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Methanolysis of *Balanite aegyptiaca* (Desert Date) Oil using CaO as Catalyst

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ABSTRACT

Biodiesel is a trans-esterified vegetable oil which is renewable energy source that can be considered as a pivotal solution to combating global warming, climate stabilization through the reduction of greenhouse gas emissions and dependence on mineral diesel. In this work Methanolysis of *Balanite aegyptiaca* (Desert date) seeds oil was done using a heterogeneous catalyst (CaO). The transesterification was carried out at 55 °C for a period of 1 h. and catalyst loading of 0.4%. FTIR as well as the physico-chemical parameter analysis of the biodiesel obtained were carried out; the FTIR spectrum shows major peaks at 3007 cm^{-1}, 2921 cm^{-1}, 1745 cm^{-1}, 1163 - 1210 cm^{-1}, 1439 cm^{-1}, 1033 cm^{-1}correspond to C-H stretching of alkene, C-H stretching of alkane, C=O of esters, O-C stretching of ester, CH_3 asymmetric bending, O-CH_3 of ester respectively. The results show a high yield of biodiesel was obtained (96.3%). Physico-chemical results show the density of 0.9 g/cm^3, iodine value 96.95, and acid value 0.9. Thus, it can be concluded that Desert date (*Balanite aegyptiaca*) seed oil can be used as a good feedstock for the biodiesel production with high percentage yield.

Keywords: Biodiesel, Desert date, Heterogeneous catalyst, Methanolysis, Physico-chemical properties

INTRODUCTION

Biodiesel is a renewable, biodegradable, less pollutant emitting; particulate matter, volatile organic compounds and unburned hydrocarbons, non-toxic, more environmentally-friendly fuel and reduces greenhouse gas emissions **(**Bankovic-llic *et al*., 2012). Nigeria presently imports about 80% of her petroleum based products from oversea and the fall in price of crude oil and other micro-economic activities had led to recession since 2015 (Oniya and Bamgboye, 2012). Known petroleum reserves are limited and will eventually run out. Various studies put the date of the global peak in oil production between 1996 and 2035 (Demirbas, 2007). Biomass energy technologies use waste or plant matter to produce energy with a lower level of greenhouse gas emissions than fossil fuel sources (Sheehan *et al*., 1998). Various scenarios have put forward estimates of biofuel from biomass sources in the future energy system. In the most biomass-intensive scenario, by 2050 modernized biomass energy will contribute about one half of the total energy demand in developing countries (IPCC, 1997). The availability of biofuel resources is important for the electricity, heat and liquid fuel market. There are two global biomass-based liquid transportation fuels that might replace gasoline and diesel fuel. These are bioethanol and biodiesel. Transport is one of the main energy-consuming sectors, it is assumed that biodiesel will be used as a fossil diesel replacement and that bioethanol will be used as a gasoline replacement. Biomass-based energy sources for heat, electricity, and transportation fuels are potentially carbon dioxide neutral and recycle the same carbon atoms.

The purpose of the trans- esterification process is to lower the viscosity of the oil. Ideally, trans-esterification is potentially a less expensive way of transforming the large, branched molecular structure of bio-oils into smaller, straight-chain molecules of the type required in regular diesel combustion engines. Biodiesel esters are characterized by their physical and fuel properties including density, viscosity, iodine value, acid value, cloud point, pour point, gross heat of combustion, and volatility. Biodiesel fuels produce slightly lower power and torque and consume more fuel than No. 2 diesel (D2) fuel but is better than diesel fuel in terms of sulfur content, flash point, aromatic content, and bio-degradability (Bala, 2005). If the biodiesel can be utilized efficiently as alternative energy source, it would be of great benefit for the environment and the local population; job creation and provision of modern energy carriers to rural communities.

The seed oil of *Balanite aegyptiaca* is reported to be rich in saturated fatty acids and is used as cooking oil (NRC, 2008). It also contains steroids (saponins, sapogenins, diosgenins) used as raw material for industrial production of contraceptive pills, corticoids, anabolisants and other sexual hormones (UNIDO, 1983). Reports on studies of *B. aegyptiaca* seed oil (Hussain *et al*., 1949.; Cook *et al*., 1998; Mohamed *et al*., 2002) indicate that the seed oil consists of four major fatty acids; linolein, olein, stearic and palmitic acid but in varying proportions across study sites. Some studies (WIPO, 2006; Deshmukh and Bhuyar, 2009) have demonstrated and recommended use of Balanites oil for biodiesel production. Therefore, there is growing interest in the development and use of *B. aegyptiaca* as a potential resource for improving livelihoods of dry land communities.

