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Synthesize of Biodiesel from High Acidity Neem oil Using a Two Steps Approach

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Abstract

In this study, biodiesel was obtained from the neem oil (N-oil) through a two-stage process: esterification and transesterification. In the first stage, N-oil was esterified with HCl, while in the second stage, the esterified N-oil was converted to biodiesel via the synthesized activated corn waste. The produced biodiesel properties were examined and compared with the recommended standard.

Results show that N-oil has a high acid value (10.50 mg KOH/g oil) and is non-edible. This oil (N-oil) was converted to a low acid (2.56 mg KOH/g oil) value using HCl at 1.90% concentration in the first stage (esterification). Activated catalyst from corn waste was found to be heterogeneous and rich in quartz, illite, orthoclase, and other minerals that are bio-based in nature. Biodiesel synthesized using the activated catalyst was found to be at its maximum (95.40% (wt./wt.) at a methanol-oil molar ratio of 7:1, and the properties of the biodiesel were found to be in agreement with the biodiesel recommended standard. The study concluded that the produced biodiesel is environmentally friendly and can be used with or without blends.

Keywords: Biodiesel; Neem oil; Esterification; Transesterification; Corn waste; Quartz; Environmentally friendly

1. Introduction

Concerns regarding the rate of depletion of petroleum reserves, the destruction of the ozone layer causing climatic changes, and their rising cost have grown among those involved in the oil and gas business as a result of global urbanization and industrialization and the increased use of petroleum (fossil fuel). The search for alternate energy sources must be stepped up if we are to mitigate climate change. One strategy to avoid the looming threats at present and in the future is to use agricultural solid wastes to create fuel for energy needs. Crops, fruits, and other agricultural wastes may be used to produce energy; additionally, using the agricultural wastes to produce energy can solve the problem of waste disposal as well as the food threat (Sumera et al., 2022; Mamoona et al., 2022). Biogas and biofuel production have both utilized the agricultural wastes ever reported and have similar approaches (Mamoona et al., 2022).

Biodiesel, an alternative fuel to traditional diesel, is less harmful, more affordable, renewable, environmentally friendly, and sustainable. This biodiesel can be produced via transesterification, esterification, or both methods (Adepoju et al., 2022; Nyorere et al., 2024). Although it has been noted that agricultural seeds contain a high oil percentage (triglycerides), which may be utilized as a main raw material for the manufacturing of biodiesel, reports indicated that the use of waste seeds proved to be sustainable to prevent food insecurity [8, 9]. Neem seed is one type of agricultural seed that is widely available but always has a disposal issue, and it has been tagged as agricultural waste seed with a disposal problem. The seed can be used to obtain the oil needed for industrial application. According to reports, neem oil's fatty acid composition primarily consists of oleic acid, palmitic acid, stearic acid, and linoleic acid. Oleic acid is often the most abundant, ranging from 45.9% to 73.57%. Other significant fatty acids include linoleic acid (8-16%), palmitic acid (13-15%), and stearic acid (14-19%) (Adepoju, 2020).

More than 1.15 billion metric tons of corn are generated globally [26]. According to Vancetovic et al. (2017), kernels make up between 30 and 52% of all maize fruits and are always available as trash. According to Nyoyere et al. (2024), the composition of the cob has been observed to be rich in quartz (68%), orthoclase (7.1%), ibise (9.8%), and illite (15%). These minerals contained alkalis needed for the conversion of oil to biodiesel in the transesterification process.

Therefore, this study employed the produced neem oil from research institutes for the synthesis of biodiesel in two steps (esterification and transesterification). The characteristics of the oil were first determined after purification, and the pure oil was converted to biodiesel with acid as well as a bio-based catalyst developed from corn waste (corncobs, stalks, husks) (Fig. 1). The biodiesel produced was characterized and compared with the biodiesel recommended standard (ASTM D6751 and EN 14214).

Fig. 1: Corn plant, fruits, and waste

2. Materials and Methods

2.1 Materials

Neem oil was obtained from NIPRD (Center of Excellence in Research and Development) located in Abuja, Nigeria. The oil was preheated at 100°C for 30 min and was filtered to obtain pure oil. The neem oil was kept in a tight container for further processing.

Corn waste was collected from a nearby market where corn processing takes place. The waste was manually made into small particle size and was oven-dried to constant weight. The dried corn waste was thermally burnt in an open furnace until the ash was formed. The corn waste ash (CWA) was sieved with a mesh size of 40 µm to obtain fine carbonated waste ash catalyst (CWAC) and was stored in a tight container for further analysis.

