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EFFECT OF ALUMINUM AND ZINC OXIDES NANOPARTICLES AND THEIR BLEND ON YIELD AND QUALITY OF BIODIESEL FROM BLENDS OF NEEM AND WASTE COOKING OIL

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Abstract: **The effect of aluminum oxide (Al_2O_3), zinc oxide(ZnO) nanoparticles and their blend on yield and quality of biodiesel from blends of Neem (Azadirachtaindica) and waste cooking oils has been evaluatedin this study. Characterizing using the X-ray diffraction(XRD) technique reveals that both nanoparticles are crystalline and are within the nanoparticles size range with grain sizes of 9.61nm and1.31nm, respectively.Acid values and %FFA of blends of Neem and waste cooking oil were also observedto be suitable for transesterification without the need for prior esterification.Results show that all the sample blends gave biodiesel yields that are above 70% with a maximum yield of 97.1±0.8% by100wt%NMO:0wt%WCO sample blend, when treated with a combination of Al_2O_3 and ZnO nanoparticles.This shows that the combination of Al_2O_3 and ZnO nanoparticles is a promising catalyst for biodiesel production.Biodiesel samples were also analyzed for pour points, cloud points, flash points, saponification values, iodine values, cetane numbers and calorific values to unveil the oil quality. Analysis results show that most of the determined fuel properties of the biodiesel samples were within ASTM standards.**

Keywords: **Biodiesel production, Nanoparticles' effect, Neem,Waste cooking oil, Enhanced yield and quality**

I. INTRODUCTION

For decades, fossil fuels such as natural gas, coal and oil have been the major supplier of energy, of which about 90% are consumed as liquid fuels for transportation and energy generation. The negative environmental impacts of utilizing fossil fuels as primary energy sourceshas led to research on technologies and sources of alternative renewable energy/fuels, such as biodiesel, that can complement fossil fuels [1, 2]. As reported by recent life cycle assessment studies, the use of biodiesel can reduce emissions of carbon dioxide and carbon monoxide by 8–41% [3]. However, production cost and the overlap with food consumption are two factors affecting the consumption of biodiesel, worldwide[4].Many standardized procedures (such as blending, micro emulsification, thermal cracking and transesterification) are available for production of biodiesel; however, transesterification of vegetable oils is the most commonly used. Alcohols like methanol and ethanol are usually used in this process, in the presence of a catalyst. The catalyst can be homogenous, heterogeneous or enzymatic. In recent times, nanotechnology-based biodiesel production has gained global recognition because of the evolution of the most promising nanocatalysts[5-7].Thus, the use of nanoparticles as catalysts has shown promise in increasing biodiesel yield and improving its properties, by reducing its

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free fatty acid content and improving cold flow properties [6].

Several researchers have explored the use of various nanoparticles as catalysts in biodiesel production from Neem and waste cooking oils. Noreen et al. [8]synthesized Fe, Ni, and Cu doped ZnO nanocatalysts and employed them in biodiesel production from neem oil. Their study results revealed biodiesel yields of 95%, 80%, and 85% for Fe, Ni, and Cu respectively. Besides, results of analysis of produced biodiesel samples unveiled that the Fe, Ni, and Cu doped ZnO nanocatalysts are promising heterogeneous catalysts.In the optimization study conducted by Zahid et al. [9], Ni doped ZnO heterogeneous catalyst was used in conversion of neem oil to biodiesel by transesterification. A maximum biodiesel yield of 90.18%, under reaction conditions of 60 °C, 1:10 oil-to-methyl alcohol ratio, and 0.9 g catalyst, was obtained. Farokhi et al.[10]used spinel type $Ni_xZn_{1-x}Fe_2O_4$ magnetic nanocatalysts for conversion of neem oil into biodiesel via transesterification, and obtained a maximum biodiesel yield of 93%.In the study carried out by Velmurugan and Warrier[11], mesoporous MgO-SnO_2 nanocomposite was used in conversion of waste cooking oil (WCO) to biodiesel. A biodiesel yield of 80% was obtained in the first 20min but the yield increased to 88% at 120mins. Gada et al. [12]used a mixture of H_2SO_4 and ZnO nanoparticles to enhance the yield of biodiesel obtained from transesterification of waste cooking oil. Results showed that the use of H_2SO_4 as control resulted in a biodiesel yield of 71.3%, but the yield increased to 81.94% when H_2SO_4 was mixed with ZnO nanoparticles at catalyst loading of 0.5% (w/w).

However, in this novel study, Al_2O_3 and ZnO nanoparticles and their blends were synthesized, characterized, and used, for the first time, in biodiesel production from various blends of Neem and Waste cooking oil. The produced biodiesel samples were also analyzed to unveil the effect of the nanoparticles and their blend on the biodiesel quality. Results of this study willnot only provide valuable information for effective biodiesel production, but also will serve as an efficient method for recycling waste cooking oil, beside unveiling the economic viability of biodiesel production from neem and waste cooking oils.