Therefore, there is need to look into other alternatives for the source of energy. Also there is improper utilization of desert date seed (*Balanite aegyptiaca*).

The industrialization of oil seeds is one of the most important agro industrial activities in the world today. Oil from plant and animal are employed in the formulation of foods, cosmetics, and drugs in many industrial activities (Sayyar *et al.,* 2009). The importance of fats and oils to the global economy becomes clear when considering the amount of oilseed and fruit grown worldwide. The importance of these oils and fats will increase considerably in the future because they represent a vast potential of naturally regenerating raw materials in which the chemical and pharmaceutical industries have a special interest. Until the previous century, the utilization of fats and oils as food went hand in hand with their use as fuel, predominantly for purposes of illumination. Even today, the name "lampante" for certain qualities of olive oil refers to this. (Sayyar *et al.,* 2009). As a base for ointments and cosmetics, they are still in use today, just as in the earliest periods. There are many areas where oils and fats are used for non-food purposes. Thus, detergents, soaps, glycerine and polymers, inks, lubricants, and biodiesel may be derived from fatty acids and their derivative (Sayyar *et al.,* 2009).

Natural vegetable oil and fats are increasingly becoming important worldwide in nutrition and commerce because they are sources of dietary energy, antioxidants, biofuels and raw material for the manufacture of industrial products. They are widely used in food, cosmetic, pharmaceutical and chemical industries. According to FAO (2007), vegetable oils account for 80% of the world's natural oils and fat supply. Nutritional information on Balanites oil will prove useful to nutritionists, policymakers, development agencies and the general public where nutrition and health benefits would be most beneficial. Most of the reported biological activities included the use Balanites seed extract as anticancer and fruit mesocarp extract as fasciolicidal related to polar constituents (Koko *et al*., 2000). The plant contains high amount of nutritive oil (38.2–54.5%, wt/wt) extracted from Balanites seeds with petroleum ether using soxhlet extraction; the majority of studies focused on that oil and oil from seed of fruits prepared by oil pressing as edible oils (Mohamed *et al*., 2002). Unsaturated fatty acids are reported to have anticancer and anti-mutagenic activity (O'Hagan and Menzel, 2003); in addition, fatty acids had antimicrobial activity (Abdelrahman *et al.,* 2003).

In Nigeria, especially in the Northwest part, there is high abundance of the Desert Date trees, the seed oil obtained from *B. aegyptiaca* has been used, as substitute to groundnut oil which is usually relatively expensive. The oil is used for frying food and adding flavor to the food. It is also used to add flavor to tea. This is in addition to medicinal uses such as treatment of skin disease and rheumatism. However, despite such wide spread use, there is limited literature on the possible effects of long term consumption of the oil (Abdel-Rahim *et al.,* 1986), also there is limited attention on its practical use as substrate as alternative energy source from this region.

The aim of this work is to produce biodiesel from *B. aegyptiaca* (desert date) oil using CaO as heterogeneous catalyst, characterize the biodiesel for available functional groups, using analysis and analyze the physiochemical properties of the biodiesel. The characterization will be limited to readily available resources and instrumentation. The *B. aegyptiaca* (desert date) plant, from which the seed (source of the oil) was obtained is naturally available in Dutsin-Ma area of Katsina State, Nigeria.

MATERIALS AND METHODS

Various methods used in this research work for production and physico-chemical parameters evaluation are presented. Seeds of *B. aegyptiaca* (desert date) was obtained from market and the oil extracted through Soxhlet extraction process.

Biodiesel Production

The process of biodiesel production was conducted through the following stages:

Treatment of Raw Material

In this stage, 50 ml of the oil was accurately measured into a beaker and put in a water bath at 110 ºC for about 10-15 minute to remove excess water content in the oil.

Alcohol-Catalyst Mixing

Two necked round bottom flask was clamped to a retort stand and assembled on a hot plate with magnetic stirrer; thermometer was introduced through the side neck of the round bottom flask: 4 ml anhydrous methanol was added into the flask and 0.4 g calcium oxide (CaO) was also added; then condenser was fitted to the second neck of the flask; the hot plate was set at about 65 ºC and the set-up was allowed for run for about 3 mins (Kabo *et al.,* 2018).

Chemical Reaction (Methanolysis)

From the set-up in Fig. 1, 11 ml of *Balanite aegyptiaca* seed oil was added into the mixture (oil: methanol molar ratio 1:6) and the set-up was allowed to run for 1 hour maintaining the temperature at 65 ^oC (Kabo *et al., 2018)*.