2.2 Methods

2.2.1 Physicochemical properties of neem oil (N-oil)

The pure N-oil was characterized by determining its physicochemical properties using AOAC 1997 methods. Properties such as density, viscosity, moisture content, peroxide value, saponification value, iodine value, pour point, and flash point.

2.2.2 Catalyst (CWAC) characterization

The produced CWAC was characterized using a scanning electron microscope (SEM) and an x-ray diffractometer (XRD) to determine the morphological structures of the CWAC and the elemental compositions of the CWAC.

2.2.3 Acid treatments of N-oil: Esterification

Since the acid value of the N-oil has been reportedly greater than the normal vegetable oil (FFA < 1.5), hence, the N-oil was first treated with acid (HCl) with different concentrations until a low acid value was obtained. The acid treatment was as designed in five runs with a constant methanol-oil molar ratio. Table 1 displayed the variables and the number of runs needed to arrive at the lowest acid value (usually <3.0 mgKOH/g oil). The procedures adopted have been reported by Falowo and Betiku (2022). The procedures are as follows:

5 g of oil sample was dissolved in a hot mixture of 25 ml (95% v/v) diethyl ether and 25 ml ethanol in a 250 ml flask; the hot solution was neutralized with 0.1 M potassium hydroxide solution using three drops of phenolphthalein as an indicator. The acid value was calculated using equation 1.

$$Acid\ value\ (g\ KOH/g\ oil) = \frac{V\ X\ N\ X\ 282}{W}\ X\ 100 \qquad (1)$$

Where V = volume of KOH used during titration, N = Normality of KOH, and W = Weight of oil sample.

Table 1: The variables and acid concentrations' for esterification stage

Runs	HCl concentrations	Methanol-oil molar ratio (vol./vol.)
1	1.5	3
2	1.7	4
3	1.9	5

4	2.1	6
5	2.3	7

2.2.4 CWAC treatments of esterified N-oil: Transesterification

The oil obtained after treatment with acid (HCl) is known as esterified oil with a low acid value. 0 mg KOH/g oil. This esterified oil was then converted in a second step using CWAC as a catalyst to biodiesel in the transesterification stage. The procedure was as earlier reported by Falowo and Betiku (2022), with little moderation. The procedures are as follows:

Biodiesel production was carried out using the esterified oil. 200 mL of the esterified oil was measured in a reactor, and 2.5 g of CWAC was mixed in until it was dissolved. The mixture was transferred to the reactor esterified oil, and the reaction was allowed to complete at the temperature rate of 60°C/60 min. At the end of the reaction, the biodiesel was separated from the by-products (glycerol-catalyst) using downward gravity settling in the separating funnel. The purity of the biodiesel was ascertained by washing with distilled water and drying over calcium chloride. The yield of biodiesel was determined using equation (2):

$$Biodiesel\ yield\ \ \%\left(^{wt.}/_{wt.}\right) = \left(\frac{Weight\ of\ biodiesel\ produced}{Weight\ of\ oil\ used}\right) X100 \qquad (2)$$

2.2.5 Properties of biodiesel

The quality of biodiesel was examined through its properties, and these properties were compared with the biodiesel recommended standards ASTM D6751 and EN 14214.

3. Results and Discussions

3.1 Physicochemical properties of N-oil

Found in Table 2 are the properties of the N-oil. The oil's viscosity (23.40 Cst.) demonstrated that it has a high flow resistance and can congeal if left at room temperature for a period of time. The oil is of high acid value, non-edible, and requires two steps for its complete conversion to biodiesel with acid and bio-base activated catalyst, as indicated by its high acid value (10.50 mg KOH/g oil), which indicates an FFA of 5.25%. The oil's tendency to form soap during production was indicated by the saponification value; the higher value (186.70 mg KOH/g oil) found in this study suggested that the N-oil has the potential to form soap if improperly treated at high temperatures during the conversion process.

Table 2: Properties of the N-oil

Properties	**Blended oil**
Colour	Yellowish liquid
Moisture content (%)	0.02
Specific gravity	0.900
Viscosity @ 40 ^{o}C (Cst)	23.40
Acid value (mg KOH/g oil)	10.50
%FFA (as oleic acid)	5.25
Iodine value (g I_2/100g oil)	103.42
Saponification value (mg KOH/g oil)	186.70
Peroxide value (meq. O_2/kg oil)	5.30
Pour point (^{o}C)	221.00
Flash point (^{o}C)	212.00

The oil's pour and flash points, expressed in temperature units, provide information about its energy capacity when used as a raw material for biodiesel production (Mandari and Davari, 2021). Consequently, N-oil turned out to be a good raw material for biodiesel synthesis.