II. MATERIALS AND METHODS

Collection of neem and waste cooking oil

Neem oil was purchased from Kano state while waste cooking oil was obtained from road-side bean cake vendors. The Neem oil was further purified by degumming using warm water at 70^{o}C for 30 minutes while the waste cooking oil was sieved to remove impurities. Figure 1 shows the pretreated Neem and waste cooking oils.

Fig.1: Pretreated Neem and waste cooking oils

Sample characterization

The acid values of both neem and waste cooking oil were estimated by simple titration using NaOH. Thus, 200ml of ethanol was poured into a conical flask and three drops of phenolphthalein were added to it. A few drops of 0.1M NaOH were titrated into the mixture until a pink colour appeared. The conical flask was put on a weighing balance and 3.137g of the neem oil was added. The mixture was stirred vigorously for a few seconds and NaOH was titrated again into the mixture until a pink colour appeared. The same process was carried out for 3.226g of waste cooking oil.

$$\text{Acid value} = \frac{\text{T x N x 40}}{\text{W}} \quad (1)$$

Where; T = Titer volume of 0.1 M NaOH consumed by sample, N = normality/molarity of NaOH (0.1 M); W = weight in grams of the sample. The %FFAs were estimated as follows.

$$\text{Free fatty acid (\%FFA)} = \text{Acid value x } \frac{282.27}{40} \text{ x } \frac{1}{10} \quad (2)$$

Synthesis of Zinc Oxide Nanoparticles

Direct precipitation approach was used to create zinc oxide nanoparticles using zinc nitrate hexahydrate ($Zn(NO_3).6H_2O$) and potassium hydroxide (KOH) as precursors. An aqueous solution of 0.2M zinc nitrate was prepared by dissolving 13.4g of zinc nitrate in 225ml of deionized water. Solution of 0.4M KOH was prepared by dissolving 5.1g of KOH in 225ml of deionized water. Both solutions were stirred for about 5 minutes each. While the zinc nitrate was undergoing vigorous stirring under room temperature, the KOH solution was slowly added into it,

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which resulted in formation of a white suspension. The formed product was centrifuged at 4000rpm for 20 minutes. The product was washed with distilled water and centrifuged again at 4000rpm for 10 minutes, after which it was washed at last with absolute alcohol. The obtained product was dried at 80^{o}C for 4 hours after which it was calcined at 500^{o}C for 3 hours. The product was left to cool and grinded using mortar and pestle. Three batches of the zinc nitrate and KOH solution were prepared in total to give about 6g of zinc oxide nanoparticles.

Synthesis of alumina nanoparticles

γ-Alumina was synthesized by precipitation hydrothermal calcination process using Ammonia ($NH_3.H_2O$) and Aluminum chloride hexahydrate ($AlCl_3.6H_2O$) as precursors. 1M aluminum chloride solution was prepared by dissolving 54.3g of aluminum chloride in 225ml of distilled water. White precipitates formed when ammonia was added dropwise to the 1M aluminum chloride solution until the pH reached 9 while being vigorously stirred. The mixture was then transferred into a 250ml Teflon-lined stainless steel autoclave. After being kept at 200°C for three hours, the autoclave was allowed to cool to ambient temperature. The white precipitates were then centrifugally separated at 4000 rpm for 20minutes. The product was washed with distilled water and centrifuged again at 4000rpm for 10 minutes. The obtained white precipitates were dried at 80^{o}C for 9 hours. The precipitate was then calcined in a muffle furnace at 500^{o}C and it burnt between the first 5 to 15 minutes, turning the white precipitates into black. The calcination continued at this temperature for 4 hours, during which the black precipitates turned white. The product wasallowed to cool and afterward grinded into fine particles using mortar and pestle.

Experimental setup

The transesterification reaction was carried out in a round bottom flaskmounted on a hot plate with an in-built magnetic stirrer. The hot plate was used to regulate the temperature and the stirrer was used to control the speed of the reaction.

(a) (b)

Fig. 2: (a) Biodiesel mixture mounted on hot plate with in-built magnetic stirrer (b) Separating funnel

