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# A Solid Mineral (Limestone) as a Potential Catalyst for Biodiesel Production from Yellow Oleander Oil (*Thevetia peruviana)*

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**ABSTRACT**

This work considers the use ofa solid mineral (limestone) as heterogeneous catalyst for biodiesel production from yellow oleander seed oil (YOO). Limestone was crushed and reduced to less than 200 μm, the crushed limestone was separated into eight samples, all of which were prepared by calcinating at 700$^{o}$C, and four samples were pre-soaked in methanol while the other four were not. It was noted that pre-soaking pulverized limestone in methanol and calcinating for 5 hours gave the highest calcium content of 58.48% as determined by EDXRF Spectrophotometer (EDX3600B). This was used for biodiesel synthesis. The biodiesel production was performed at catalyst amount of 4 g, reaction time of 70 minutes and methanol/oil ratio of 0.1. The biodiesel yield under this condition was 86.00 % (v/v) this was validated by running three experimental explicate. The physical state of the biodiesel was found to be liquid/reddish-brown at room temperature, acid value of 0.508 (mgKOH/g oil), FFA value of 0.254, iodine value of 73.20 (g $I_2$/100g oil), saponification value of 26.648 (mgKOH/g oil), cetane number of 234.580 among others. Qualities of the yellow oleander biodiesel (YOB) were compared to standards set by ASTM D6751 and EN 14214.

**Keywords:** Limestone, Catalyst, Biodiesel, Yellow Oleander Oil

## INTRODUCTION

Mineral resources are naturally occurring matters which comprises of industrial mineral, valuable metals, of which are solid, liquid or gaseous material in or on the Earth's crust in such form and amount that economic extraction of the commodity from the concentration is currently or potentially feasible [1,2].According to Professor Donatus Maduka Orazulike moderate mineral resource potential exists where geologic, geochemical and geophysical characteristics are favourable for resource accumulation are known or can reasonably be interpreted to be present but where evidence for

economic ore accumulation is vague or has not yet been found.

Homogeneous catalysts are catalysts which are in the same phase with the reactants; this type of catalyst has been successfully used for transesterification of biodiesel production. Dhoot et al. [3] produced biodiesel using alkali catalysed methanolysis. Ana[4] used Hexane/Ether mixture as catalyst to produce biodiesel. A major disadvantage of this type of catalyst is the difficulty of their recovery from reaction medium, and they are corrosive to equipment. It has also been reported that the use of homogeneous catalyst result in consequent problems (i.e. saponification, excess reactant consumption, environmental pollution, high alcohol to oil molar ratios and additional separation costs) which increase the overall cost of biodiesel production [5,6].

Ferdous *et al.,* [7] reported that heterogeneous catalytic process which involves the use of solid base catalyst was easy to separate from the transesterified product. For the purpose of studying heterogeneous catalytic process, researchers have tested a variety of solid base for the catalytic activity. Several studies have been carried out on various oxides used as heterogeneous catalyst which include; Granados et al. [8], Wang et al. [9], Alonso et al. [10], Yang and Xie [11], Albuquerque *et al.,* [12], Refaat, [13] among others.

Xie *et al.,* [14] prepared potassium loaded on alumina as the solid base catalyst; the prepared catalyst was employed for transesterification of soybean oil at reflux of methanol. Tin oxide was active for soybean oil methanolysis in a heterogeneous system reported by Abreu et al. [15]. It was reported that reaction yields up to 93 % in 3 h at 60°C. The catalyst was recovered and reused three times without any loss of catalytic activity. Zirconium oxide, titanium oxide and zinc oxide are among metal oxides that have attracted attention for biodiesel production due to their acidic properties [16].The base-catalyzed activities of single metal oxides, $La_2O_3$, MgO, CaO, and ZnO were compared by Bancquart et al. [17] and the results confirmed that stronger basicity of the catalysts resulted in their higher activity for transesterification.

Kim *et al.,* [18] reported that heterogeneous catalyst is recoverable, less corrosive, produce no soap, and can be reused. Its continual use minimize

separation and purification costs, makes it economically viable to compete with commercial petroleum based diesel fuels [5]. Several studies such as Kakati *et al.,* [19] have also examined the use of heterogeneous catalyst in the production of biodiesel.

The aim of this study is to determine the potential of limestone as a catalyst for biodiesel production, to analyze the elemental composition using EDXRF Spectrophotometer (EDX3600B) at calcinating temperature of 700$^{o}$C and at different time of 4, 5, 6, and 7hr. using the optimum condition to carry out biodiesel production.

## MATERIALS AND METHODS

### Yellow Oleander (*Thevetia peruviana*) Oilseeds

The YOO used in this work were collected from Government Secondary School, Ile Ife, Osun state, Nigeria. They were washed to remove dirt and sundried, thereafter the mesocarp and epicarp of the oilseeds were removed; the fruits were manually shelled to remove the kernels, which were milled using a blending machine.

