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PHYSICO-CHEMICAL PROPERTIES OF BIODIESEL OBTAINED FROM *JATROPHA CURCAS* SEEDS OIL USING $CoMgFe_2O_4$ and $MgFe_2O_4$ AS NANOCATALYSTS

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ABSTRACT
The chemical evaluation of *Jatropha curcas* (barbados nut) seeds was carried out to ascertain the proximate composition, ascorbic acid content of the seeds, elemental analysis and physicochemical properties of the biodiesel produced from *Jatropha curcas* seeds oil. Standard Analytical Methods were employed in the analysis. The result of the proximate composition was shown to be moisture (4.00%), ash (6.00%), fat (40.00%), fibre (8.00%), protein (27.65%) and carbohydrate (18.35%). The ascorbic acid content was found to be 5.16%. The seeds of *Jatropha curcas* yield 432 ml which represents 36% of the extracted oil without any catalyst. In the presence of $CoMgFe_2O_4$ nanocatalyst the yield was 2174 ml which is 92 % biodiesel produced. It was observed that the $MgFe_2O_4$ nanocatalyst was not a very good catalyst for the system studied as compared to $CoMgFe_2O_4$. Some of the parameters that were considered include; time, temperature, catalysts concentration and reactant ratio, the best combination of the parameters was found as 7:1 molar ratio of methanol to oil, 0.5 % $CoMgFe_2O_4$ nanocatalyst, 60 ^oC reaction temperature and 180 minutes of reaction time. Physico-chemical analysis of the biodiesel produced gave a flash point of (87 min.), specific gravity of 0.87, FFA (18.06 mgKOH/g), viscosity (3.8 mm^2/s^{-1}), iodine value (110 mg/I_2), peroxide value (0.30 mg/I_2), saponification value (189 mgKOH/g), refractive index 1.26 and density (0.89g/cm^3). This study revealed that *Jatropha curcas* seeds have low moisture content, high fat and protein and could be a good source of oil for biodiesel production using $CoMgFe_2O_4$ nanocatalyst.

Keywords: *Jatropha curcas* oil, $CoMgFe_2Co_4$ Nanocatalysts, $MgFe_2Co_4$ Nanocatalysts, biodiesel, Transesterification.

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1 Introduction

The continuous increase in civilization and population of the world has generally led to increase in the use of fossil fuel. However, the use of fossil fuel is very limited and associated with some drawbacks. Ojolo *et al.* (2011) reported that the world crude oil reserve shall be exhausted in the next few decades. Whereas there has been a continuous increase in price of petroleum fuel, uncertainties in supply and availability, and the emission of CO_2 from combustion of fuel engine has contributed to global warming (Wang *et al.* 2006). This situation has led to the search for an alternative fuel, which should not only be

sustainable, but also environmental friendly. Biodiesel is considered to be the best sustainable source of fuel because it is clean, biodegradable, non-toxic, renewable, economically viable, technologically feasible and environmental friendly. (Israel, Sunday, Mansong, and Ubong, 2016; Bugaje *et al.* 2012; Magu *et al.*,2017).

Jatropha curcas oil is the best sustainable alternative feedstock because of its huge benefits for production of biodiesel (Chinmoy *et al.* 2009). Jatropha oil diesel yields easily during conversion process by transesterification and it requires lower oil catalyst ratio. It can be blended directly with diesel, (Ma and Hanna, 2008). Moreover, *Jatropha curcas* serves to decrease the amount of carbon dioxide (CO_2), oxides of nitrogen (NOx) and particulate matter from combustion engine, thus reducing environmental hazard caused by global warming (Kazi *et al.* 2009; Nyong and Ekwenchi, 2017). The production of biodiesel is limited by land area but Jatropha curcas trees can be cultivated in any kind of land (Kazi *et al.* 2009).

Generally, Biodiesel productions still face a big problem of cost when it comes to commercialization of the product. Because of its renewable nature and eco-friendly properties, it is important to study the concentration of different nanocatalysts that will be best suitable for biodiesel production from Jatropha curcas oil (Nakpong and Woothikanokkhan 2010). The study of biodiesel production from *Jatropha curcas* oil has been conducted by several researchers, but with different production processes, optimum conditions, and methyl ester yields. Due to the tremendous problems being faced by the international community on the use of fossil fuel, replacing fossil fuel with renewable biodiesel from Jatropha oil still requires enormous work to be done most especially on the catalyst concentration of the production process. That is why this research work intends to investigate the behavior of different nano catalysts ($CoMgFe_2O_4$ and $MgFe_2O_4$) in the transesterification reaction of *Jatropha curcas* oil in the production of biodiesel.