Transesterification process

Transesterification reactions were first performed without addition of nanoparticles (i.e., the control experiments) using the sample blends: 100wt%NMO:0wt%WCO, 75wt%NMO:25wt%WCO, 50wt%NMO:50wt%WCO, 25wt%NMO:75wt%WCO and 0wt%NMO:100wt%WCO, respectively, with KOH as catalyst at a methanol to oil ratio of 1:1. For 100wt%NMO:0wt%WCO sample blend, 50g of the pretreated Neem oil was heated in round bottom flask to 60^{o}C. The methoxide solution was prepared by dissolving 0.6g of KOH (i.e., 1.2wt% of the oil) in 50g of methanol and was heated to 50^{o}C and added to the heated oil. The mixture was stirred at 100rpm for 1 hour while maintaining the temperature between 55^{o}C to 65^{o}C. After the reaction, the mixture was transferred into a 500ml separating funnel and a fast separation was observed. The mixture was left to settle for 24 hours after which the mixture separated into two well-defined layers of glycerol at the bottom, and biodiesel at the top. The glycerol was run out from the funnel and the biodiesel was collected. The reaction was also performed for the remaining sample blends keeping all the parameters constant. Likewise, transesterification reactions were also performed, however, with addition of the nanoparticles, AL_2O_3, ZnO and their blend (at 1:1), respectively, using the same feedstock blending ratios. Thus, for the reaction with AL_2O_3 nanoparticles, 0.5g of Al_2O_3 nanoparticles (i.e., 1wt% of the oil) was added to the heated oil, followed by the methoxide solution. The mixture was then stirred at 100rpm for 1 hour while maintaining the temperature between 55^{o}C to 65^{o}C. After the reaction, the mixture was transferred into a 500ml separating funnel and a fast separation was observed. The mixture was left to settle for 24 hours after which it separated into three well-defined layers of Al_2O_3 nanoparticles at the bottom, glycerol at the middle, and biodiesel at the top. The nanoparticles and glycerol were run out from the funnel and biodiesel was collected. The reaction was also carried out for the remaining sample blends, keeping all the parameters constant. Similarly, transesterification reactions were also performed with the ZnO NPs and the blend of Al_2O_3 and

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ZnO NPs accordingly. However, for the reactions with the blend of AL_2O_3 and ZnO nanoparticles, 0.25g of each of Al_2O_3 NPs and ZnONPs were mixed together to make up for the required 0.5g of nanoparticles to be added to the heated oil, followed by the methoxide solution.

Characterization of biodiesel samples to unveil effect of nanoparticles on their quality

Determination of cloud point, pour point and flash point

The cloud points of produced biodiesel samples were determined using the cloud point apparatus. The cloud point apparatus is mainly made up of 12cm high glass tubes of 3cm diameter. To further lower the system's temperature, the tubes were encased in an air jacket that was containing a freezing combination of broken ice and sodium chloride crystals. Likewise, the temperature at which fuel motion was initially detected for five seconds after tilting the tube to a horizontal position was determined to be the pour point, while the flash points of the produced biodiesel samples were measured by Pensky-Martens closed cup tester (ASTM D93).

Determination of saponification value

The method described by Balami et al. [13] was used in estimating the saponification value of the produced biodiesel. Thus, the flask was filled with 2g of the oil. After adding 25 ml of 0.5N alcoholic sodium hydroxide, it was boiled under reflux for an hour. Using 0.5 ml of a 1% alcoholic solution of phenolphthalein as an indicator, the excess alkali was identified by titrating with 0.5N hydrochloric acid while the mixture was still hot. Additionally, a blank was calculated under the same conditions but without the sample.The saponification value of the produced biodiesel was estimated using the equation below.

$$S.V = \frac{56.1 \text{ x } (B - S) \text{x } N}{W} (3)$$

W is the weight of oil utilized, N is the normality of HCL, B is the volume of standard HCL needed for the blank (ml), and S is the volume of standard HCL needed for the sample (ml).

Determination of iodine value

The iodine values (IV) of the biodiesel produced from various sample blends were determined according to Getahun and Gabiyye[14]and Leal et al., [15]using equation (4). Thus, 1 g of the biodiesel sample was mixed together with 10 mL of chloroform and 25 mL of Hanus solution, and the resultant mixture was kept in a dark place for 30 minutes. The combination of 10 mL of 15% potassium iodide solution and the mixture was titrated against standardized sodium thiosulphate. The titrant volume, V_t, consumed by the sample was then recorded. The same process was used for blank titration, but without the biodiesel sample. The titrant volume, V_b, consumed by the blank solution was also noted. Likewise, the titration processes were repeated, and the average values of titrant volume were estimated.

$$I.V = \frac{M_{iodine} \cdot C_t \cdot (V_b - V_t)}{W_s} (4)$$

Where: C_t is the concentration of standardized sodium thiosulphate (N),,M_{iodine} depicts the molecular weight of iodine (g), and W_s represents the weight of biodiesel sample (g).

Determination of calorific value and cetane number

The Calorific value (CV) or high heating value (HHV) and cetane numbers (CN) of the biodiesel produced from various sample blends were determined using ASTM D 613 standard procedures via empirical formula as applied by Cocks and Vanrede, [16] and Getahun and Gabiyye, [14], respectively. Computation of the HHV and CN of the biodiesel wereperformedwith the results of the saponification values (SV) and iodine values (IV) using equations (5) and (6), respectively.

$$HHV = 49.43 - \left[\frac{(0.041.SV) + (0.015.IV)}{W_s}\right] (5)$$

$$CN = 46.3 + \left(\frac{5458}{SV}\right) - (0.225.IV) (6)$$

Statistical analysis

SPSS (IBM, v. 20) was used to perform statistical analysis. To assess the level of significance, the data were statistically examined using a one-way analysis of variance and the least significant difference test at the probability level ($P < 0.05$. The mean ± standard deviation (SD) of three replicates was used to present the results.