### Chemicals

All chemicals used were of analytical grade. They include: n-Hexane, sodium hydroxide, potassium hydroxide, calcium chloride, methanol, ethanol, phenolphthalein, starch, potassium hydroxide, $CCl_4$, sodium thiosulphate, ethanoic potassium hydroxide, hydrochloric acid, isooctane, diethyl ether, iso-octane and ethyl alcohol.

### Yellow Oleander Oil Extraction

Soxhlet apparatus was used in this study, and n-hexane as extraction solvent. The apparatus was charged with 200g of powdered yellow oleander seeds, which was packed in a muslin cloth. A round bottom flask containing 250ml of n-hexane was fixed to the end and a condenser was tightly fixed at the bottom end of the extractor. The whole set up was heated up in a heating mantle at temperature of 60$^{o}$C. The extraction solvent in the solvent-oil mixture was recovered and recycled by distillation

### Analysis of Physiochemical Properties of Yellow Oleander Oil and Biodiesel

The physiochemical property of YOO extracted and biodiesel produced were analyzed. Standard ASTM D6751 methods were used to find acid value (ASTM D664), density (ASTM D5002), moisture content (ASTM D2709), specific gravity (ASTM

D287), cetane number (ASTM D613), free fatty acid (FFA) (ASTM D5555), iodine value (ASTM D1959) and saponification value (ASTM D464). Peroxide value was determined based on American Oil Chemists' Society [20]. Iodine value was estimated by applying Wijs method [21, 22].

**Catalyst Preparation and Activation**

The limestone samples were crushed and grinded to reduce the particle size to >200μm to ensure large surface area per unit mass. The catalyst activation was performed by calcinations of 4 samples of limestone each weighing 50g in a (Carbolite AAF 1100) furnace for 4, 5, 6 and 7 hours each. This same procedure was repeated for another set of 4 samples each weighing 50g pre-soaked in methanol in order to ascertain the sample with highest $Ca^{2+}$. The calcinated limestone samples were packed into a screwed bottle. The elemental composition of the limestone samples was carried out using EDXRF Spectrophotometer (EDX3600B) by Skyray Company, China. The machine was calibrated using silver standard as recommended while the analysis was carried out using ore standard calibration curve.

**Biodiesel Production**

The base catalysed reaction was carried out according to the work of Betiku and Ajala, [6]. In this work, 50ml of YOO was poured into 250 ml capacity spherical flat bottom flask placed on a hot plate with magnetic stirrer, set at a temperature of 60$^{o}$C.A known weight of calcinated limestone was dissolved in a known volume of anhydrous methanol and was quickly transferred into the preheated oil on the hot plate with magnetic stirrer. A uniform temperature of 60$^{o}$C was maintained throughout the reaction process.At the end of the experiment the resulting mixture was transferred to a separating funnel for glycerol and methyl ester separation, the product was allowed to separate by gravity for 24 hr. Two phases separated clearly, the less dense methyl ester at the upper layerwhile the denser phase of glycerol at the lower layer. Glycerol was tapped off leaving behind methyl ester in the separating funnel. The methyl ester left in the funnel was washed thrice with warm distilled water to remove residual catalyst, glycerol, methanol and soap. The washed methyl ester left in the separating funnel was tapped into a pyrex flask where it was dried over heated calcium chloride powder (1 g) placed in heating mantle to

absorb the untapped water. The dried methyl ester obtained was decanted into a clean pyrex flask to remove the hygroscopic calcium chloride sediment at the bottom of the heated flask. The biodiesel yield was determined by Eqn. 1.

$$Yield\ (\%) = \frac{YOO\ volume\ (ml)}{Biodiesel\ (methyl\ ester) volume\ (ml)} \quad (1)$$

## RESULTS AND DISCUSSIONS

### Properties of Oil Extracted

In this study, YOO obtained was liquid, orange-yellowish colour at room temperature, having moisture content of 0.0131, specific gravity of 0.8984 g/cm$^3$, and density of 0.774 g/cm$^3$.Acid and FFA values are 1.8048 and 0.9024 respectively; these are in close concordance with other researches such as Deka et al. [23] reported lower acid value of 0.568 andFFA value of 0.284 while Yarkasuwa *et al.,* [24 ]reported higher acid value 4.7 and FFA value of 2.4. The low FFA content of YOO obtained in this study was indicative of the good resistance of this oil to hydrolysis. Peroxide value measures the content of hydroperoxides in the oil [25] and its low value of 23.8 meq$O_2$/Kg oil indicates high resistance to oxidation.Other fuel property such as cetane number of the YOO wasdetermined to be 140.998. Cetane number is a measure of the fuel's ignition delay and combustion quality, since standard specification of cetane number for biodiesel is minimum of 40 [26, 27]. The cetane number shows that it had a high fuel potential.Transesterification of YOO could improve its fuel properties.

