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# SUSTAINABLE PRODUCTION OF BIO-LUBRICANTS FROM NEEM SEED OIL USING EGGSHELL-DERIVED CALCIUM OXIDE CATALYST

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**ABSTRACT**

Power and energy are prerequisites for material driving. Nowadays in developing countries (Nigeria), more work needs to be done to find inexpensive and environmentally benign energy fuels to replace home and vehicle lubricants. This will signal a shift away from the use of fossil fuel-based products and toward cleaner, greener products as an alternative to the current energy system. The process of turning Neem seed oil into biolubricant is being studied in this work. Additionally, calcium oxide was produced by calcining egg shells and then activated using a solution of phosphoric acid. TGA and FT-IR were used to characterize the activated calcium oxide that was generated. Using activated calcium oxide as a catalyst, methanol was also used to transesterify Neem seed oil (biodiesel), which was then transesterified once more using trimethylolpropane (TMP). The target Biolubricant was produced under reflux at various reaction conditions, and it was then characterized using FT-IR and GC-MS. The biolubricant's physicochemical properties were examined using techniques approved by the American Society for Testing and Materials (ASTM). The analysis of parameters like viscosity (53.2), cloud point (2.8), pour point (-8.7), flash point (218), and viscosity index (128) of the Biolubricant revealed results that were in line with the ASTM specification for lubricant.

**Keywords**: Neem seed oil, Eggshell, calcium oxide, Methanol, TMP,

## I.INTRODUCTION

Growing concern over the effects of fossil fuels on the environment has led to a renewed interest in the usage of lubricants made from vegetable oils. Numerous businesses have created and sold bio-based lubricants [1,2]. Since bio-based lubricants maintain the technical criteria of traditional lubricants, they represent a possible substitute for mineral oils. According to Babatope and Rachael [3] bio-based lubricants have a high lubricity, viscosity index, and flash point. They are biodegradable lubricants made from both edible and non-edible vegetable oils.

However, these synthetic oil-based lubricants are much more expensive than mineral oil-based lubricants [4]. The improper after-use disposal of the available lubricants creates severe environmental issues by polluting the water bodies [4].

The aforementioned problems can be effectively resolved by creating an effective lubricant from a non-edible plant oil-based stock because it is renewable, biodegradable, and environmentally benign [5]. Compared to mineral oil basis stocks, vegetable oil base stocks have better lubricating qualities, low volatility, good biodegradability, high thermal stability, and non-toxicity [6]

The hunt for alternative fuel has gained new momentum due to the rising and oftentimes volatile cost of conventional lubricants and the increasing environmental concerns. However, this is limited by severe recessionary constraints brought on by a decline in demand; as a result, supply and demand for mineral oils are equal. Alternative energy sources must be investigated urgently due to the depletion of fossil fuels and the growing concern over their negative effects on the environment. However, the discovery of petroleum and the availability of inexpensive oils led to the abandonment of this concept. Crude oils derived from fossil fuels are still utilized as raw materials [7].

Since bio-based lubricants maintain the technical criteria of traditional lubricants, they represent a possible substitute for mineral oils. Given the significant discrepancy between the availability and demand for edible vegetable oil, it is not practical to use it to make lubricants and cutting fluids [7]. Although the use of lubricants derived from petroleum-based stocks has expanded widely, their non-biodegradability and non-renewability pose a serious threat to the environment and sustainability. It is now necessary to search for sustainable, environmentally friendly, and biodegradable feedstock for the lubricant industry. [8,9]. -Vegetable oils that are renewable, non-toxic, and biodegradable are now the foremost option for environmentally friendly lubricants, including grease and hydraulic oils. Consequently, altering and combining bio-based oils like Neem seed oil to provide them desirable properties for a range of lubricating uses may offer good substitutes for feedstock made of petroleum. The goal of the research is to use waste egg shell as a catalyst to create Biolubricant from Neem seed oil utilizing a CaO source [10].