III. RESULTS AND DISCUSSION

Oil samples' characterization results

Results of the %FFA of both oils were less than 2% (Table 1), indicating that the oils can be used for biodiesel production without esterification reaction.

Table 1: Results of Acid values and %FFA of Neem and Waste cooking oils.

Characterization parameters	Neem oil	Waste cooking oil	ASTMD6751 [17]
Acid value (mgNaOH/g)	2.44	0.5	≤0.05
%FFA(mgNaOH/g)	1.72	0.35	≤0.05

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Nanoparticles' characterization results

XRD patterns of synthesized Aluminum and Zinc oxides nanoparticles are described in figures 3 (a) and (b), respectively. Cu Kα radiation (1.662 Angstrom) was used to record the X-ray diffraction results. Data on intensities were gathered throughout 2θ ranges of 10–140° and 25–75° for the Aluminum and Zinc oxides nanoparticles, respectively, while the sharp peaks in figures 3 (a) and (b) indicatedthe crystallinity of thenanoparticles, respectively.For Al_2O_3 nanoparticles, a total of thirteen (13) peaks were observed at 2θ of 18.5±0.3°, 30±0.4°, 38±0.6°, 58±0.4°, 60.3±0.2°, 67±0.1°, 86±1°, 92±0.1°, 108±0.2°, 114±0.3°, 116±0.4°, 127±0.3°, and 132±2°. This was analyzed in relation to an XRD standard for gamma-alumina structure JCPDS reference no. 00-010-0425 found in the International Centre for Diffraction Data database. It was observed that the XRD peak positions 38±0.6° (311), 60.3±0.2° (511), 67±0.1° (440) and 86±1° (444) matched with the gamma-alumina standard. All the peak positions showed the presence of impurities, except the peak position 67±0.1°, which showed pure Al_2O_3.However, for ZnO nanoparticles, a total of nine (9) peaks (27.0±0.2°, 32.2±0.1°, 34.5±0.2°, 36.8±0.1°,

48.1±0.2°, 56.9±0.1°, 63.1±0.1°, 68.3±0.1°, and 69.3±0.2°) were observed at 2θ.It was observed that the XRD peak positions 32.2±0.1° (100), 34.5±0.2° (002), 36.8±0.1° (101), 48.1±0.2° (102), 56.9±0.1° (110), 63.1±0.1° (103), 68.3±0.1° (112), and 69.3±0.2° (201) aligned with the JCPDS data.Thus, all the peak positions showed the presence of impurities. Scherrer equation, as in Eq. (7)was used to calculate the average grain sizes of samples using the diffraction intensities at the Al_2O_3 and ZnO peaks, respectively, and results indicated that the average crystallite sizes of Al_2O_3 and ZnO nanoparticles were about9.61nm and 1.31nm, respectively.

$$D = \left(\frac{0.89\lambda}{\beta \cos\theta}\right) \quad (7)$$

Where λ = wavelength (Cu Kα), β = full width at the half-maximum of the nanoparticle and θ = diffraction angle.

