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# Synthesis, characterization and formation of $KNO_3$ treated CaO-MgO composite catalysts for biodiesel production using Neem seed oil

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## Abstract
Biodiesel production is a valuable process, which needs a continued study and optimization process because of its environmentally advantageous attributes and its renewable nature. The catalyst solid heterogeneous ($KNO_3$/CaO-MgO) catalysts were used in this work. The later was derived from $Ca(NO_3)_2.4H_2O$ and $Mg(NO_3)_2.4H_2O$, the activity of the catalyst was improved by doping the solid composite (CaO-MgO) with $KNO_3$ via impregnation method followed by calcination at 600°C for 3 h. The catalyst characterization was conducted using FT-IR and SEM. The fuel properties such as specific gravity, kinematic viscosity, flash point, fire point and acid value were determine and compared with the ASTM standard. The $KNO_3$/CaO-MgO catalyst yield maximum biodiesel of 78% was obtained at optimum reaction condition of catalyst loading 0.9% w/w; reaction temperature of 50-55°C; reaction time 24 h; methanol to oil molar ratio of 12:1 and stirring speed of 600rpm. From the obtained results it was apparent that the produced biodiesel fuel was within the recommended standards of biodiesel as fuel.

## 1. Introduction
Over the decades, an effort has been devoted to the search for renewable energy as an alternatives to fossil fuels [1, 2]. Biodiesels, consisting of long-chain fatty acid methyl esters and as an alternative renewable energy, has fascinated a significant interest regarding the limited fossil fuel reserves and the intensified environment pollution [3, 4, 5]. Biodiesel production is generally carried out using catalytic transesterification of animal or vegetable oils with methanol. Unlike the homogeneous catalysts, the heterogeneous catalysts can be easily recovered, regenerated, and reused and thus known to be eco-friendly. A variety of solid-based heterogeneous catalysts such as alkali earth metal oxides (CaO, MgO, SrO, and BaO), transition metal oxides (ZrO, $TiO_2$, ZnO and $SiO_2$), and zeolite were used in the transesterification reactions without the presence of free fatty acid (FFA) and water [6, 7]. Heterogeneous catalysts have gained a significant interest. They simply separated from the reaction mixture and reused which in turns simplify the biodiesel process and eliminate the downstream processing steps. Moreover the heterogeneous catalysts are environmental friendly and attracted the researcher's attention [8, 9]. Neem (*Azadirachtaindica*) is a tree in the mahogany family Meliaceae which is abundantly grown in

varied parts of Nigeria. The Neem grows on almost all types of soils including clayey, saline and alkaline conditions. Neem seed obtained from this tree are collected, de-pulped, sun dried and crushed for oil extraction. The seeds have 45% oil which has high potential for the production of biodiesel. Neem oil is generally light to dark brown, bitter and has a rather strong odour that is said to combine the odours of peanut and garlic. It comprises mainly of triglycerides and large amounts of triterpenoid compounds, which are responsible for the bitter taste. It is hydrophobic in nature and in order to emulsify it in water for application purposes, it has to be formulated with appropriate surfactants [10, 11]. The methanolysis was found to be the most effective suitable process for the heterogeneous catalytic production of biodiesel from plant materials. The performance of ethanolysis was not as good as in methanolysis due to the higher water content of ethanol (0.44%) compared to methanol (0.08%) [12, 13]. In this paper solid catalyst derived from calcium nitrate and magnesium nitrate which was doped with potassium nitrate via impregnation method was synthesized and used as a catalyst for transesterification reaction of Neem seed oil to produce biodiesel.

## *2. Material and Methods*

### *2.1 Chemical*

n-hexane, methanol, ammonium hydroxide, potassium nitrate was obtain from Ideal scientific Calcium nitrate, Magnesium nitrate (Analar BDH), Ethanol, Phenolphthalein (Sigma Aldrich) and the deionized water was used throughout the investigation. The reagents were use as received without further purification.

#### *2.1.1 Seed Collection and Purification*

Fresh Neem seed were collected at Ringim Local government area of Jigawa state, the seed were shade dried for two weeks, grounded into powder using mortar and pestle, the powder material was packed in polythene bags for further use.

### *2.2 Oil Extraction from Neem Seed Extract*

Hundred grams (100g) of dried powder was put into the filter paper and rounded like cylindrical shape and place into the thimble, 250 ml n-hexane was placed in to round bottom flask and connected to the thimble, the thimble was also connected to a condenser, the whole soxhlet apparatus were placed on a hot plate connected to a power supply. The extraction begins for 4 hours, it was then the oil extracted completely from the seed.

$$\%\ \text{yeild} = \frac{massofextact}{massofsample} \times 100 \qquad (1)$$

This result of extract was use for the determination of free fatty acid, acid value and also for the production of biodiesel respectively.