3.2 CWAC Analysis using SEM Analyzer

The structural and morphological picture (1000x: Mag.) of the CWAC that was acquired during SEM examination is shown in Fig. 2. It was noted that the picture is jointed, stiff, and has a fully bound shape. It also has a black-whitish color and a crack outlook. This can be ascribed to heat treatment using open-air burning for corn waste. The catalyst's heterogeneous atoms, which give it its many forms and sizes, are the result of the entire breakdown. The hue suggested that ash had formed during heat treatment. The fractured views show the porosity area needed for the transesterification base reaction, in which the alkalis are leaching on the powder's surface, to interact with the methanol-oil layer. Additional compounds, as shown by XRD, are in charge of cloud formation and burning bone-like observed. They also act as a hub for the adsorption of catalytic molecules on the oil surface, which displaces water molecules.

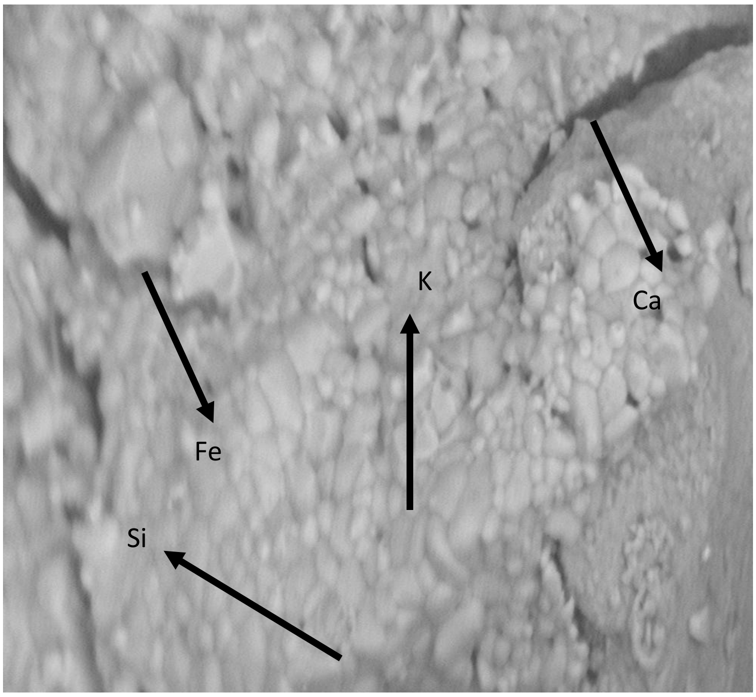

Fig. 2: SEM analysis of CWAC Analysis

3.3 XRF-FS Analysis of CWAC

XRF-FS is an analysis tool widely used for the elemental analysis and chemical analysis of materials. It can be used to identify the elements and the compounds present in solid catalysts. This tool was used to analyze the produced developed catalyst CWAC. It was observed that the phase angle produced high intensity for quartz, followed by illite and then albite. The last compound found was orthoclase (Fig. 3). The presence of quartz indicates the presence of SiO_2 salt, which is responsible for the catalytic current that helped in the oscillatory vibration of the 2θ phases. The 2theta angle of the XRF crystalline structure of the compound is approximately 90.2°, as determined by high-resolution X-ray diffraction (Sumera et al., 2017; Nyorere et al., 2024).

The components of illite, a salt, include hydromica, hydrous illite, hydromuscovite, hydrous mica, K-mica, micaceous clay, and sericite. The material can produce biodiesel while retaining its stability and capacity to hold onto moisture. Transesterification is the process by which biodiesel is transformed into oil, and it requires the NaAlSi3O8 chemical albite, which has a high base strength. Orthoclase is the potassium-aluminate-silicon-containing portion of the potassium-sodium feldspar solid. Pure orthoclase is rare since it frequently includes some sodium in its structure. This supports the idea of using catalysis to turn oil into biodiesel.

