Value	MJ/kg	-	65.34±2.20
Kinematic Viscosity	mm^2/sec	1.9 to 6.0	4.50±0.02
Flash Point	^{0}C	93 min	147±1.50
Cloud Point	^{0}C	-3 to 12	3.50±0.65
Pour Point	^{0}C	-15 to 16	-10.20±0.8
Acid Value	mgKOH/g	0.05 max	0.09±0.01
Sulphur Content	%	0.05 max	0.02±0.001
Iodine Value	gI_2/100g	-	45.59±0.40
Aniline Point	^{0}F	-	103.30±2.5
Water & Sediment	%	0.05 max	0.04±0.001

4. Conclusion

Zinc oxide nanoparticles (ZnO-NPs) were successfully synthesized by solution-based method. The synthesized ZnO-NPs was used as catalyst in the conversion of waste frying oil (WFO) to biodiesel via transesterification method. The results from this research confirmed the formation nanosized zinc oxide with higher thermal stability. The result also reveals that, all the fuel properties tested are within the ASTM limits, indicating that the biodiesel produced could be used as an alternative diesel fuel.

Conflict of Interest

The author declares that there is no conflict of interest.

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