#### *3.2.1 Pretreatment of oil:*

40.7 g of the extracted oil was mixed intensively with 33.7 g of methanol and 8.2 g of 25% methanolic solution of tetramethylammonium hydroxide for 30 min. the resultant mixture was allowed to separate overnight and the phases so obtained were subsequently withdrawn and analyzed

### *2.3 Preparation of CaO-MgO Composite catalyst*

2 M solution of calcium nitrate tetrahydrate $Ca(NO_3)_2{\cdot}4H_2O$ and magnesium nitrate tetrahydrate $Mg(NO_3)_2{\cdot}4H_2O$ were prepared followed by addition drop wise $NH_4OH$ solution until co precipitate, the precipitate was filtered and wash with distilled water and dry at 110$^o$c over night and then calcinated at

600°c for 3 hours using muffle furnace, the catalyst were impregnated by adding 2 M potassium nitrate solution then filtered and dry at 110°C then calcinated at 600°c.

*2.4 Determination of free fatty acid*

5 g of the oil was placed in a 250 ml volumetric flask, 25 ml of ethanol was added followed by 2-3 drops of phenolphthalein indicator, and the mixture was then heated for 10 minutes with constant shaking. The mixture was titrated against prepared solution of potassium hydroxide (0.1 M) until color change.

Calculation

$$\text{Free fatty acid} = \frac{0.5 \times FW \times M \times V}{m} \quad (2)$$

Where

FW= formula weight of KOH in g/mol

M= molarity of KOH in mol/dm$^3$

V= titer value

m = mass of oil

*2.5 determination of acid value*

The same procedure as in 2.2 above was repeated

Calculation

$$\text{Acid value} = \frac{FW \times M \times V}{m} \quad (3)$$

*3.6 Production of the biodiesel*

Biodiesel fuel blend can be conventionally prepared by using alkali or acid as catalyst. 50g of refined neem oil was mixed with 6g of methanol and 0.5g calcium oxide-magnesium oxide (CaO-MgO) was mixed. The experiments were conducted in a manner similar to Soxhlet extraction apparatus This mixture is taken in a 500ml round bottomed flask .The amount of catalyst that should be added to the reactor varies from 0.5% to 1% w/w. Using magnetic stirrer and heater equipment the above mixture is thoroughly mixed and maintained at a temperature of 50-55 °C for two hours. The mixture is then allowed to settle for 24 hours at which two separate layers are obtained. The top layer will be methyl ester of neem oil (fatty acid methyl ester (FAME) i.e. biodiesel) and the bottom one glycerin. Using a conical separating funnel the glycerin is separated at the bottom. To separate the FAME (fatty acid methyl ester) from glycerol, catalyst (CaO-MgO) and methanol, washing was carried out with warm water. Further water and methanol will be removed by distillation. Then the NaOH, Glycerol, methanol and water was treated with phosphoric acid for neutralizing the catalyst. Finally glycerin is obtained as a byproduct in case of alkali transesterification process.

*3.7 Determination of Fuel Properties of the Biodiesel*

A method of ASTM (American society of Testing and Materials) was used for the determination of fuel properties of biodiesel produce. The properties such as kinematic viscosity, specific gravity, cloud point, flash point, fire point, and sulfur content were carried out at Kaduna refining and petrochemical company (KRPC) to ensure quality of biodiesel produced.

*3. Results and discussion*

*3.1 Fuel Properties of Biodiesel:*

In this research the fuel properties of oil, biodiesel were determined and the result was shown in Table-1. From table, it can be seen that the properties of biodiesel and its blends appeared to be much closer to those of petro-diesel. However, the properties of Neem oil were found to be much higher values when compared to those of petro-diesel. Prior to and after extraction of the Neem oil, pretreatment, acid value and free fatty acids values are given in Table 1. Neem oil was found to have high acid value (9 mg KOH/g) before treatment but after treatment the acid value decline to 0.34 mg KOH/g which is nearest to that of Diesel which has the value of 0.35 mg KOH/g while for free fatty acid prior to treatment 5.4mgKOH/mg than value decline to 0.502 mgKOH/mg compared to the value of diesel 0.175 mgKOH/mg [14]. Due to exceedingly high fuel properties such as flash point (261°C), kinematic viscosity (44 $mm^2/s$), specific gravity (913.2), Fire point (222) and Pour point (28.6), the Neem oil must be upgraded or converted to another form prior to application as fuel [15].