2 Materials and method

Sample collection and preparation

Fruits of *Jatropha curcas* were obtained from Pankshin Local Government Area, of Plateau State of Nigeria, in June, 2016. The seeds were then removed from the fruit, cracked and placed on the asbestos pad and dried in the oven at a temperature of 60 -70^oC. They were brought out and kept for air circulation. The dried sample was ground into powdered form and stored in an air tight container for further analysis.

Synthesis and Characterization of $CoMgFe_2O_4$ and $MgFe_2O_4$ Nano Catalyst

The $CoMgFe_2O_4$ and $MgFe_2O_4$ nanocatalysts were synthesized, characterized and supplied by Ehi-Eromosele, C. O. (2015). Synthesis, Surface Modification and Characterization of Optimized Magnetic Nanoparticles for Potential Biomedical Applications Ph.D dissertation from the Department of Chemistry in Covenant University, Ota Ogun State, Nigeria**.**

Extraction of oil from *Jatropha curcas* seed.

Extraction of oil from the *Jatropha curcas* seed was done according to the method described by (Gubitz *et al.* 1999).

Proximate analysis

Proximate analysis involves determination of moisture, ash, crude fibre, crude protein, fat and carbohydrate contents (Verma 2010). Carbohydrates were calculated while ash, moisture, fats, fibre and crude protein were determined through methods described by (A. O .A. C.).

Determination of moisture content (A. O. A. C.)

The powdered sample of the seeds was weighed (5g) into pre-weighed beaker and placed in an oven for six (6) hours at a temperature of 100^oC to a constant weight. The loss in weight was expressed as a percentage of the initial weight. Thus the different in weight indicates the amount of water contained in the sample.

$$\% \text{ moisture} = \frac{loss\ in\ weight\ on\ drying}{initial\ sample\ weight} \times \frac{100}{1}$$

Weight of empty beaker (a_1) = 30.1g

Weight of empty beaker + sample (a_2) = 35.1g

Weight of empty beaker + dry sample (a_3) = 30.3g

% moisture content = $\frac{a_3 - a_1}{a_2 - a_1} \times \frac{100}{1}$

= $\frac{30.3 - 30.1}{35.1 - 30.1} \times \frac{100}{1}$ = $\frac{0.2}{5} \times \frac{100}{1}$ =

$0.4 \times 100 = 4\%$

Determination of ash content (A.O.A.C.)

The 5.0g of the powdered sample was weighed into a pre-weighed labelled crucible and placed in the muffle furnace at a temperature of 50 ^{o}C for 20 minutes. The furnace was allowed to cool before removing the crucible with its content. The crucible was later cooled in a desiccator and reweighed to get the ash content.

Weight of empty beaker (b_1) = 30.1g

Weight of empty beaker + sample (b_2) = 35.1g

Weight of empty beaker + dry ignited sample (b_3) = 30.4g

% Ash = $\frac{b_3 - b_1}{b_2 - b_1} \times \frac{100}{1}$

= $\frac{30.4 - 30.1}{35.1 - 30.1} \times \frac{100}{1}$ = $\frac{0.3}{5} \times \frac{100}{1}$ = $0.06 \times 100 = 6\%$

Determination of crude fat content (A.O.A.C.)

The 5.0g of the powdered sample was put into the soxhlet extractor thimble wrapped with a filter paper and plugged tightly with cotton wool. 150 ml of petroleum ether (bpt 60 – 80^{o}C) was poured into 300 ml round bottom flask containing anti-bombings and the soxhlet extractor assembled. The sample was extracted for 4hrs until the extract become colourless. The extract was poured into a dried pre-weighed beaker and the thimble rinsed with a little quantity of petroleum ether back into the beaker. The beaker was heated on a steam bath to drive off the solvent. The extracted fat left in the beaker was dried in one desiccator and weighed.