## II.MATERIALS AND METHODS

### Materials

Methanol (99.5%), potassium hydroxide (85.0%), trymethalolpropane (98.0%), Phosphoric acid (46.0%), and sodium bicarbonate (95.0%) were all of the analytical grades and were purchased from Sigma-Aldrich (Merck).

### Methods

**Sample collection and preparation**

The eatery in Usmanu, Danfodiyo University Sokoto micro market is where the eggshell sample was obtained. The CaO catalyst was made using the calcination process on a discarded eggshell, using the modified method described by [3]. After the distilled water wash, the eggshells were sun-dried. After that, the cleaned eggshell was crushed and burned for an hour at 800 degrees Celsius in a furnace. The resulting solid product was sieved, crushed, and stored in airtight sample bottles after cooling. To avoid air contact, the sample vials were stored in the desiccator.

### Activation of CaO catalyst

Phosphoric acid was used as the active agent to impregnate a known quality of the powdered sample, thereby activating the catalyst. A mixture of 15 g of activation agent and 5 g of calcined eggshells was used for impregnation. After 30 minutes of stirring, a paste was created in this mixture, which was then left to stand for 24 hours. A filter paper was used to filter the active substrate. The filter paper holding the sample was placed over a conical flask, and the mixture was gently cleaned by pouring distilled water over it. Until neutrality, the filtrate's pH was measured on a regular basis using a pH meter. After that, the activated substrate was dried for ten minutes at 1050C in an oven [3].

### Characterization of the Raw and Activated Calcium oxide derived from eggshell

Using a Carry 630 Model Spectrophotometer, the Fourier transform infrared (FT-IR) spectroscopic study of both activated and raw calcium oxide was performed at the Central Advanced Science Laboratory, Usmanu, Danfodiyo University Sokoto. The dry calcium oxide samples were combined with potassium bromide (KBr) at a weight ratio of one to twenty, and then ground into a fine powder for analysis. After three hours of drying at 1000C, the material was formed into thin pellets using manual machinery. At this temperature, the spectra were obtained by collecting 100 scans at a wavelength of 4000 cm-1.

### Thermogravimetric Analysis (TGA) of the activated Calcium oxide

Thermal gravimetric (TG) was carried out using TA-60WS thermal analyzer. The 14.32 g of the sample were placed on a cleaned pan and inserted into the machine after calibration the heating program of the machine was 5$^{o}$c per minute starting from room temperature and raised to 800$^{o}$C. The machine started with a heating rate of 5 °C per minute, starting from room temperature up to 800°C in inert condition. Biolubricant Synthesis by Double Transesterification of Neem Seed Oil After generating methyl esters of fatty acids (biodiesel) in the first step, trimethylolpropane (TMP) was reacted with to create Biolubricant.
Methyl Ester Synthesis using CaO derived from the waste eggshell. Calcium oxide served as a catalyst in the transesterification of 400g of neem seed oil with methanol. The amount of catalyst was 0.5% w/w of the oil or 2g of catalysts, and the weight ratio of oil to methanol was 3:1, or 48g of methanol and 400g of oil. For one hour, the process was carried out at 60°C to create glycerol and biodiesel. After allowing it to settle for 20 hours, the biodiesel and glycerin were separated by gravity using a separating funnel [11].

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**Synthesis of Biolubricant**

The previously made methyl esters of Neem oil (Biodeiesel) were heated to 70˚C in a water bath after being weighed (100 ml) in a 500 ml reaction vessel. After that, 0.9 g of catalyst solution based on CaO was added. Twenty grams of TMP crystals were added to the reaction vessel after ten minutes, and the reaction was allowed to continue for four hours at 100˚C with reflux. It was decided to let the reaction mixture cool to room temperature. The mixture was then poured into a separatory funnel, and the biolubricant, or TMP triester, was collected as the bottom viscous layer [11].