**Table 1.0:** Comparisonsof Properties of neem biodiesel, crude neem oil and diesel

| Properties | Diesel | Neem oil | Neem oil biodiesel | ASTM method |
|---|---|---|---|---|
| Density($kg/m^3$) | 822 | 913.2 | 874 | D1298 |
| Viscosity at 40°c | 2.2 | 44 | 4.11 | D445 |
| Acid value(mg KOH/gm) | 0.35 | 9 | 0.34 | D664 |
| Free fatty acid(mg KOH/gm) | 0.175 | 5.4 | 0.502 | D664 |
| Pour point | -15 | 28.6 | 4 | D2500 |
| Flash point °c | 55 | 261 | 120 | D93 |
| Fire point °c | 74 | 222 | 128 | D93 |
| Hydrogen (% w/w) | 12.78 | 11.02 | N/d | - |
| Carbon(% w/w) | 81.33 | 78.31 | N/d | - |

A comparison with petro diesel shows the unsuitability of the Neem oil for use as fuel. Upon methanolysis however, the biodiesel product and its blends exhibit properties consistent with those of ASTM standard. Specifically, the specific gravity (874) is higher than that of typical biodiesel (822). The viscosity of the Neem oil biodiesel was reduced to 4.11 $mm^2/s$ which is nearest to that of diesel 2.2$mm^2/s$. Flash point and fire point value of 120 and 128 are more or near to that of diesel 55 and 74. The flash point and Fire point of Neem oil biodiesel was found to be higher than that of the blends and petro-diesel which make them safe for handling. Other oil properties Pour point was also found to be higher in Neem oil biodiesel [13]. The crude neem oil, however, was found to have much higher values of fuel properties especially viscosity, way above any of these standard limits –thus restricting its direct use as a fuel for diesel engine.

### *3.2 Effect of Catalyst Loading*

The influence of $KNO_3$/CaO-MgO catalysts was investigated at the predetermined optimum methanol-oil ratio. The methyl ester yield increased proportionally with the addition of 0.5 to 1% w/w $KNO_3$, with the highest yield (78%) corresponding to the limiting catalyst dose (0.9% w/w) (Figure 1). Therefore, $KNO_3$ loading of 0.9% w/w is optimum for the heterogeneous methanolysis.

### *3.3 Characterisation of the Catalyst*

FT-IR spectrum of CaO-MgO particle is shown in Figure 2. The peak around 547.80 wave number correspond Ca – O bond [16]. The peak at 671.25 and 856.42 wave number was Mg-O bond [17]. The absorption peak at 1141.90$cm^{-1}$ wave number is due to Ca-Mg bond. The peaks at 1411.94, 1481, 38, 1643.41 and 2360.95$cm^{-1}$ wave numbers were due to impurities present in the catalyst.