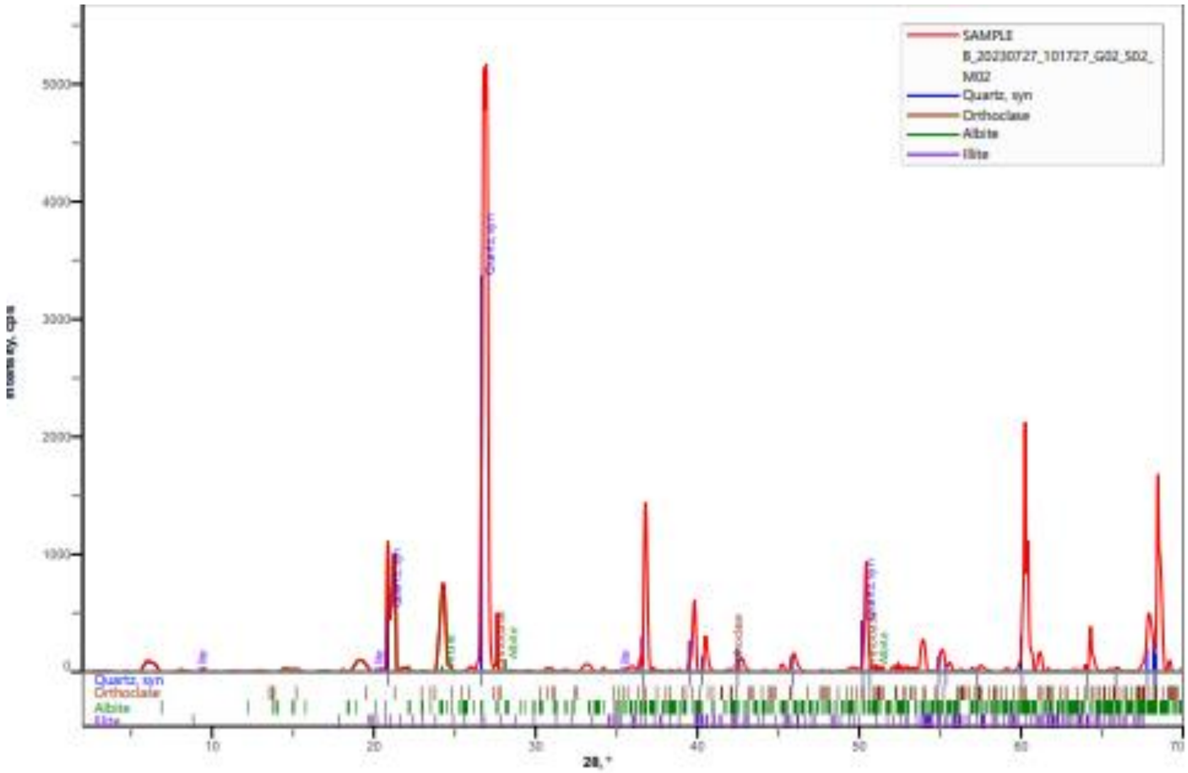

Fig. 3: Plots of XRF-FS analysis of the CWAC

3.4 Esterification of N-oil with HCl

Table 3 displayed the results of the esterified oil based on the acid values. The variables were randomized, and the values of acid values were computed. It was observed that the acid value at run 3 was the lowest value (2.56 mg KOH/g oil) at an acid concentration of 1.9% and a methanol-oil molar ratio of 5:1. This value corresponds to the FFA = 1.28 < 1.50%, which is acceptable for base catalyst transesterification for easy conversion by CWAC.

Table 3: Esterification of N-oil obtaining acid values

Runs	HCl concentrations	Methanol-oil molar ratio (vol./vol.)	Acid value (mg KOH/g oil)
1	1.5	3	5.60
2	1.7	4	4.72
3	1.9	5	2.56
4	2.1	6	2.58
5	2.3	7	2.63

3.5 Transesterification of esterified N-oil to biodiesel using CWAC

The results of biodiesel synthesized from the esterified N-oil in the presence of CWAC in methanol at different variable conditions and the yield (Table 4). It was observed that the yield of biodiesel varies at different variable conditions. The lowest yield (90.12 % (wt./wt.)) was obtained at run 1 with the lowest variable conditions, while the maximum yield of 95.40% (wt./wt.) was obtained at run 3 with a methanol-oil ratio of 7:1, a reaction time of 65 min and a CWAC concentration of 2.0 g. Nevertheless, all the yields show higher value at different concentrations. Fig. 4 displayed the plots of the yields against the number of runs. It was observed that the CWAC and methanol-oil molar ratio played a remarkably significant role in the yields of biodiesel due to higher regression parameters R^2 of 0.897 and 0.957, respectively. The reaction temperature and reaction time do not show a significant impact on the yield of biodiesel due to low R-squared values of 0.477 and 0.445. These results show that the key variable factors suggested to be considered in future work should be catalyst weight and methanol-oil molar ratio.