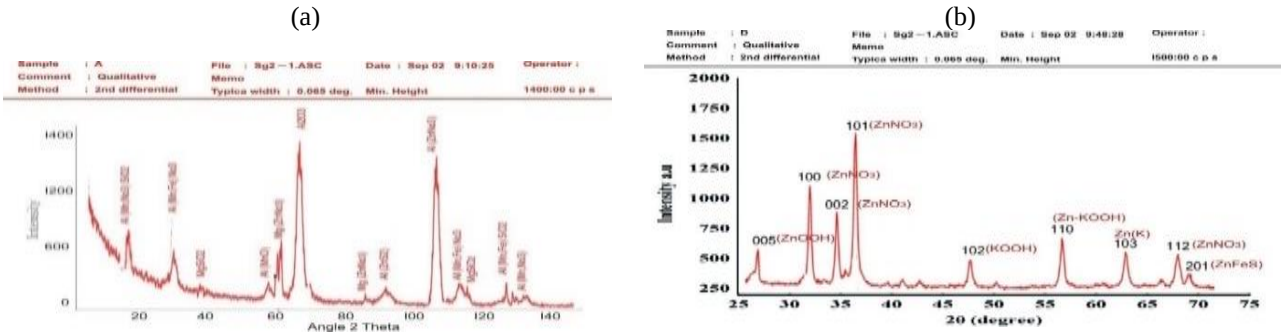

Figure 3: XRD patterns of: (a) Al_2O_3 nanoparticles and (b) ZnO nanoparticles

Effect of nanoparticles on yields of biodiesel produced

Table 2 presents percentage yields of biodiesel from blends of Neem and Waste cooking oils. From the table, the results unveiled that all the sample blends gave biodiesel yields above 70%, although the highest yield of 97.1±0.8% was obtained from the sample blend, 100wt%NMO:0wt%WCO, when treated with Al_2O_3+ZnO nanoparticles. It can also be observed from the table that the biodiesel yields of 78.6±0.9%, 79.3 ±0.7%, 85.8 ±1.1%, 79.2 ±1.2% and 72.9 ±0.9% were achieved with the oil blends of 100wtNMO: 0wt%WCO, 75wt%NMO:25wt%WCO, 50wt%NMO: 50wt%WCO, 25wt% NMO:75wt% WCO and 0wt%NMO: 100wt% WCO, respectively, when no nanoparticles were added.However, when Al_2O_3 nanoparticles was used for the reactions using the oil blends, a sharp increase in biodiesel yields was observed. Likewise, a similar trend was observed for the experiments with ZnO nanoparticles.

Table 2: Percentage yields of biodiesel produced from blends of neem and waste cooking oils

S/N	Feedstock Blends	Biodiesel Yield (%)
1.	Samplegroup without nanoparticlestreatment (Control samples): 100wtNMO:0wt%WCO	78.6±0.9[a]
	75wt%NMO:25wt%WCO	79.3±0.7[a]
	50wt%NMO:50wt%WCO	85.8±1.1[b]

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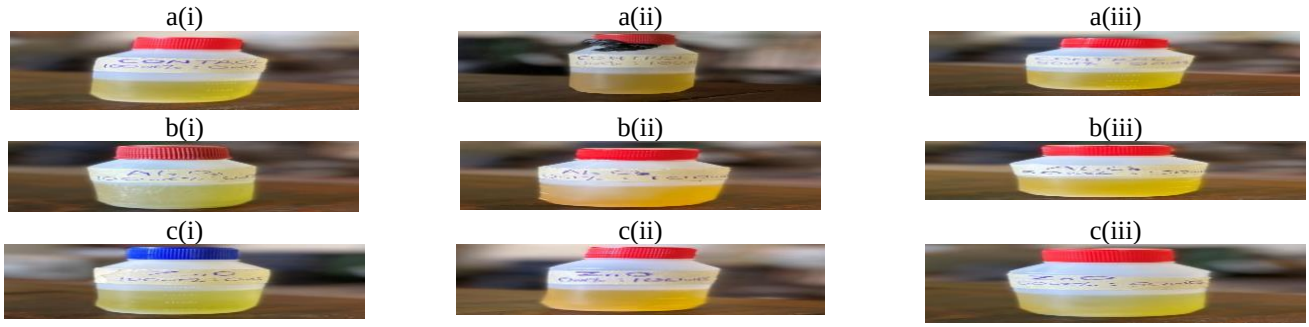
	25wt%NMO:75wt%WCO	79.2±1.2[a]
	0wt%NMO:100wt%WCO	72.9±0.9[c]
2.	Samplegroup treated with Al_2O_3nanoparticles:	
	100wt%NMO:0wt%WCO	91.7±1.1[a]
	75wt%NMO:25wt%WCO	85.9±0.5[b]
	50wt%NMO:50wt%WCO	87.1±0.8[b]
	25wt%NMO:75wt%WCO	82.4±1.2[c]
	0wt%NMO:100wt%WCO	81.8±1.1[c]
3.	Sample group treated with ZnO nanoparticles:	
	100wt%NMO:0wt%WCO	89.9 ±0.7[a]
	75wt%NMO:25wt%WCO	82.5 ±1.2[b]
	50wt%NMO:50wt%WCO	83.1 ±0.9[b]
	25wt%NMO:75wt%WCO	81.2±0.6[b]
	0wt%NMO:100wt%WCO	75.8 ±0.4[c]
4.	Sample group treated with Al_2O_3 + ZnO nanoparticles:	
	100wt%NMO:0wt%WCO	97.1 ±0.8[a]
	75wt%NMO:25wt%WCO	96.9 ±0.5[a]
	50wt%NMO:50wt%WCO	90.9 ±1.2[b]
	25wt%NMO:75wt%WCO	90.3 ±1.2[b]
	0wt%NMO:100wt%WCO	84.2±0.9[c]

valuesunder treated or untreated sample groups withthesamelettershowedinsignificantdifference (atP≤0.05).

Figure 6 presents samples of biodiesel obtained from some sample blends during reactions with Al_2O_3 NPs, ZnO NPs, and blends of Al_2O_3 and ZnO nanoparticles as well as during reactions without nanoparticles.