### Effect of Time on Catalyst Activation

Figure 1and 2 shows the elemental composition of the calcinated limestone samples analyzedusing EDXRF Spectrophotometer (EDX3600B). Limestone samples A1,B1,C1, and D1 were presoaked in methanol then calcinated for 4, 5, 6, and 7 hours respectively while limestone samples A2, B2,C2, and D2 were not presoaked in methanol, they were also calcinated for 4, 5 , 6, and 7 hours respectively in a (Carbolite AAF 1100) furnace at 700$^o$C.

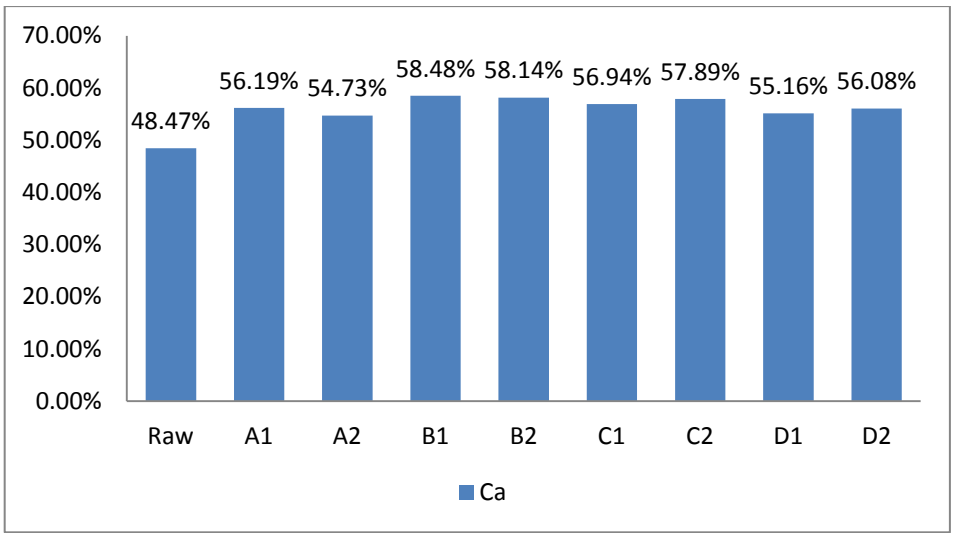
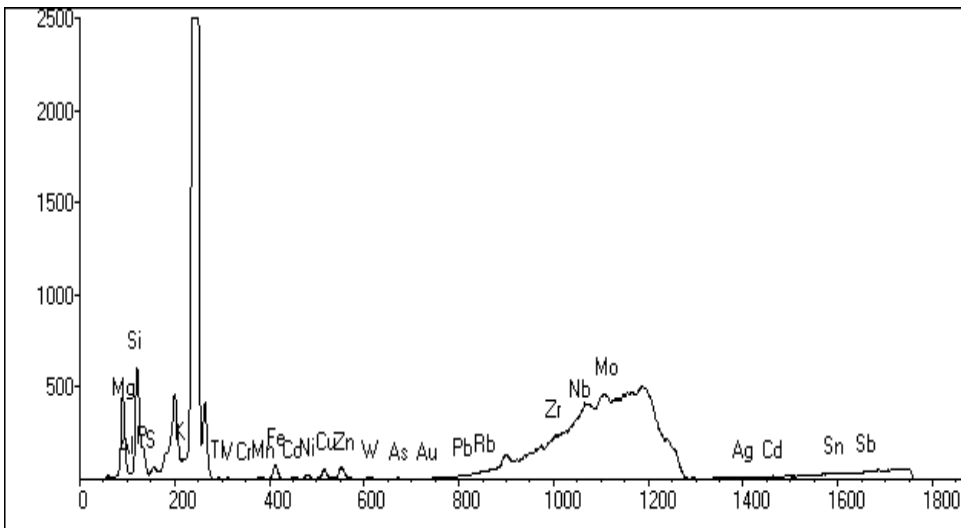