The percentage crude fat was calculated as follows;

Weight of empty round bottom flask (c_1) = 23.3g

Weight of round bottom flask + sample (c_2) = 28.3g

Weight of round bottom flask + (dry fat), lipid (c_3) = 25.3g

% crude fat = $\frac{c_3 - c_1}{c_2 - c_1} \times \frac{100}{1}$

= $\frac{25.3 - 23.3}{28.3 - 23.3} \times \frac{100}{1}$ = $\frac{2}{5} \times \frac{100}{1}$ = $0.40 \times 100 = 40\%$

Determination of crude fiber content

The 5.0g of powdered sample was put in a pre-weighed beaker. 50ml of 1.25% H_2SO_4 solution was added and made up to 200 ml with distilled water and stirred. The mixture was heated with continuous stirring for thirty (30) minutes and allowed to cool and settle. Distilled water was added and allowed to settled then decanted, decantation was repeated for six (6) times consecutively to make the mixture acid free. 50ml of 1.25% NaOH was added to 200ml with distilled water in a beaker and heated for thirty (30) minutes with continuous stirring. It was cooled and allowed to settle. Distilled water was added and decanted for six (6) times consecutively. The mixture was filtered with filter paper and kept for forty-five (45) minutes for water to drain completely and the weight taken.

Weight of empty beaker (d_1) = 97.7g

Weight of empty beaker (d_2) = 102.7g

Weight of empty beaker + dry fibre (d_3) = 97.7g

% crude fibre = $\frac{d_3 - d_1}{d_2 - d_1} \times \frac{100}{1}$

= $\frac{97.7 - 97.7}{102.7 - 97.7} \times \frac{100}{1}$ = $\frac{0.4}{5} \times \frac{100}{1} = 0.08 \times 100 = 8\%$

Determination of total carbohydrate content

This was obtained by taking each percentage value of protein, fat, fibre and ash content from the total dry matter.

Protein= 27.65%

Fat= 40.00%

Fibre= 8.00%

Ash= 6.00%

= 81.65%

% Total carbohydrate content

= 100 – 81.65

= 18.35%

Determination of crude protein content (Modified Kjeldahl method)

The analysis was carried out in three (3) stages, these were;

- The digestion stage
- The distillation stage
- The titration stage

Digestion Stage: The powdered sample was weighed out 5g into a 250ml kjeldahl flask. 2g each of the kjeldahl catalysts (Copper Sulphate and Sodium Sulphate) were weighed into the kjeldahl flasks. Anti-bumping granule was added and 30ml of concentrated Sulphuric acid was also added to the flask. The digestion flask was then placed on the heating mantle for an hour before being transferred to electric stove. The digestion process proceeds with occasional swirling until a clear solution was obtained. The clear solution was transferred into a 100ml standard flask and made up to the mark with distilled water.

Distillation Stage: The 10ml of the digest was measured into the micro distillation apparatus. 12.5ml of 1.25% NaOH was also added to the flask. A condenser was connected from the distillation apparatus to a volumetric flask containing 10ml of 5% boric acid and 2 drops of double indicator (methyl red and methyl blue). The distillate was collected in a flask and then titrated with 0.1ml standard hydrochloric acid until a pale pink colour end point was obtained.

$$\% \text{ Nitrogen} = \frac{(sample) - ml\ of HCl(blank) \times molarity of HCl \times 100 \times 100 \times 14}{weight\ of\ sample \times ml\ of\ digest \times 1000}$$

% Protein = % Nitrogen × Protein factor

= 4.424 × 6.25

= 27.65%

Determination of ascorbic acid content. (Redox titration using Iodine solution)

The solution of iodine 5.0×10^{-3}M was prepared, 5g of the powdered sample was weighed and made into a paste by further grinding with mortar and pestle. 100ml of distilled water was then added to the paste. The solution was filtered with a filter paper. 10ml of the filtrate was pipetted into a conical flask. It was than titrated with the iodine solution until a dark blue-black colour was obtained. The titration was repeated with further aliquots (10 ml) of sample solution until concordant results were obtained.

Result of ascorbic acid content

Burette Readings	1st (cm^3)	2nd (cm^3)	3rd (cm^3)
Final	5.80	25.70	43.60
Initial	0.00	20.40	37.90
Volume of iodine used	5.80	5.30	5.70

Average Volume of iodine used = $\frac{(5.80 + 5.30 + 5.70)}{3} cm^3$

$= \frac{16.8}{3} cm^3 = 5.60 cm^3$

Volume of blank titre = $18.5cm^3$

Volume of iodine used = $5.60cm^3$

Standard Ascorbic Acid in 10ml of H_2O = 0.20g/l

Weight of Sample = 5g

% Ascorbic acid $= \frac{18.5 - 5.60 \times 0.20 \times 100}{10 \times 5} = \frac{258}{50} = 5.16$