## III. RESULTS AND DISCUSSION

FTIR was used to analyze the functional groups of the raw and activated calcium oxide that were produced during the calcination of eggshells. It was noted that the functional groups differed before and after the calcium oxide was activated as shown in table 1 and figure 1&2. The OH group of calcium hydroxide is responsible for the broad band seen in the FTIR spectra of both raw and activated calcium oxide at 3459 $cm^{-1}$. According to Rafah [12] the presence of $CO_3^{2-}$ ions is indicated by the absorption bands at approximately 1397 $cm^{-1}$, while the presence of $HCO_3^{2-}$ ions is indicated by the absorption at 712.3 $cm^{-1}$.

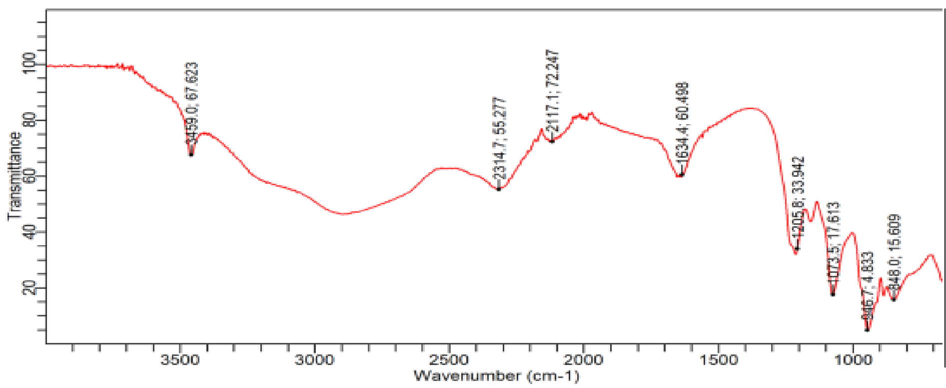


Figure 1, show FTIR spectrum of activated eggshell

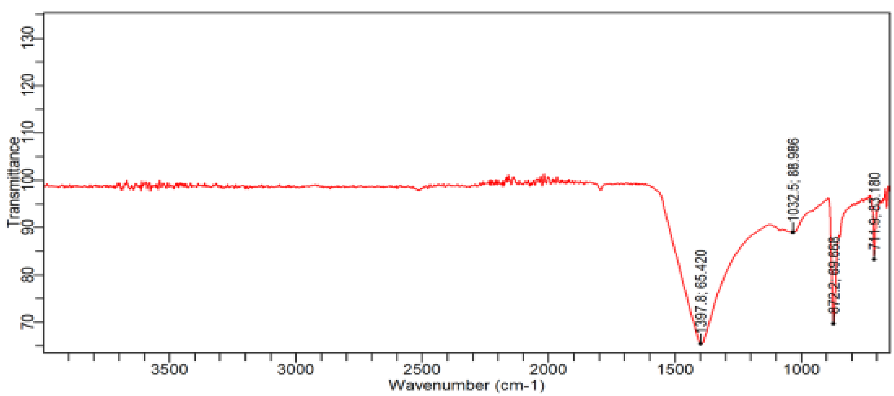


Figure 2: show FTIR spectrum of raw eggshell

Additionally, absorption at about 848 cm1 was noted, indicating the existence of CaO. Ahmad [8] likewise reported an identical absorption. The spectrum showed specific absorption at 2314 $cm^{-1}$ indicating the existence of P-OH[8]. After activation by acid, however, almost the same peaks were seen, albeit with varying intensities of vibrational peaks, except the peak of the phosphoric group observed at 2314 $cm^{-1}$ for the P-OH bond. For example, as compared to that of inactivated calcium oxide, the peak of the CaO group of activated calcium oxide, which was observed at 848 $cm^{-1}$, became less broad [12].