**Figure 1: Elemental analysis of limestone samples and their corresponding calcium content**

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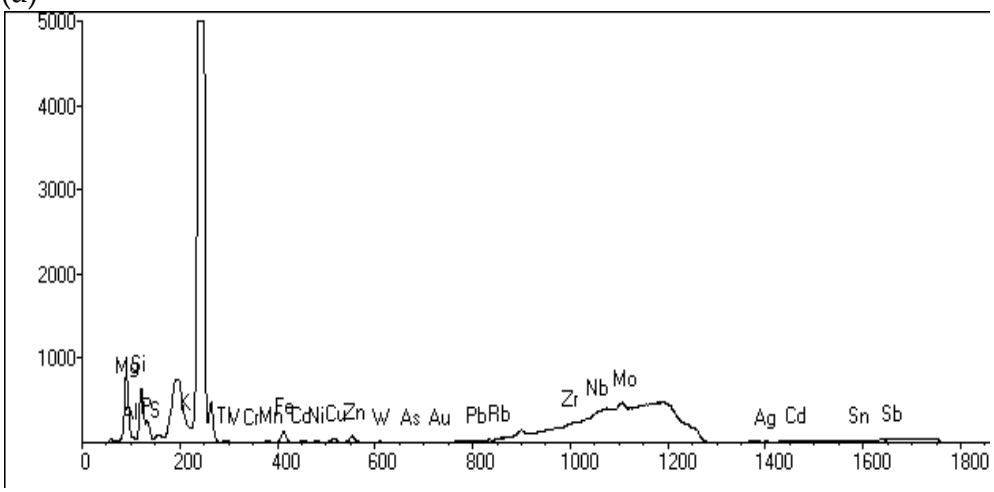