Physico-Chemical Analysis of the produced Biodiesel

Determination of Specific gravity

An empty 50 ml measuring cylinder was washed, dried weighed and labeled as (w_o). The 20 ml of oil sample was transferred into the cylinder and weighed (w_1). The weight of the oil was determined by subtracting the weight of the initial empty cylinder from the weight of the final measuring cylinder filled with oil. The specific gravity of the oil was obtained by the expression below (Sani, 2013)

$$\text{Specific gravity} = \frac{\text{weight of oil}}{\text{weight of water}}$$

$$\text{Specific Gravity} = \frac{W_o - W}{W_1 - W} \quad (3.1)$$

Determination of Free Fatty Acid

The free fatty acid was determined by method used by Ma and Hanna (2008). A mixture of ethanol and toluene in the ratio 1:1 was first prepared and was neutralized by potassium hydroxide solution in the presence of two drops of phenolphthalein indicator per 100 ml of mixture. 2 g of sample was then weighed into 250 ml conical flask plus 50 ml of previously neutralized mixture of toluene and ethanol. A few drops of phenolphthalein indicator were added again and the content titrated against 0.1 ml/litre solution of ethanolic potassium hydroxide solution until the indicator changes to pink colour. Two determinations was carried out for the sample. The acidity value was expressed as:

$$\text{Acid value} = \frac{Titre\ value \times 0.1\ M\ KOH \times 56.10}{Weight\ of\ sample(g)} = mgKOH/g$$

$$\text{Acidity value} = \frac{VxCx56.1}{m} \quad (3.2)$$

Where,

V = ethanolic potassium hydroxide solution

C = exact concentration of ethanolic potassium hydroxide solution used

m = Mass of the test sample

56.1 = molar mass expressed in grams per mole of potassium hydroxide

Flash point of the biodiesel

The flash point of the biodiesel was determined by the method of ASTMD-93, using the Penky-Martens closed cup tester. The determination of the flash point of the biodiesel was done at 60^0c by an automated Pensky-Martens closed cup apparatus according to the standard method of testing flash point (ASTMD-93). This was done by heating a sample of the fuel in a stirred container and passing flame over the surface of the liquid, when the temperature was at or above the flash point, the vapour was ignited and an easily detected flash point was observed. The fire point produced sufficient vapour to maintain a continuous flame (Babgy *et al.* 1987).

Determination of Peroxide Value

The experiment was carried out in a diffused daylight. The 2 g of sample was weighed into a 100 ml conical flask, 10ml of chloroform was added to dissolve the sample quickly by stirring, then 15 ml of acetic acid was added and 1ml of freshly prepared saturated potassium iodide solution was added. The flask was then closed immediately, stirred for 1 minute and kept for exactly 5 minutes away from light at room temperature. The 75 ml of water was added as indicator. The liberated iodine was then titrated against 0.01 N sodium thiosulphate solutions. The same procedure was carried out for other samples and the blank test was carried out by the same procedure but omitting test sample. Two determinations were carried out on each sample. The peroxide value was expressed in milli equivalent of active oxygen per kilogram of sample given by:

$$\text{Peroxide value} = \frac{(V_1 - V_0) \times T \times 1000}{m} \quad (3.3)$$

Where:

V_0 = volume of the sodium thiosulphate solution used for blank

V_1 =volume of the sodium thiosulphate solution used for determination of sample

T = the normality of the sodium thiosulphate used

m = mass of oil sample in gram.

Determination of Viscosity

The oil sample was purified with a sintered glass and charged into a viscometer via suction force in a viscometer bench apparatus. The viscometer bath was set to a temperature of 40 ^{o} C and the sample was allowed to come through the bath

after 15 minutes. Suction force was then applied to the Viscometer's thinner arm to draw the sample slightly above the upper timing mark. Afflux time of the sample as it flows freely from the upper timing mark to the lower timing mark was recorded**.** The viscosity was determined by ASTM method (ASTM D – 93). The viscosity was determined using the following expressions:
Kinetic viscosity = Time of fall x Stoke constant

Determination of Iodine Value
The Iodine value was determined by ASTM method (ASTM D – 93). The 2.0 g of the oil sample was weighed into a 50 ml glass conical flask. The 20 ml of carbon tetrachloride and 25 ml of wiji's iodine solution was added to the flask. A stopper was then fixed and the content of the flask swirled vigorously. The bottle was placed in the dark and allowed to stay for 30 minutes, after which 10 cm^3 of 15 % KI solution was added. This solution was titrated against a standard 0.1 M sodium thiosulphate solution. Titration was done with constant shaking until a yellow color of iodine almost disappeared. The 2 cm^3 of 1 % starch indicator was added and titration continued, when the color disappeared, the titration was stopped and shaken vigorously, so that any iodine in the organic solvent layer passed into the water layer. Finally, when the titration was completed the titer values were recorded. Blank determination was carried out on 5 ml of chloroform and of equal proportion of wiji's solution allowing the precipitate to dissolve for same length of time as for the sample analyzed.