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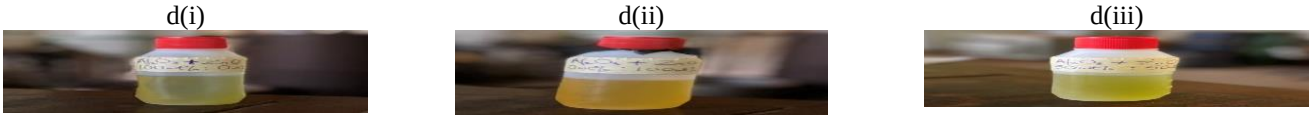

Figure 6: Samples of biodiesel obtained from: a(i-iii) reactions without nanoparticles, b(i-iii) reactions with Al_2O_3NPs,c(i-iii) reactions with ZnO NPs, and d(i-iii) reactions with blends of Al_2O_3 andZnONPs for 100wt%NMO:0wt%WCO, 0wt%NMO:100wt%WCO and 50wt%NMO:50wt%WCO sample blends, respectively.

Effect of nanoparticles on quality of biodiesel produced

Table 3: Fuel properties of the samples of biodiesel produced.

	Feedstock Blends	Pour point (^oC)	Cloud point (^oC)	Flash Point (^oC)	SV (mgKOH/g)	IV (mg I_2/100g)	CN	HHV (MJ/Kg)
ASTM standards (ASTM D6751)	100wt%NMO:0wt%WCO 75wt%NMO:25wt%WCO 50wt%NMO:50wt%WCO 25wt%NMO:75wt%WCO 0wt%NMO:100wt%WCO	-15 to 10	-3 to 12	≥ 130	0 to 370	≤ 120	≥ 47	≥ 42
Blends without NPs	100wt%NMO:0wt%WCO	-10	-1	179	183.54	52.43	64.24	39.04
	75wt%NMO:25wt%WCO	-9	0	176	165.91	51.57	67.59	39.96
	50wt%NMO:50wt%WCO	-8	-1	175	160.53	50.89	68.85	40.23
	25wt%NMO:75wt%WCO	-10	0	173	165.27	61.03	65.59	39.82
	0wt%NMO:100wt%WCO	-8	-2	168	179.31	85.31	57.54	38.64
Blends with Al_2O_3NPs	100wtNMO:0wt%WCO	-10	0	184	153.83	51.26	70.25	40.59
	75wt%NMO:25wt%WCO	-10	-1	181	140.27	45.82	74.90	41.38
	50wt%NMO:50wt%WCO	-8	0	183	136.32	41.64	76.97	41.66
	25wt%NMO:75wt%WCO	-9	-2	180	138.94	45.71	75.30	41.45
	0wt%NMO:100wt%WCO	-9	-1	171	141.61	66.35	69.91	40.93
Blends with ZnO NPs	100wt%NMO:0wt%WCO	-9	0	182	173.52	47.34	67.10	39.65
	75wt%NMO:25wt%WCO	-8	1	179	155.91	46.73	70.79	40.56
	50wt%NMO:50wt%WCO	-9	-1	181	150.55	45.98	72.21	40.85
	25wt%NMO:75wt%WCO	-9	1	177	155.26	56.31	68.78	40.42
	0wt%NMO:100wt%WCO	-10	-2	170	169.34	80.13	60.50	39.25
Blends with Al_2O_3 + ZnO NPs	100wt%NMO:0wt%WCO	-10	-1	187	148.37	42.71	73.48	41.03
	75wt%NMO:25wt%WCO	-8	1	183	135.93	33.13	79.00	41.84
	50wt%NMO:50wt%WCO	-9	0	185	132.91	31.16	80.36	42.03
	25wt%NMO:75wt%WCO	-8	1	183	133.23	37.27	78.88	41.90
	0wt%NMO:100wt%WCO	-9	-1	174	136.82	47.53	75.50	41.53

* NPs=Nanoparticles; IV=Iodine value; CN=Cetane number, HHV= High heating value

Effect of nanoparticleson pour points of produced biodiesel samples

The ASTM (D6751) standard for pour point of biodiesel is -15 to 10^oC (Table 3). The biodiesel produced without nanoparticles showed -10^oC, -9^oC, -8^oC, -10^oC and -8^oC pour point values for 100wt%NMO:0wt%WCO, 25wt%NMO:75wt%WCO, 50wt%NMO:50wt%WCO, 75wt%NMO:25wt%WCO, and 0wt%NMO:100wt%WCO oil blends, respectively. However, biodiesel samples produced in the presence of Al_2O_3 nanoparticles gave pour point values of -10^oC, -10^oC, -8^oC, -9^oC, and -9^oC, respectively for the same oil blends. Similarly, biodiesel samples produced in the presence of ZnO nanoparticles showed pour point values of -9^oC, -8^oC, -9^oC, -9^oC and -10^oC for the oil blends, respectively. While biodiesel samples produced in the presence of a combination of Al_2O_3 and ZnO nanoparticles showed pour point values of -10^oC, -8^oC, -9^oC, -8^oC and -9^oC for the oil blends, respectively.Thus, the pour points of the entire samples showed values within -8^oC to -10^oCwhich is within the ASTM (D6751) standard, however with varying degrees owing to nanoparticles addition.This is comparable to the result obtained by Fadhil et al. [18]. The researchers reported a value of $<-10^oC$ for biodiesel sample produced from castor seed oil. Kumar et al. [19] reported a value of -8^oC as the pour point value obtained from the analysis of the 50:50 mixture of castor and karanja oil.