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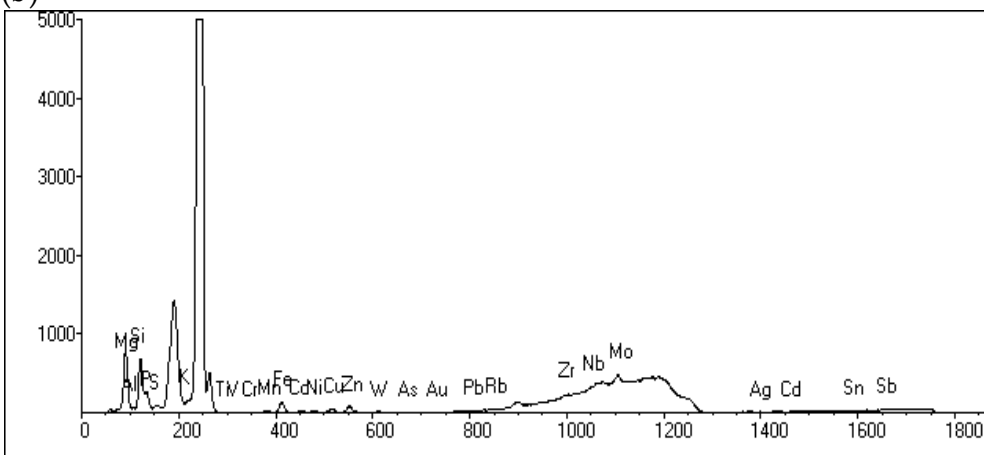
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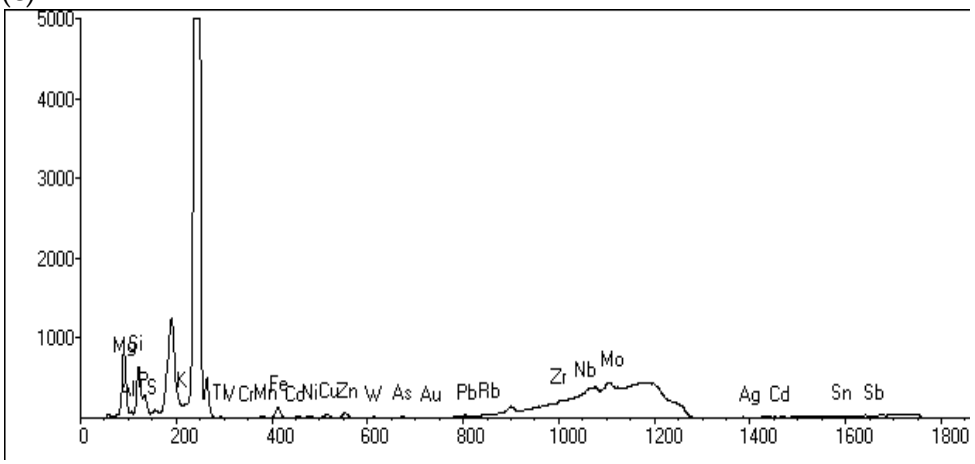
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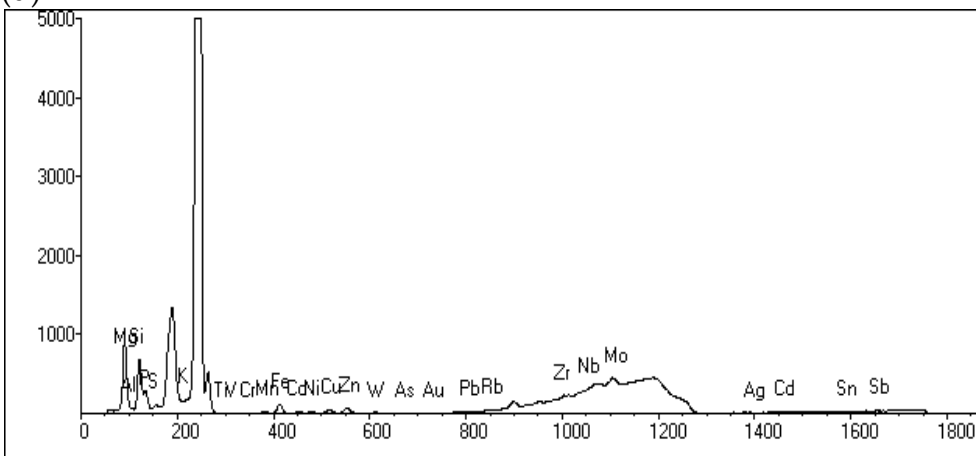
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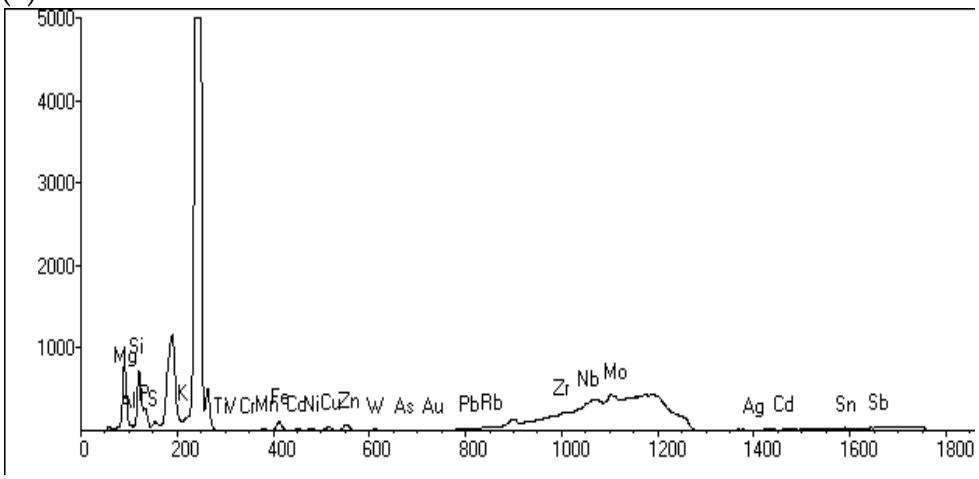
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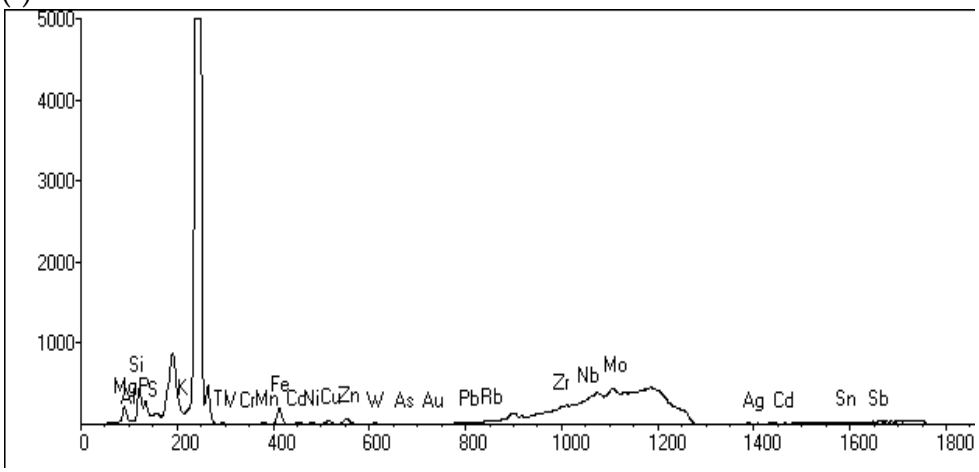
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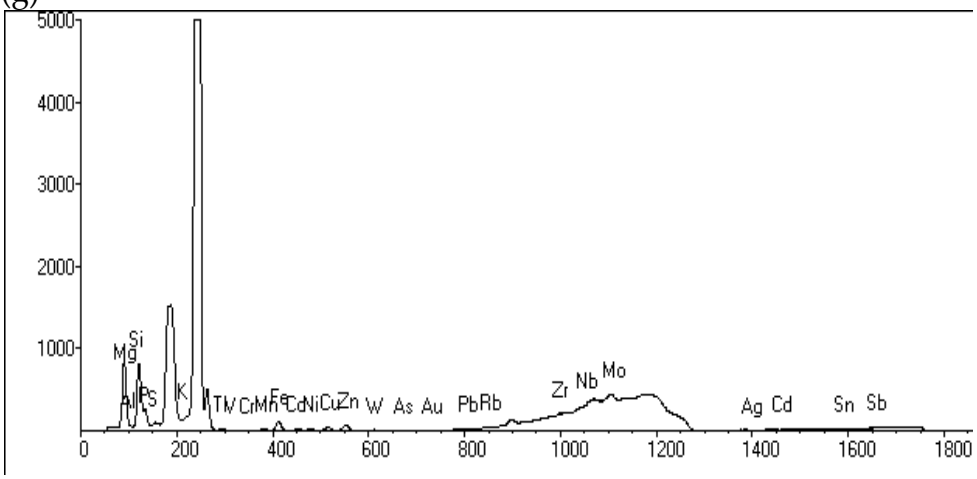
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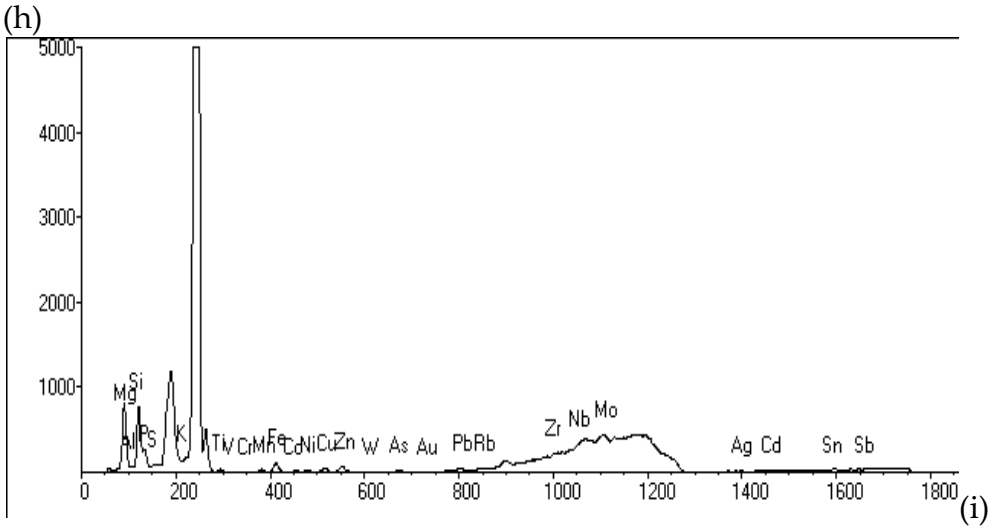