Iodine value = $\frac{12.69.C(V_1-V_2)}{M}$ (3.4)

Where:
C= concentration of sodium thiosulphate
V_1 = Volume of sodium thiosulphate solution used for blank test
V_2 =Volume of sodium thiosulphate solution used for determination
M = Mass of the oil sample

Determination of Water Content
A known weight of the biodiesel sample was heated at a constant temperature of 100 ^oC in an oven for 50 minutes. The sample was removed and placed in the desiccator to prevent water mixture to the oil, Then every 10 minutes the sample was removed and re-weighed. The process was repeated until a constant weight was obtained.

Determination of Saponification Value
The saponification value was determined by ASTM method (ASTM D – 93). The oil sample was purified with a sintered glass. The 2 g of the oil sample was weighed into flask and 20 ml of alcoholic KOH was added from burette by allowing it to drain for 10 mins. A blank was also prepared by taking only 20 ml of alcoholic KOH allowing it to drain for the same 10mins. A reflux condenser was connected to the flasks and the content of the flasks allowed to boil gently for one hour. The flasks and condenser were removed after condensation has taken place. One drop of phenolphthalein indicator was added and titrated against 0.5 M HCl until the pink color disappeared.
Saponification value, $(S.V) =$

$$\frac{56.1\times T(V_B-V_S)}{M}\ mgKOH/g$$

Where, T = Molarity of KOH, V_S=Volume of acid used for the titration with oil sample,
V_B= Volume of acid used for the titration of the blank solution,
M= Mass of the oil sample used.

$$FFA = \frac{Acid\ value}{2} = mgKO \quad (3.5)$$

Density of the biodiesel:
The density of the biodiesel (0.89glcm^3) is within the range of biodiesel density standard (0.860 - 0.900glcm^3).

- The dark brown colour of the biodiesel produced compare to the colour of other biodiesel obtained from conventional oil seed such as groundnut (yellow), cotton seed (brown) and can be attributed to the seeds that were used for the extraction of oil from the blended *Jatropha curcas* seeds and the catalyst used during the mixture. – Is the weight per unit volume. Oils that are denser contain more energy. For example, petrol and diesel fuels give comparable energy by weight, but diesel is denser and hence gives more energy per liter. The aspects listed

above are the key aspects that determine the efficiency of a fuel for diesel engines. There are other aspects/characteristics which do not have a direct bearing on the performance, but are important for reasons such as environmental impact etc.

The density was determined using a density bottle and was estimated as shown,

$$Density = \frac{mass\ of\ oil}{volume\ of\ biodiesel}$$

Mass of bottle = 24.00g
Mass of bottle + H_2O = 74.40g
Volume of water = 50.40g
Mass of biodiesel = 44.90g

$$Density = \frac{44.90g}{50.40cm^3} = 0.891g/cm^3$$

$$Density \simeq 0.89g/cm^3.$$

Production of biodiesel from *Jatropha curcas* seed oil.

Biodiesel production process procedure was according to Joao F.*et al* (2012)