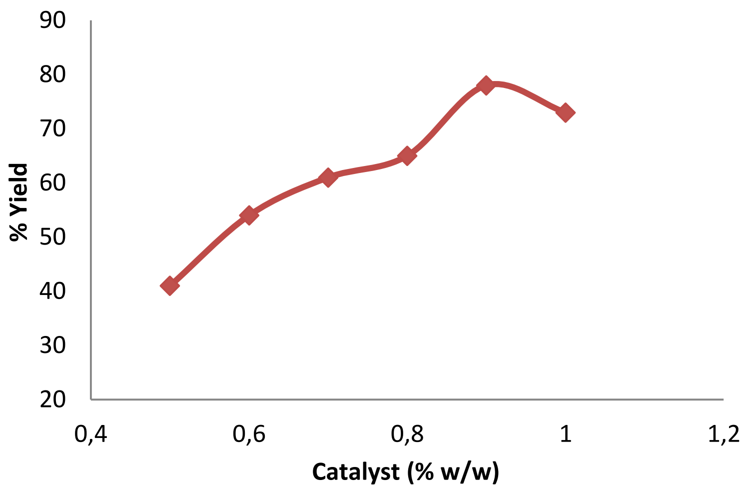


**Figure 1:** Effect of $KNO_3$/CaO-MgO catalyst for the biodiesel production

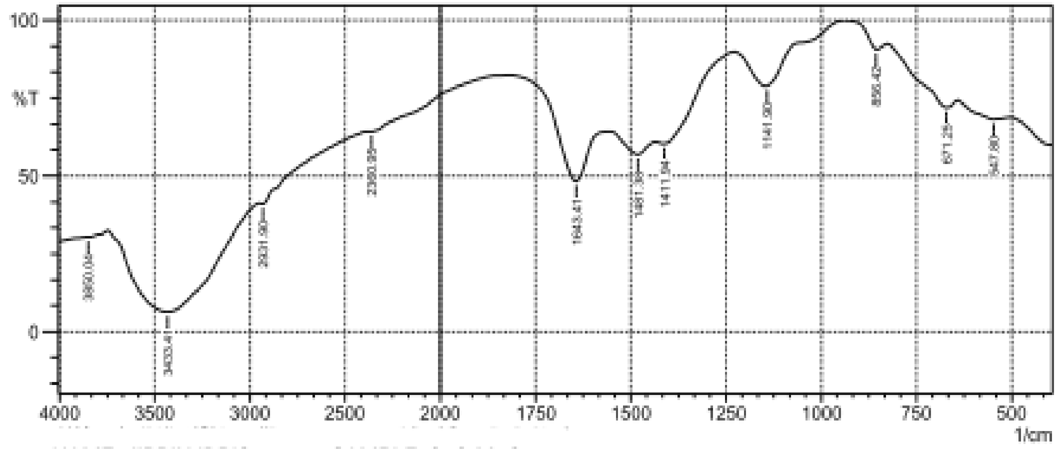


**Figure 2:** FT-IR spectrumof CaO-MgO Composite catalysts

The scanning electron microscopy (SEM) technique was used to obtain the information of the morphology and size of the CaO-MgO synthesized catalysts as shown in figure 3, the SEM image of catalysts indicated the structural morphology of the synthesized CaO-MgO [18-21].

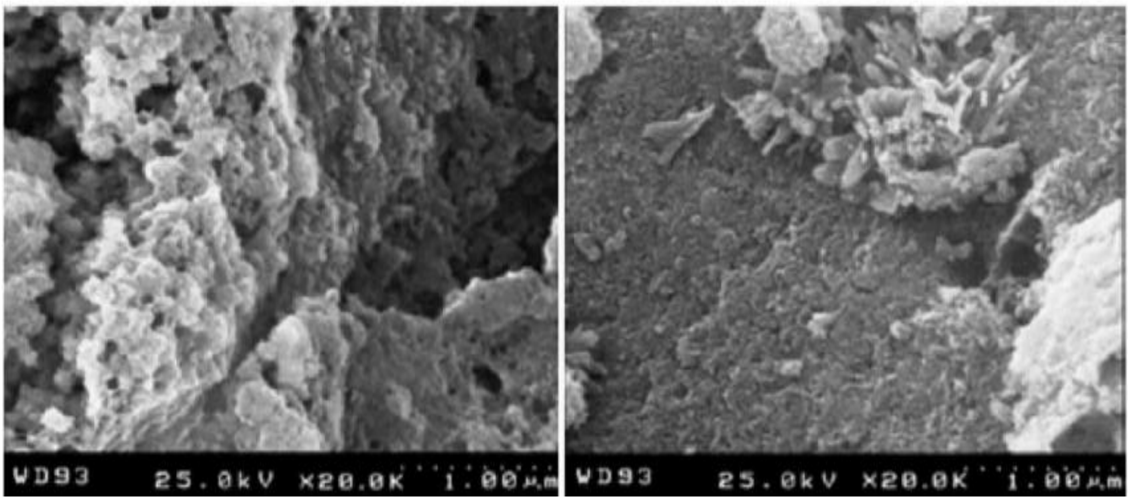


**Figure 3:** SEM image for CaO-MgO Heterogeneous catalysts

The particle morphology and size were directly imaged using SEM. SEM image shows lump of organized grains, the analysis informs the of the dimension of the grains to be in the order of hundred nano meter [22,23].

## Conclusion

The use of biodiesel as an alternative fuel has turned the technological aspect of energy evaluation to a growing change. The conversion of vegetable oil such as Neem oil to biodiesel has performed and a remarkable change of the fuel properties were observed. From the observed properties of biodiesel it is shown that properties were very close to diesel properties. During the production of biodiesel from Neem oil, the challenge is to reduce the cost of production low enough that it can compete with diesel, which will come as biodiesel producers improve and automate production operations. Physical properties of biodiesel such as relative density, viscosity, flash point, heating value and ester content were determined using standard test methods according to ASTM.

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