**Figure 2: EDXRF Spectrophotometer curve for limestone samples**

Figure 2 shows EDXRF Spectrophotometer curve for limestone samples where (a) is for the raw sample, (b), (c), (d), (e), (f), (g), (h), (i) are for samples A1, A2, B1, B2, C1, C2, D1, D2 respectively. It can be deduced that B1 has the highest content of calcium at 58.48%, whileA2 has the lowest amount of calcium at 54.73%. This shows there was an increase in the calcium content when compared with the raw sample which was not pre-soaked and not calcined having 48.47% calcium content. Therefore, pre-soaking pulverized limestone in methanol followed by calcination increased the elemental composition of calcium present in the limestone sample by reducing the composition of other elements present.

**Properties of Biodiesel Produced**

At room temperature, YOB produced was reddish-brown in colour with moisture content of 0.0044%. From Table 1, the density of the biodiesel produced was found to be 0.816 g/cm$^3$; this was in concordance with that reported by Deka et al. [23], Dhoot *et al.*, [3], and Adebowale et al. [28].This was within the range specified by EN 14214. The specific gravity was determined as 0.91, which is slightly higher than that specified by ASTM D6751 and EN 14214. The acid value of YOB was found to be 0.5076 (mgKOH/g), which was higher than that prescribed by EN 14214 but still below the limit specified by ASTM D6751.Iodine value of YOB (73.2 g$I_2$/100g) is far below the maximum limit of 120 prescribed in EN 14214.