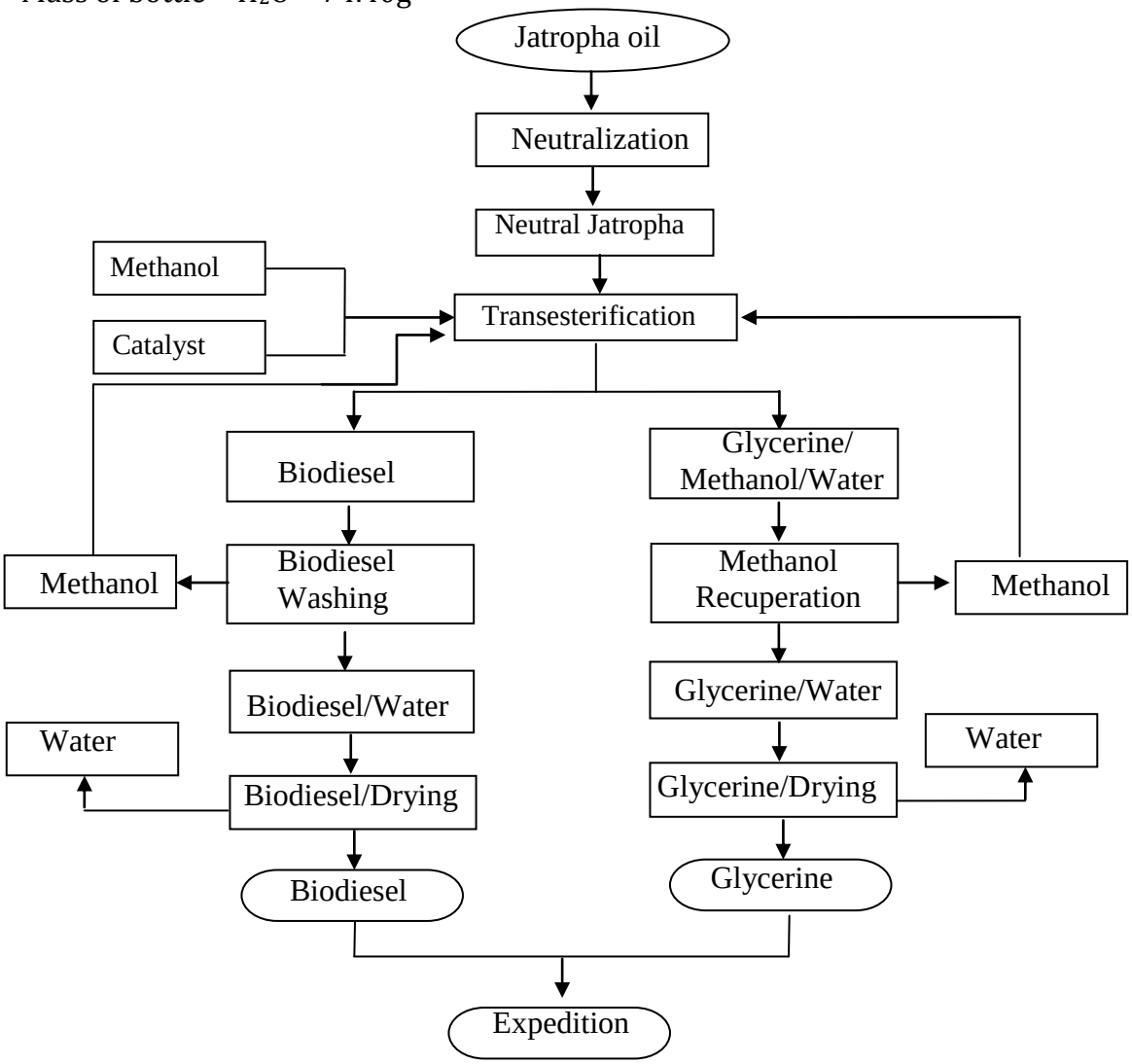


Figure 1**:** Schematic process diagram of Biodiesel

The *Jatropha curcas* oil contains average amount 17 % free fatty acids in nature. It must free before been taken into actual conversion process. Acid catalysed esterification is used to reduce the FFA to >1 % FFA using HCl as catalyst.

The production of biodiesel from Jatropha Curcas seeds was comprised of three major steps:

- Extraction of seed oil: A solvent extraction method was used to extract the oil from crushed Jatropha curcas seed flakes.

- Treatment of seed oil: The free fatty acid content in the seed oil was reduced by acid-catalyzed transesterification to give a higher biodiesel yield product.
- Conversion of seed oil to biodiesel: This step utilized base- catalyzed transesterification process which effectively produced biodiesel from the treated *Jatropha curcas* seed oil.

Pre-treatment through Acid esterification:
The oil was dehydrated by heating it above 100 ^{o} C on a hot plate to evaporate the water content. The dehydrated oil was then esterifies by agitating it with a mixture of methanol and HCl to oil in 1000ml beaker was placed on a magnetic hot plate with a constant agitation and equipped with a thermometer; the oil was heated to 60 ^{o} C and was allowed to run for three hours. The mixture was then allowed to settle in a separating funnel into two layers at the end of reaction time. The upper layer contained methanol and water while the lower layer containing vegetable oil. The oil was carefully removed and the methanol was distilled to dry the water content. The free fatty acid was now determined and found to be less than 2 %.