**Table 1: Absorption bands and functional groups of activated calcium oxide and Raw eggshell**

| Absorption band ($cm^{-1}$ | Raw Eggshell | Absorption band | Activated CaO |
|---|---|---|---|
| 3592 | O-H | 3459 | O-H |
| 1032 | $CO_{23-}$ | 1397 | $CO_{23-}$ |
| 872 | $HCO_2^{3-}$ | 713 | $HCO_2^{3-}$ |
| 711 | CaO | 848 | CaO |
| Nil | Nil | 2324 | P-OH |

The starting weight of the refluxed calcined eggshell is 13.25 mg, as shown by the TGA and DTA curves of the synthesized CaO catalyst from the eggshell in Figure 3. The weight began to decrease to 13.10 mg at 3.22 minutes as the temperature increased to 62.77 °C, which may have been caused by moisture loss and its high hydrophobicity. This could be because of the loss of very low volatile impurities and carbonates attached to the surface of CaO, respectively, when the temperature rises over 699.370 °C, from 12.19 to 8.65 mg at 105.54 minutes [12]. Following that, the curve steadied, signifying the termination of thermal degradation

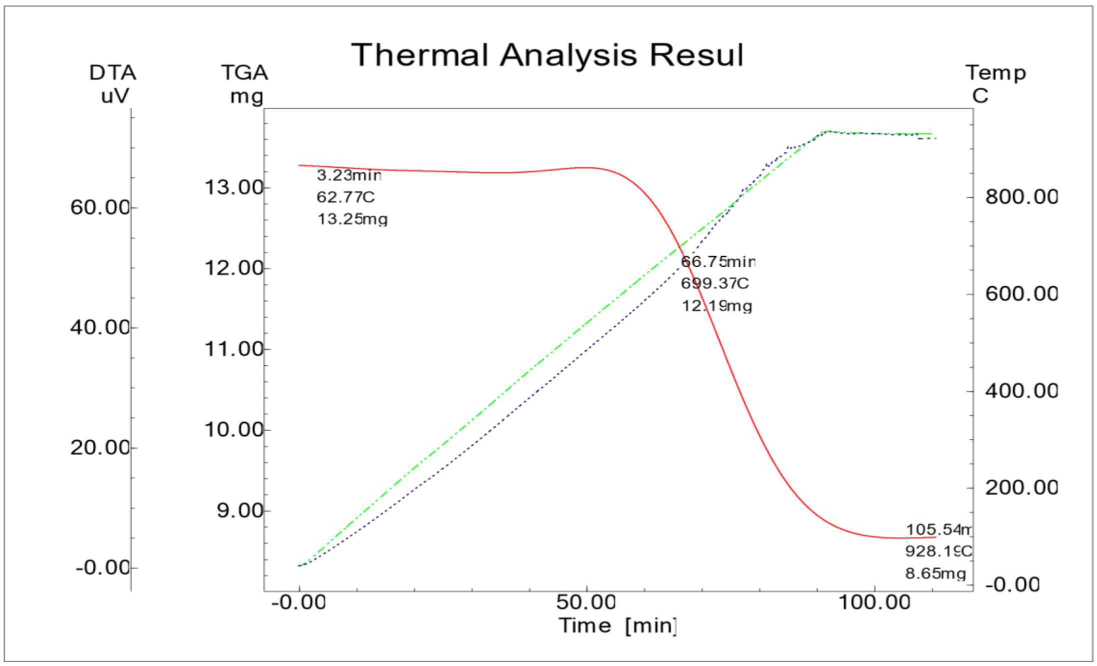


Figure 3: Thermogravimetric analysis (TGA) of calcium oxide produced

**Characterization of the Biodiesel and Biolubricant produced**

Utilizing activated calcium oxide made from eggshells as the catalyst, the biodiesel' and Biolubricant FT-IR studied as shown in Table 2, reveals the primary absorption band's frequency at 2929$cm^{-1}$, illuminating the C-H bond vibration of alkanes. A distinct ester group absorption as shown in figure 4, by the stretching absorption of C=O, which can be seen at approximately 1748 $cm^{-1}$, and the alcohol's C-O-H bending vibration is most likely indicated by a sharp stretching absorbance band at 1377 $cm^{-1}$.