Table 4: The variables and the biodiesel yields

Runs	Reaction temperature (°C)	Reaction time (min)	CWAC weight (g)	Methanol-oil molar ratio (vol./vol.)	Biodiesel yield % (wt./wt.)
1	50	55	.1.0	3:1	90.12
2	55	60	1.5	5:1	92.24
3	60	65	2.0	7:1	**95.40**
4	65	70	2.5	9:1	94.80
5	70	75	3.0	11:1	93.50
6	75	80	3.5	13:1	92.76

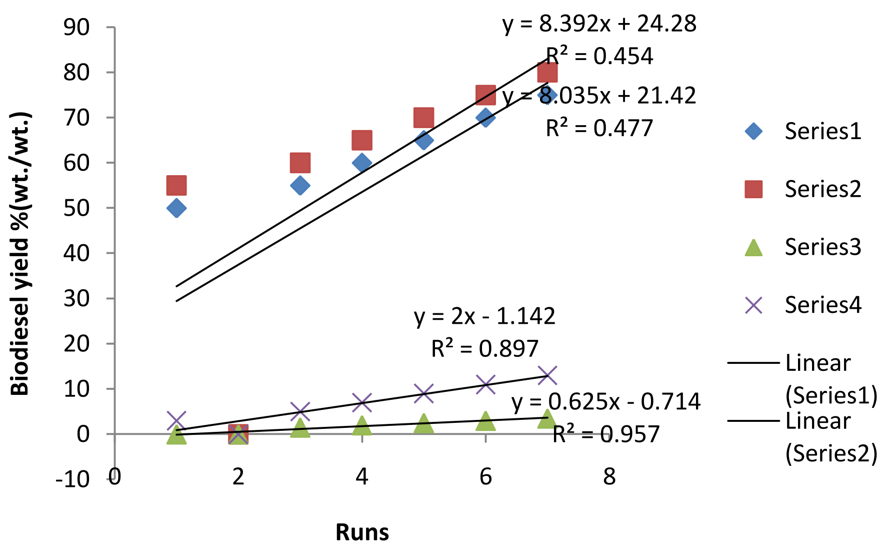

Fig. 4: Plots of biodiesel yield Vs. Runs number

3.6 Properties of synthesized biodiesel from N-oil

Depicted in Table 4 are the properties of the produced biodiesel as compared with the international standard recommended standard ASTM D6751 and EN 14214. The properties of the produced biodiesel were in agreement with what was reported for the set standard for fuel properties, and the biodiesel was found to be environmentally friendly and cheap due to waste utilization during the production process.

Table 4: Properties of biodiesel as compared with recommended standard

Parameters	BOB	ASTM D6751	EN 14214
Specific gravity	0.860	-	860-900
Viscosity @ 25 °C/ (mm^2/s)	1.92	1.9-6.0	3.5-5.0
Moisture content (%)	<0.01	<0.03	0.02
%FFA (as oleic acid)	0.22	0.40 max	0.25 max
Acid value (mg KOH/g oil)	0.44	0.80 max	0.50 max
Iodine value (g I_2/100g oil)	98.72	-	120 max

Saponification value (mg KOH/g oil)	123.40	-	-
Peroxide value (meq. O_2/kg oil)	8.76	-	12.85
HHV (MJ/kg)		-	-
Cetane number		57 min	51 min
API		39.95 max	-
Diesel index		50.4 min	-
Cloud point (^oC)	+12	9 min	-
Flash point (^oC)	100	50 min	-
Pour point	--15	-2	-28

Conclusion

The study concluded that neem oil has a high acid value (10.50 mg KOH/g oil) and is non-edible. This oil (N-oil) was converted to a low acid (2.56 mg KOH/g oil) value using HCl at 1.90% concentration. The heterogeneous catalyst used was derived from waste corn, and it was found to be rich in quartz, illite, orthoclase, and other minerals that are bio-based in nature.

Biodiesel production was at its maximum at a methanol-oil molar ratio of 7:1, and the properties were found to be in agreement with the biodiesel recommended standard. The study concluded that the produced biodiesel is environmentally friendly and can be used with or without blends.

Declarations

Ethics approval and consent to participate

Not Applicable

Consent for publication

All authors consented and agreed to take part in this study as research participant.

Competing interests

Authors declares no competing interests whatsoever

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