Alkaline Transesterification

- The 100 ml of *Jatropha* oil was heated to 60 ^{o} C in four 1000 ml round bottom flasks on a hot plate magnetic stirrer equipped with thermometers to drive off moisture, when stirred vigorously. The oil was then allowed to cool to 45 ^{o} C and maintained at this temperature.
- The 0.5 g $CoMgFe_2O_4$ and 0.5 g $MgFe_2O_4$ pellets were measured and poured into the four 1000 ml beakers; 500 ml of methanol was poured into the beaker containing 0.5g of $CoMgFe_2O_4$ and 0.5g of $MgFe_2O_4$ each. The catalysts dissolved completely. The resulting solution of methoxide was poured into the flask containing the oil and the reaction time was 180 minutes.
- After 180 minutes the reaction was stopped. The mixture was poured into 1000 ml separating funnel and allowed to settle under gravity for 24 hours. The mixture separated into two separate layers, the layer containing biodiesel, methanol soap, and residual catalyst. The lower layer contained glycerol. The glycerol was gradually drained off. The pH of biodiesel was measured and found to be around pH of 9 which is alkaline; phosphoric acid was added to neutralize the residual catalyst.
- The upper layer was then cleaned thoroughly by washing in distilled water with 50 ml warm distilled water at 45 ^{o} C to remove methanol, residual catalyst and soaps. During washing the solution was gently agitated to emulsion formation.
- After separation of the layer for 5 – 10 minute, the wash water layer was drained off from the bottom of the funnel. The washing process was repeated until the ester layer became clear to the eye.
- For each washing process the pH of wash water and biodiesel layer were constantly measured until a pH of 7 was reached. The washing process was stopped. The biodiesel was then heated on a hot plate in a 1000 ml beaker to evaporate any water present. The end product was a clear amber yellow liquid depending on the catalyst been used though and with viscosity similar to that of petroleum diesel according to (ASTM D-93) standard 1.3-4.5.

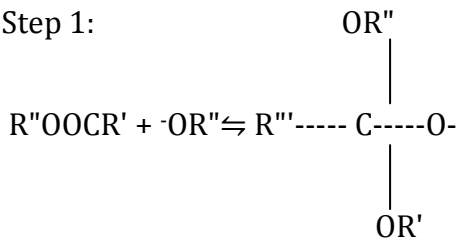
Chemistry of transesterification

The transesterification or alcoholysis reaction occurs in a sequence of three consecutive reversible reactions in which the triglyceride molecule is converted step by step into ester and glycerol. In the first step triglycerides are converted to diglycerides, and diglycerides to monoglycerides and monoglycerides to glycerine. Pre-step:

$^{-}OH- + R''OH \leftrightharpoons R''O- + H_2O$ or (2.1)

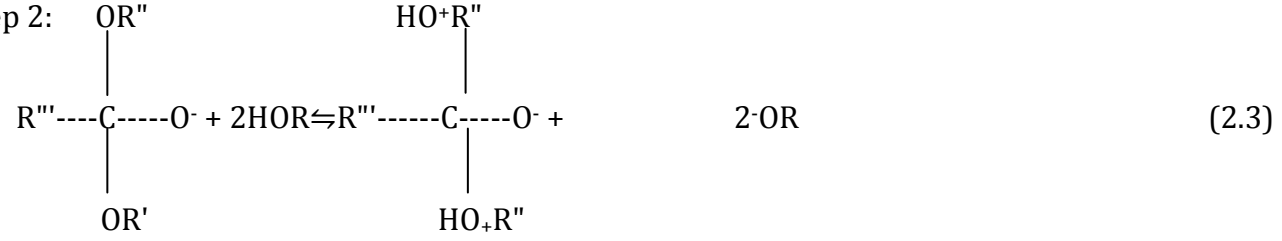
$KOR'' \leftrightharpoons R''O- + K^{+}$

Step 1:



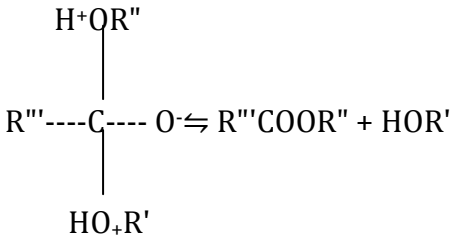
(2.2)

Step 2:



(2.3)

Step3:



(2.4)

In each step one mole of alcohol is consumed and one mole of ester is liberated. In order to shift the equilibrium to the right, methanol is added in an excess over the stoichiometric amount in most commercial biodiesel production plants.

Another advantage of methanolysis as compared to transesterification with higher alcohols is the fact that the two main products, glycerol and fatty acid methyl esters (FAME), are hardly miscible thus form separate phases – an upper ester phase and lower glycerol phase. This process removes glycerol from the reaction mixture and enables high conversion.