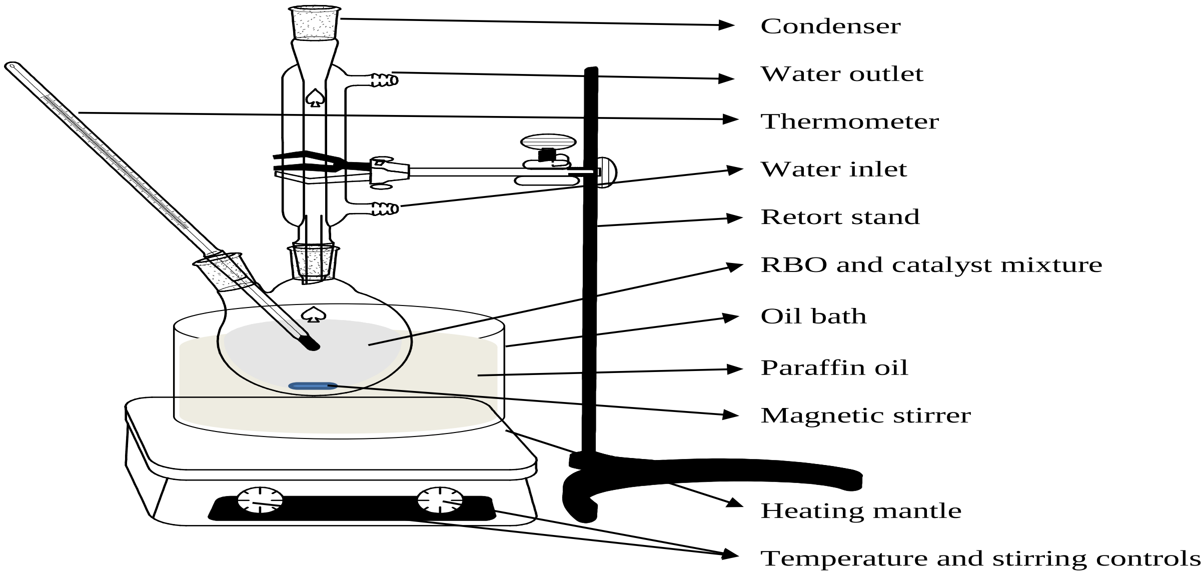

Figure 1: Experimental Set-up for Methanolysis Reaction

Separation of the Product

After completion of the methanolysis reaction, the product obtained was transferred into a test tube and centrifuged at 1000 rotation per minute for 10 mins to get three distinct layers of solid catalyst, biodiesel and glycerol.

FTIR Analysis of Biodiesel

The oil and products obtained were analyzed using Shimadzu FTIR-8400S at a range of 4000-650 cm^{-1} and a resolution of 8 cm^{-1} and spectra was generated. Characterization by FTIR was carried out for functional groups identification. The functional groups in Desert Date seed oil and its fatty acid methyl ester (FAME) or biodiesel analyzed were compared to confirm the conversion of oil to biodiesel.

Determination of Percentage Yield

Determination of percentage yield of biodiesel was done by taking the weight of the oil sample use and the weight of the biodiesel after separating it from catalyst and excess methanol. The yield was obtained using Equation (1) (Capreda, 2013).

$$Yield = \frac{w_1}{w_2} \times 100\% \quad (1)$$

Where: w_1= weight of biodiesel; w_2= weight of oil sample used

Determination of Specific Density

The biodiesel (25 mL) was measured in a pre-weighed measuring cylinder. The weight of the cylinder and the biodiesel was taken; the weight of the biodiesel was obtained by subtracting the weight of the cylinder from the weight of the biodiesel and cylinder. The specific density of the biodiesel is obtained using the Equation (2) (John, 2008). Same procedure i.e. repeated for oil (Capreda, 2013).

$$S.D. = \frac{(w_1 - w_o)}{v_o} \quad (2)$$

Where;
w_1= weight (in g) of empty measuring cylinder + biodiesel,
w_o= weight (in g) of measuring cylinder,
v_o= volume (in ml) of biodiesel

Determination of acid Value

Into a dried 250 mL conical flask was placed 2.0 g of the biodiesel sample followed by 25 mL of absolute ethanol and 3 drops of phenolphthalein indicator. The mixture was heated in a shaking water bath for 5 minutes. While hot, it was titrated against 0.1 M KOH until pink color appeared. Vigorous shaking was done when approaching the end point to ensure thorough mixing. The volume of 0.1 M KOH consumed by an acid was recorded. The acid value was calculated as using Equation (3). The acid value of the oil is determined using same method (Capreda, 2013).

$$A.V. = \frac{56.1 \times v \times M}{m} \quad (3)$$

Where v= volume of KOH used; M = molarity of KOH and m = mass of sample.