Additionally, absorption at 1456 $cm^{-1}$, which is indicative of CH2 alkane absorption, was noted. Alcohol was also shown to exhibit C-O stretching absorption at 1162 $cm^{-1}$, as well as acute absorption at 721 $cm^{-1}$, which suggested CH aromatic bending vibration. Zayyanu et al [13] also reported absorptions that resembled the ones shown in the present work. But the spectrum derived from the biodiesel analysis reveals the existence of three main peaks: one for carbonyls (C=O absorption), one for alkyls (C-H), and one for esters (C-O absorption band)

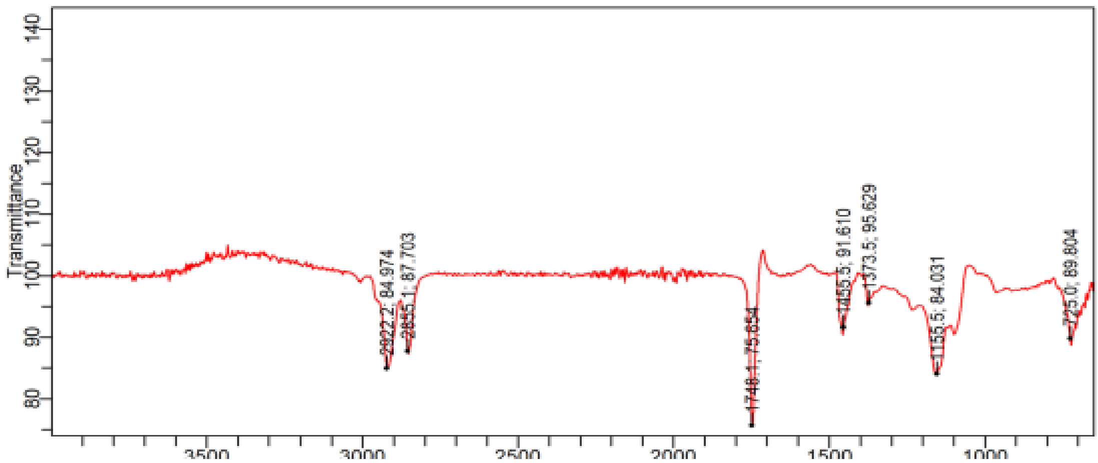


Figure 4: showing the FTIR spectrum of biodiesel

Double esterification of methyl esters generated from the transesterification of Neem seed oil, was also study by using FTIR. A sharp stretching absorbance band at 1168 $cm^{-1}$ most likely reflects C-O stretching for C-O-C linkage in the ester, and the stretching absorption of C=O observed at about 1742 $cm^{-1}$ shows a typical absorption of the carbonyl group.

However, the spectrum acquired during the Biolubricant analysis examination reveals the existence of prominent peaks that correspond to the O-H absorption for alcohols, the C=O absorption for carbonyls, and the C-O absorption band for esters. It is reasonable to conclude that the spectrum found corresponded to an alcohol compound that was joined to the ester group. Once more, Table 3 displays the absorption band and potential functional groupings found [13]

**Table 2: Shows FTIR absorption bands and functional groups of biodiesel and Biolubricant**

| **The absorption band of Biodiesel ($cm^{-1}$)** | **Bond** | **Absorption band of Biolubricant** | **Bond** |
|---|---|---|---|
| **1377** | O-H | 3226 | O-H |
| **1758** | C=O | 1752 | C=O |
| **1162** | C-O | 1159 | C-O |
| **2939** | C-H | 2817 | C-H |
| **1456** | CH2 | Nil | Nil |

**GC-MS analysis of the biodiesel Product**

Eggshell-derived activated calcium oxide was used as a catalyst in an esterification process between methanol and Neem seed oil. GC-MS reveals the presence of four organic compounds in both biodiesel and Biolubricant as shown in Table 3 namely: methylpalmitate, methylcarboxylate, linoleic acid, methyl stearate, and methylmyristic acid, octadecanoic acid, hexadecanoate, and palmitica acid respectively. Zayyanu [13 ] also noticed similar esters are produced in its Biolubricant.