Effect of nanoparticles on cloud points of produced biodiesel samples

The ASTM (D6751) standard for cloud point is -3^{o}C to 12^{o}C. Biodiesel samples produced without nanoparticles showed -1^{o}C, 0^{o}C, -1^{o}C, 0^{o}C and -2^{o}C cloud point values for 100wt%NMO:0wt%WCO, 25wt%NMO:75wt%WCO, 50wt%NMO:50wt%WCO, 75wt%NMO:25wt%WCO, and 0wt%NMO:100wt%WCO oil blends, respectively. However, biodiesel samples produced in the presence of Al_2O_3 nanoparticles gave cloud point values of 0^{o}C, -1^{o}C, 0^{o}C, -2^{o}C, and -1^{o}C for the same oil blends, respectively. Similarly, biodiesel samples produced in the presence of ZnO nanoparticles showed cloud point values of 0^{o}C, 1^{o}C, -1^{o}C, 1^{o}C and -2^{o}C for the oil blends, respectively. Finally, biodiesel samples produced with a combination of Al_2O_3 and ZnO nanoparticles gave cloud point values of -1^{o}C, 1^{o}C, 0^{o}C, 1^{o}C and -1^{o}C, respectively for the same oil blends. The cloud points of the whole biodiesel samples were within the range of -2^{o}C to 1^{o}C, which is within the ASTM standard, however with varying degrees owing to nanoparticles addition.This is also comparable to the result obtained by Fadhil and Ahmed [20]. Their result showed a cloud point value of -3^{o}C for biodiesel obtained from castor bean oil.

Effect of nanoparticles on flash points of produced biodiesel samples

From Table 3, biodiesel produced without nanoparticles showed 179^{o}C, 176^{o}C, 175^{o}C, 173^{o}C and 168^{o}C flash point values for 100wt%NMO:0wt%WCO, 25wt% NMO: 75wt% WCO, 50wt% NMO: 50wt% WCO, 75wt% NMO:25wt% WCO, and 0wt% NMO: 100wt% WCO oil blends respectively. However, with addition of Al_2O_3 nanoparticles, the flash point values were increased to184^{o}C, 181^{o}C, 183^{o}C, 180^{o}C, and 171^{o}C for the same oil blends, respectively. A similar trend was also observed with addition of ZnO nanoparticles as the flash point values of 182^{o}C, 179^{o}C, 181^{o}C, 177^{o}C and 170^{o}C were obtained for the oil blends, respectively. Likewise, biodiesel samples produced in the presence of Al_2O_3 +ZnO nanoparticles gave higher flash point values of 187^{o}C, 183^{o}C, 185^{o}C, 183^{o}C, and 174^{o}C for the oil blends respectively. The flash points of the whole biodiesel samples were within the range of 168^{o}C to 187^{o}C, which is within the ASTM standard, however with varying degrees owing to nanoparticles addition.Khan et al. [21] reported a flash point value of 184.5^{o}C for the 50:50 mixtures of Ceibapentandra oil and Nigella sativa oil. Similarly, Damanik et al. [22] reported a value of 175^{o}C for the 50:50 mixtures of C. inophyllum oil and Palm oil.

Effect of nanoparticles on saponification values of producedbiodiesel samples

From Table 3, it can be observedthat the saponification valuesofbiodiesel samples produced without nanoparticles addition are within the range of 160.53 to 183.54 mgKOH/g. However, biodiesel samples produced in the presence of Al_2O_3 nanoparticles gave lower saponification values, ranging from136.32 to 153.83 mg KOH/g. A similar trend was observed,in the saponification values of biodiesel samples,which ranges from 150.55 to 173.52 mgKOH/g,on addition of ZnO nanoparticles.Besides, biodiesel samples produced in the presence of Al_2O_3 +ZnO nanoparticles gave the lowest range of saponification values of 132.91 to 148.37 mg KOH/g. However, saponification values of the whole biodiesel samples were within the range of 132.91 to 183.54 mg KOH/g, which is within the ASTM standard, but the lower the saponification value of a diesel fuel, the better the fuel.This result is also comparable to the result obtained by Gupta et al. [23]. The researchers reported a saponification value of 179.5 mg KOH/g for biodiesel obtained from Karanja oil. Similarly, Falowo et al. [24] reported a value of 178.86 mg KOH/g for biodiesel produced from neem oil. Kumar et al. [19] also reported a value of 177.76 mg KOH/g for biodiesel obtained from the 50:50 mixtures of karanja and castor oil.