**Table 1: Properties of Extracted Yellow Oleander Oil and Biodiesel in Comparison to Biodiesel Standards**

| Parameters | Yellow Oleander seed Oil | Yellow Oleander Biodiesel | ASTM D6751 | EN 14214 |
|---|---|---|---|---|
| Density ($g/cm^3$) | 0.774 | 0.816 | 0.84 | 0.86-0.90 |
| Moisture content (%) | 0.0131 | 0.0044 | < 0.03 | 0.02 |
| Specific gravity | 0.8984 | 0.913 | 0.86-0.90 | 0.85 |
| Acid value (mg KOH/g oil) | 1.8048 | 0.508 | < 0.80 | 0.5 max |
| Saponification value (mg KOH/g oil) | 57.5025 | 26.648 | - | - |
| Iodine value (g $I_2$/100g oil) | 97.6 | 73.2 | - | 120 max |
| Peroxide value (meq $O_2$/kg oil) | 23.8 | - | - | - |
| Cetane number | 140.998 | 234.58 | 47 min | 51 min |

Fuel properties such as saponification value and cetane number of the YOB weredetermined to be 26.648 and 234.58. Cetane number is a measure of the fuel's ignition delay and combustion quality. Fuels with low cetane number are difficult to start, therefore it smokes,the higher the cetane number, the shorter the delay interval and the greater the combustibility. Standard specified value of cetane number for biodiesel is within the range of 47-51 (ASTM D6751 and EN 14214). The YOB cetane number obtained in this study showed that it is of a very high fuel potential. These results showed that further improvements on the fuel properties such as acid value andspecific gravity of YOB could adequately serve as an alternative to conventional diesel.

**Fuel Properties of Yellow Oleander Biodiesel Produced**

It was observed from Table 1 that conversion from the parent oil (YOO) to biodiesel reduce the moisture content by 66.4%, which showed a very low moisture content of biodiesel, which is required in order to prevent or eliminate engine knockout effect. Specific gravity increased by 1.6%, which showed a significant increase in heat of vaporization and this will speed up ignition

when combustion occurs. Iodine value reduced by 24.69%, this implied that the biodiesel produced has low level of unsaturation [29], while acid value was reduced by 71.8%, indicating that the biodiesel have a long shelf life [30], saponification value reduced by 30.86%, suggesting low concentration of triglycerides in biodiesel. However, cetane number increased by 33.89%, which encourages greater combustion process. The moisture content, density, and cetane number obtained were well within the ASTM D6751 and EN 14214 standards exceptacid value and specific gravity of the YOB.

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**REFERENCES**

1. Onuiri E. E., Ogbonna A. E., Alli-Shehu B. and Maduakolam C. (2015) Mineral Resources Management Information System. *European Journal of Computer Science and Information System*, 3(2), 13-23

2. U.S. Geological Survey, (1980) Circular 831.

3. Dhoot, S. B., Jaju, D. R., Deshmukh, S. A., Panchal, B. M., Sharma, M. R., (2011) Extraction of *Thevetia peruviana* Seed Oil and Optimization of Biodiesel Production Using Alkali-catalyzed Methanolysis. *Journal of Alternate Energy Sources and Technologies*, 2 (2), 8-16.

4. Ana Godson R. E. E., Udofia Bassey G. (2015) Characterization of Oil and Biodiesel Produced from *Thevetia peruviana* (Yellow Oleander) Seeds. *International Journal of Sustainable and Green Energy*. Vol. 4, No. 4, 150-158.

5. Guo, F., and Fang, Z. (2011). Biodiesel Production with Solid Catalysts, Biodiesel - Feedstocks and Processing Technologies, Dr. Margarita Stoytcheva (Ed.), ISBN: 978-953-307-713-0, InTech, Available from: http://www.intechopen.com/books/biodiesel-feedstocks-and-processing-technologies/biodiesel-productionwith-solid-catalysts

6. Betiku E., Ajala S.O., (2014). Modeling and optimization of Thevetia peruviana (yellow oleander) oil biodiesel synthesis via Musa paradisiacal (plantain) peels as heterogeneous catalyst: A case of artificial neural network vs. response surface methodology. *Industrial Crops and Products* 53, 314-322

7. Ferdous, K. M., Uddin, M. R., Khan, R. M., Islam, M. A., (2013) Preparation of biodiesel from soybean oil by using heterogeneous catalyst. *International journal of energy and environment*. 4 (2), 243-252

8. Granados, M. L., Poves, M. D. Z., Alonso, D. M., Mariscal, R., Galisteo, F. C., Moreno-Tost, R., Santamaria, J., Fierro, J. L. G., (2007). Biodiesel from sunflower oil by using activated calcium oxide. *Applied Catalysis B: Environmental*, 73 (3-4), 317-326

9. Wang, H.; Wang, M.; Liu, S.; Zhao, N.; Wei, W. and Sun, Y. (2006). Influence of preparation methods on the structure and performance of CaO–$ZrO_2$ catalyst for the synthesis of dimethyl carbonate via transesterification. *Journal of Molecular Catalysis A: Chemical*, 258 (1-2), 308-312

10. Alonso, D. M.; Mariscal, R.; Granados, M. L.; Maireles-Torres, P., (2009). Biodiesel preparation using Li/CaO catalysts: Activation process and homogeneous contribution. *Catalysis Today*, 143 (1-2), 167-171