Determination of Iodine Value

About 0.25 g of the biodiesel sample was added in a 250 mL conical flask 10 mL of chloroform was added followed by 30 mL of Hanus iodine solution. The flask was securely closed and the solution was left shaken for 30 minutes in the dark. This was followed by adding 10 mL of 15% potassium iodide solution and then shaken, after which 100 mL of distilled water was added. The mixture was then titrated with the iodine solution against 0.1 M Sodium thiosulfate. The iodine value is calculated using Equation (4). Same procedure was repeated for the determination of iodine value of oil sample (Capreda, 2013).

$$I.V. = 12.69 \times C \times \frac{(v_1 - v_2)}{m} \quad (4)$$

Where C = Concentration of $Na_2S_2O_3$ used; v_1 = volume of $Na_2S_2O_3$ used for the blank; v_2 = Volume of $Na_2S_2O_3$ used for sample; m = mass of the sample.

Saponification Number of Biodiesel

Two grams of the biodiesel sample was added to a flask with 30 cm^3 of ethanolic KOH and was then reflux for 30 minutes to ensure the sample is fully dissolved. After sample was cooled, 1 cm^3 of phenolphthalein was added and titrated with the 0.5 M HCl until a pink endpoint has reached. (Capreda, 2013). The procedure is repeated for oil sample.

Saponification value was calculated from Equation (5).

$$S.V. = \frac{(S-B) \times M \times 56.1}{Sample\ weight\ (g)} \quad (5)$$

Where S = sample titre value
B = blank titre value
M = molarity of the HCl
56.1 $gmol^{-1}$ = molecular weight of KOH

RESULTS AND DISCUSSION

Biodiesel was produced, characterized using the methodology explained earlier. The results obtained are presented as follows.

Fourier Transform Infrared (FTIR) Results

The FTIR spectra for the sample of Desert date *(B. aegyptiaca)* oil and its FAME (fatty acid methyl ester) obtained with the conditions of catalyst concentration 0.4 %, reaction time of 1 hour and oil: alcohol ratio of 1:6 are presented in the Fig. 2. Rather subtle differences can be observed between the spectra, since the product of the trans-esterification process (FAME) is almost chemically similar to its oil precursor. The main difference being the presence of peaks associated with methyl esters.