**Table 3: Common Name of compound Present in Biodiesel and Biolubricant produced using GC-MS.**

| Biodiesel | Molecular formula | Biolubricant | Molecular formula |
|---|---|---|---|
| **Methylpalmitate** | C17H34O2 | Methylmyristic acid | C15H24O2 |
| **Methylcarboxylate** | C11H18O4 | Octadecanoic acid, methyl ester | C12H24O2 |
| **Linoleic acid** | C19H34O2 | Hexadecanoate methyl ester | C17H34O2 |
| **Methyl stearate** | C19H36O2 | Palmitic acid ethyl ester. | C10H38O4 |

**Physicochemical Parameters of Biolubricant produced**

Physical-chemical Characteristics of the Produced Bio lubricant along with the oil's applications, the physicochemical qualities are crucial criteria that provide valuable information. Kinematic viscosity, pour point, cloud point, flash point, and density are a few of these characteristics. Table 6 displays the physicochemical characteristics of the biolubricant generated in accordance with the ASTM D5 criteria [12].

**Table 4: physicochemical Properties of Biolubricant in Comparison with ASTM Standards**

| Properties | Biolubricant produced | ASTM Limits D5 |
|---|---|---|
| Kinematic Viscosity | 53.20 | >41.4 |
| Pour point oC | -8.70 | < -10 |
| Cloud point oC | 2.80 | -15 to 5 |
| Flash point oC | 218 | 220 |
| Viscosity index oC | 128 | >90 |

**Kinematic Viscosity**

Since kinematic viscosity influences fuel atomization, lubricity, and fluidity, it is the most significant attribute of oil. Fuels with high viscosity result in inefficient combustion and increase exhaust emissions, while fuels with low viscosity may not offer enough lubrication, leading to wear[14]. According to Table 4, the kinematic viscosity of the Biolubricant produced at 40 °C is 53.20. A similar value was obtained by [3] investigated the synthesis of Biolubricant from Neem seed oil catalyzed by calcium oxide from snail shell; they came to a similar conclusion (54.87). The viscosity of the Biolubricant derived from Neem seed oil satisfied the standard values of ASTM standards. The result of kinematic viscosity obtained is highly favorable in terms of ignition due to the lower value of viscosity, which is capable of improving the properties of oil and is effectively used for better engine performance.

**Pour point**

The temperature at which a liquid loses its ability to flow is known as its pour point. The lowest temperature at which oil can be poured out of a container is its definition. In this work, the pour point (-8.70) was used to calculate the sample's freezing point. The ASTM permitted pour point limit is less than -10 °C, which is comparable to [3, 13] result of -90 °C.

**Cloud point**

The temperature at which dissolved materials become partially soluble and precipitate as a second phase, giving the fluid a cloudy appearance, is known as the cloud point [14]. As shown in Table 4, the ASTM regulation for the maximum permitted values of cloud point falls between -15 and 5 °C. The cloud point of the Biolubricant produced (2.80). This is similar to the work of Bosede and Attamah (2018) to be 2.8 °C. It is evident from the outcome that the values obtained for the lubricating oil are within the ASTM criteria as reported by [13].

**Flash point** The flash point of the synthesized Biolubricant was found to be 218 0C. Rengasamy *et al.* [14]. also obtained a similar result (215 °C) when t studied the production of Biolubricant from castor-based oil. The result obtained in this work was also in conformity with the ASTM specifications, as shown in Table 6. What is meant by the term "flash point" is the minimum temperature at which fuel gives a momentary flash on ignition under specified test conditions

**Viscosity index**

When temperature variations are applied, the lubricant viscosity properties are displayed by the viscosity index. The synthesized bio-based lubricant's viscosity index of 128 was found to be similar to that of other plant-based Biolubricant and the result of [13] which is 136.43 the outcome was likewise in compliance with the ASTM criteria.

## IV.CONCLUSION

This study showed how to produce a Biolubricant by esterifying methyl esters with TMP over eggshell-prepared activated calcium oxide. By activating and calcining eggshells with phosphoric acid solution, egg shells can be effectively used as a source of calcium oxide for the synthesis of solid acid catalysts (activated calcium oxide). The esterification reaction with TMP was successfully and efficiently catalyzed by the generated catalyst, yielding Biolubricant.

## ACKNOWLEDGMENTS

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