11. Yang, Z., and Xie, W. (2007). Soybean oil transesterification over zinc oxide modified with alkali earth metals. Fuel

Processing Technology, 88 (6), 631-638

12. Albuquerque, M. C. G., Jiménez-Urbistondo, I., Santamaría- González, J., Mérida-Robles, J. M., Moreno-Tost, R., Rodríguez-Castellón, E., Jiménez-López, A., Azevedo, D. C. S., Cavalcante Jr, C. L., Maireles-Torres, P. (2008). CaO supported on mesoporous silicas as basic catalysts for transesterification reactions. *Applied Catalysis A: General*, 334 (1-2), 35-43

13. Refaat, A. A., (2011). Biodiesel production using solid metal oxide catalysts. *International Journal of Environmental Science and Technology*, 8 (1), 203-221.

14. Xie, W., Peng H., Chen, L. (2006) Transesterification of soybean oil catalyzed by potassium loaded on alumina as a solid-base catalyst. *Applied Catalysis*, 300, 67–74.

15. Abreu, F. R.; Alvez, M. B.; Macêdo, C. C. S.; Zara, L. F.; Suarez, P. A. Z., (2005). New multi-phase catalytic systems based on tin compounds active for vegetable oil transesterificaton reaction. *Journal of Molecular Catalysis A: Chemical*, 227 (1-2), 263-267

16. Zabeti, M.; Wan Daud, W. M. A. and Aroua, K., (2009). Activity of solid catalysts for biodiesel production: A review. *Fuel Processing Technology*, 90 (6), 770-777

17. Bancquart, S., Vanhove, C., Pouilloux, Y., Barrault, J. (2001). Glycerol transesterification with methyl stearate over solid basic catalysts. I. Relationship between activity and basicity. *Applied Catalysis A: General*, 218 (1-2), 1-11

18. Kim, H. J., Kang B. S., Kim, M. J., Park, Y.M., Kim D. K., Lee, J. S., Lee, K. Y., (2004) Transesterification of vegetable oil to biodiesel using heterogeneous base catalyst. *Catalysis Today*, 93, 315-320.

19. Kakati, D. K., Boraa, M. M., Gogoib, P., Dekaa, D. C. (2014) Synthesis and characterization of yellow

oleander (*Thevetia peruviana*) seed oil-based alkyd resin. *Industrial Crops and Products* 52, 721– 728

20. American Oil Chemists' Society (AOCS), 1980. Official and Tentative Methods of the American Oil Chemists' Society, third ed. American Oil Chemists' Society, Champion, IL.

21. AOAC (1993). Iodine value of fats and oils, AOAC Official Method. 20.

22. Pocklington W. D. (1990) Determination of iodine value of oils and fats. *Pure and Applied Chemistry*, 62 (43).

23. Deka, D. C., Basumatary, S. (2011) High quality biodiesel from yellow oleander (*Thevetia peruviana*) seed oil. *Biomass Bioenergy*, 35, 1797–1803.

24. Yarkasuwa, C. I., Wilson, D., Michael, E., (2013) Production of Biodiesel from Yellow Oleander (*Thevetia peruviana*) Oil and its Biodegradability.*Journal of the Korean Chemical Society*, 57(3), 377– 381.

25. O'Brien R. D. (2004) Fats and Oils: Formulating and processing for applications. CRC Press LLC, 2000 N. W. Corporate Blvd., Bova Raton, Florida 33431.

26. Meher, L. C., Sagar, D. V., Naik, S. N. (2006) Technical Aspect of Biodiesel Production by Transesterification- A Review. *Renewal and Sustainable Energy Reviews*. 10: 248.

27. Ramos, L. P., Domingo, A. K., Saad, E. B., Wilhelm, H. M. (2008). Optimization of the methanolysis of *Raphanus sativus*(L. Var.) crude oil applying the response surface methodology. *Bioresources Technology*, 99:1837–45.

28. Adebowale, K.O., Adewuyi, A., Ajulo, K.D. (2012). Examination of fuel properties of the methyl esters of *Thevetia peruviana* seed oil. *International Journal of Green Energy*, 9, 297–307.

29. Nakpong, P. and Wootthikanokkhan, S. (2010). Roselle (*Hibiscus sabdariffa L.*) oil as an alternative feedstock for biodiesel production in

Thailand. *Fuel*, 89:1806–1811.

30. Mahmoud, A. A., Khaled. A., Selim, K.A., Abdel-Baki., M.R., (2011) Physico-chemical and oxidative stability characteristics of roselle (*Hibiscus sabdariffa L.*) seed oil as by-product, Retrieved March 10 2016 from www.fayoum.edu.eg/Agriculture/FoodSciences/pdf/DrKhaled3.pdf.