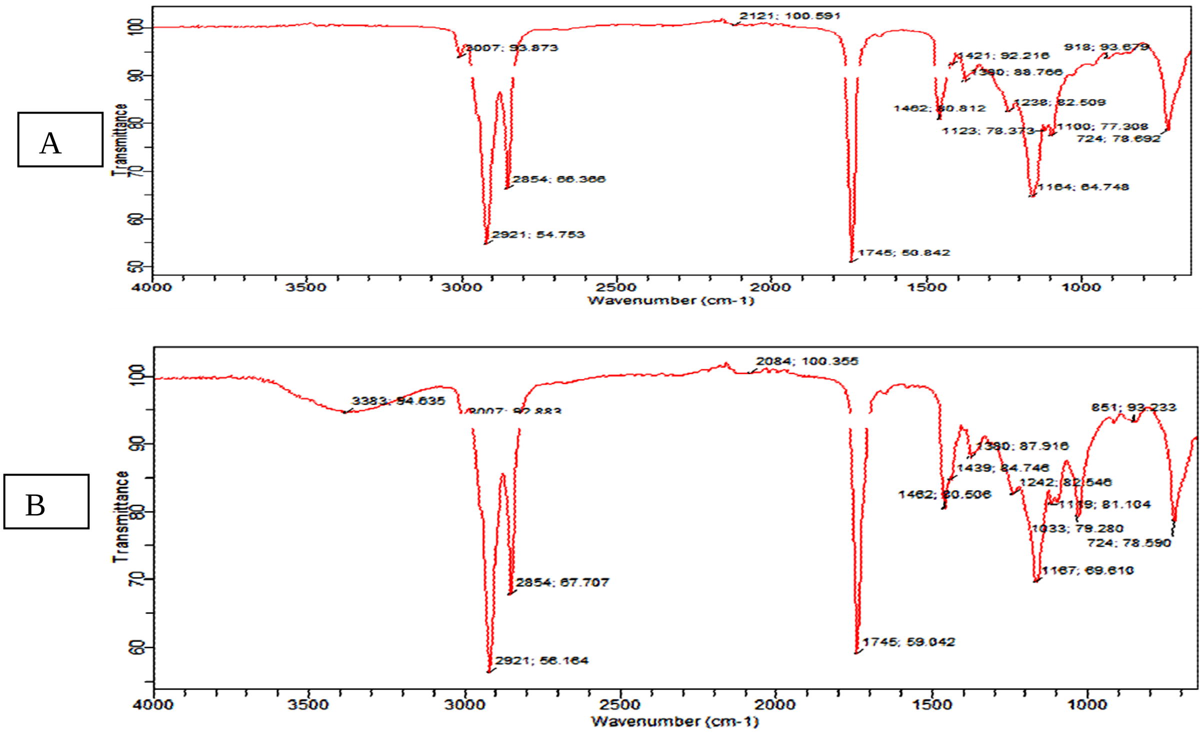

Figure 2: FTIR spectrum of oil (A) and *B.aegyptiaca* biodiesel/FAME (B)

The peak at 3007 cm^{-1} correspond to C-H stretching typical for alkene and thus common for both the oil and it's FAME, the peak at 2921 cm^{-1} corresponds to C-H stretching of alkane appear in both spectra, and the peak 1745 cm^{-1} observed is attributed to C=O typical for esters and thus are common to both FAME and the oil, the peak 1210-1163 cm^{-1} correspond to O-C stretching of ester and thus present in both spectra, the peak 724 cm^{-1} correspond to C=C bending of alkene and thus present in both spectra. The band at 1439 cm^{-1} correspond to CH_3 asymmetric bending present only in biodiesel spectra, the peak at 1033 cm^{-1} is attributed to O-CH_3 of ester present only in the biodiesel spectra and absent in the Desert date oil spectra. This result indicates the presence of methyl ester peaks in biodiesel samples, thus confirming the conversion of oil to methyl esters (biodiesel)

Physico-Chemical Analysis of the Biodiesel

Table 1 shows the different physical and chemical parameters of biodiesel and *Balanites aegyptiaca* seeds oil (Hoekmana *et al.,* 2012). From the results it was observed that the saponification, iodine value, and density fall within the range of accepted biodiesel standards. The acid value is a little bit high but unrefined oil was used and challenge can be overcome by purification.

Table1: Comparison of Physico-Chemical Parameters of Biodiesel and oil from *Balanite aegyptiaca* Seeds

Parameters	Values	
	Biodiesel	Oil
Biodiesel yield (%)	96.3	Nil
Saponification value (mgKOH/g)	0.80	2.5
Iodine Value (I.V.) (gI_2/100g)	96.95	98.74
Acid Value (mgKOH/g Oil)	0.6	2.66
Density (g/ml)	0.9	0.94

The colour of the biodiesel obtained was pale yellow owing to the colour of the substrate oil which contain carotene that remained unaffected after the reaction. The iodine value (I.V.) indicates level of unsaturation in the hydrocarbon chain. I.V. of 96.95 for biodiesel and 98.74 for oil indicates that there is no significant difference between the unsaturation of oil and biodiesel as they are from the same substrate. I.V. is used to measure the stability of the biodiesel as the double bonds can easily be oxidized by oxygen which results in degrading the product, a value of 120 was set as the maximum accepted level by EN 14214 (Hoekmana *et al.,* 2012). However, USA ASTM D6751 - 08 does not specify an iodine value. The iodine value does not necessarily make the best measurement for stability as it does not take into account the positions of the double bond available for oxidation. The acid value 0.6 is slightly higher than the value recommended by ASTM D6751 - 08 (0.5 max). This could be attributed to the fact that the oil was used without purification. The difference is not high enough to cause significant effect and can be addressed by further purification of the substrate. The density 0.9 falls within the standard range of ASTM D6751 - 08 (0.87-0.9) for biodiesel. Density and gravities are important parameters for diesel fuel injection system. The value must be maintained within tolerable limit to allow air to fuel ratio for complete combustion (Hoekmana *et al.,* 2012).

CONCLUSION

The transesterification reaction of desert date oil in the presence of methanol and CaO as catalyst was successfully achieved. The FTIR data from the biodiesel produced confirms the conversion from oil to FAME. Weights measurements show a good yield of 96.3%. The physico-chemical parameters all agrees with the international standards. The acid value of 0.6 which is higher than the 0.5 maximum is not significant considering the nature of crude oil used in the process.

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