Effect of nanoparticles on iodine values of produced biodiesel samples

The iodine valuesof biodiesel produced without nanoparticles range from 50.89 to 85.31mgI_2/100g for the entire oil blends, while the iodine valuesof41.64 to 66.35 mgI_2/100gwere obtained for the same oil blends on addition of Al_2O_3 nanoparticles. Likewise, biodiesel samples produced in the presence of ZnO nanoparticles showed iodine values of 45.98 to 80.13 mgI_2/100g for the same oil blends.However, biodiesel samples produced, in the presence of Al_2O_3 +ZnO nanoparticles,from the same oil blends gave the lowest range of iodine values of 31.16 to 47.53 mgI_2/100g.Thus, the iodine values of the whole biodiesel samples were within the range of 31.16 to 85.31 mgI_2/100g, which are within the ASTM standard, but with varying degrees owing to nanoparticles addition.

Effect of nanoparticles on cetane numbers of produced biodiesel samples

From Table 3, it can be observed that the cetane numbers of biodiesel samples produced without nanoparticles addition were in the range of 57.54 to 68.85. However,biodiesel samples produced in the presence of Al_2O_3 nanoparticles gave higher cetane numbers in the range of 69.91 to 76.97. A similar trend was observed for the biodiesel samples produced in the presence of ZnO nanoparticles, which showed cetane numbers of 60.50 to 72.21.However, biodiesel samples produced in the presence of Al_2O_3 +ZnO nanoparticles gave the highest range of cetane numbers of 73.48 to 80.36.The cetane numbers of the whole biodiesel samples were within the range of 57.54 to 80.36, which is within the ASTM standard, however, the higher the cetane number of a diesel fuel, the better the fuel.In comparison to

these results, Falowo et al. [24]also reported a value of 57.71 for biodiesel produced from neem oil.

Effect of nanoparticles on calorific values of produced biodiesel samples

Calorific values of biodiesel produced from the oil blends without nanoparticles addition are in the range of 38.64 to 40.23 MJ/Kg.However, biodiesel samples producedin the presence of Al_2O_3 nanoparticles using the same oil blends gave higher calorific values of 40.59 to 41.66 MJ/Kg.Likewise, biodiesel samples produced in the presence of ZnO nanoparticles using the same oil blends also showedcalorific values of 39.25 to 40.85 MJ/Kg which are slightly higher than those obtained from the control experiments.However, biodiesel samples produced in the presence of Al_2O_3 +ZnO nanoparticles gave the highest range of calorific values of 41.03 to 42.03 MJ/Kg.The calorific values of the entire biodiesel samples were within the range of 38.64to 41.90 MJ/Kg, which is within the ASTM standard. Falowo et al. [24] reported values of 39.32, 40.82, and 40.25 for biodiesel produced from rubber seed oil, neem oil, and a mixture (40:60) of both, respectively. Khan et al. [21] reported values of 39.49, 39.25, and 39.37 MJ/Kg for biodiesel produced from Ceibapentandra oil, Nigella sativa oil, and a mixture (50:50) of both, respectively.

IV. CONCLUSION

Effect of Al_2O_3,ZnO nanoparticles and their blend on yield and quality of biodiesel produced from blends of Neem and Waste cooking oil has been investigated in this work.The Al_2O_3 and ZnO nanoparticles were synthesized and then characterized using X-ray diffraction technique. The XRD patterns of both nanoparticles revealed that both nanoparticles are crystalline and are within the nanoparticles size range with the grain sizes of 9.61nm and 1.31nm, respectively, for the Al_2O_3 and ZnO nanoparticles. Transesterification reactions were then performed with the synthesized nanoparticles, (Al_2O_3, ZnO and Al_2O_3+ZnO), using the following sample blends: 100wt.%NMO: 0wt.% WCO, 75wt.%NMO:25wt.%WCO, 50wt.% NMO:50wt.% WCO, 25wt% NMO:75wt% WCO and 0wt% NMO:100wt% WCO, while sample blends without nanoparticles served as the control samples. A methanol to oil ratio of 1:1 was used, at a reaction time of 1 hour and temperature of 60^{o}C. Results unveiled that all the sample blends gave biodiesel yields above 70%, although the highest yield of 97.1±0.8% was obtained from the sample blend, 100wt%NMO:0wt%WCO, when treated with Al_2O_3+ZnO nanoparticles. This shows that a combination of Al_2O_3 and ZnO nanoparticles is a promising catalyst for biodiesel production. Biodiesel samples were also analyzed for pour points, cloud points, flash points, saponification values, iodine values, cetane numbers and calorific values to unveil the oil quality. Analysis results showed that most of the determined fuel properties of the biodiesel samples were within ASTM standards.

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