Finally regardless of the type of alcohol used, some form of catalyst has to be present to achieve high ester yields under comparatively mild reaction conditions. The above reaction is Transesterification reaction. Where, R', R" and R"' represent the different fatty acid derivatives (long unbranched aliphatic tail (chain), which is either saturated or unsaturated) (Chinmoy 2009).

Trans-Esterification Process

Mixing of Alcohol and Catalyst: 0.5g of $CoMgFe_2O_4$ and 0.5 $MgFe_2O_4$ nano catalysts each were mixed with 500 ml and 700 ml of methanol inside a strong heat resistant glass 1000 ml beakers. The mixture was heated

gently at 60 ^{0}C lower than the boiling point of methanol to obtain a methoxide

- The Methyl Ester Mixture: The methoxide solution was mixed in 1000ml beaker containing the treated *Jatropha curcas* seed oil. It was poured into a beaker containing methanol of 5:1 and 7:1 ratio then placed in magnetic mechanical stirrer for 180mins (3hrs) to obtain a homogenous mixture using a flat plate magnetic stirring.
-
- Separation of the Biodiesel and Glycerine: After stirring, the mixture was poured into a separating funnel and was allowed to stand for 24 hours. Once the separation was completed two major products existed. These were glycerine and biodiesel and were washed with distilled water to remove some traces of soap and other contaminants. The washed biodiesel was collected into a beaker and gently heated in an oven, at 150^{o}c to evaporate the excess water and methanol in the biodiesel. The biodiesel yield was 92% in the ratio of 7:1, 88% 5:1 using $CoMgFe_2O_4$ nano catalyst and yield 71% on the ratio of 7:1, 57% in 5:1 ratio using $MgFe_2O_4$ nano catalyst at the end of the purification process.
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3 Results and Discussion

Proximate composition

The result of the proximate composition of *Jatropha curcas* seed is presented in Table 8.

Moisture content

The result of the analysis (Table 1) shows the moisture content of the seed to be 4.00%. This value is lower than 22.00% reported by Eromosele *et al* (2003) for *Chrysophyllum cainito* seed. This reveals that this *Jatropha curcas* seed will have a very short shelf life compare to the seed of *Chrysophyllum cainito.* This is because the moisture content of seeds, fruits and vegetables is indicative of their shelf life. The higher the moisture content, the more susceptible the seeds, fruits, vegetable is to microbial attack and reduce its shelf life.

Ash content

The result of the analysis (Table 1) shows the ash content of the seed to be 5.03%. This is higher than 4.00% reported by Odoemelam (2005) for seeds of African oil bean. This composition shows that *Jatropha curcas* seed has a high content of minerals.

Fat content

Table 1 shows the result of the analysis for crude fat. The result obtained is 40.00%. This is quite high. Seeds with high lipid contents are usually compared with those of soya bean oil, locust bean and cotton seed; 19.10g/100g, 20.20g/100g and 14.05g/100g crude fat respectively. These are commercially exploited and classified as oil seeds. This makes *Jatropha curcas* a good fat content source for both industrial and commercial use (Ayodele *et al*. 2000).

Fibre content

The result analysis (Table 1) shows the fibre content of the seed to be 8.08%. This value is higher than 6.00% reported by Akintayo *et al.* (2002) for soybean seed. Fibre helps in the maintenance of human health and has been known to reduce cholesterol level in the body.

Protein content

The result of the analysis (Table 1) shows the protein content of the seed to be 27.65%. This value is higher than 23.6% reported by Ayodele *et. al.* (2000) for cowpea, the result however, suggests that *Jatropha curcas* seed could be used as an alternative source of protein supplement.

Carbohydrate content

The result of the analysis (Table 1) shows the carbohydrate content of the seed to be 18.35%. This value is lower compared with 60.0% reported by Ayodele *et al.* (2000) for cowpea. However, this result revealed that *Jatropha curcas*seed is not a good source of carbohydrate.

Results for the proximate composition of *Jatropha curcas* seed

S/N	Parameters	Raw Values (%)
1	Moisture content	4.00± 0.028
2	Ash content	6.00± 0.41
3	Crude fat content	40.00± 0.42
4	Crude Fibre content	8.00± 0.10
5	Protein content	27.65 ±3.01
6	Total carbohydrate content	18.35 ±1.08

The results of the analysis (Table 1) shows the moisture to be 4.00%, ash 6.00%, lipid 40.00%, Fibre 8.00%, protein 27.65% and carbohydrate 18.35%.

Ascorbic acid content

The result of the analysis (Table 2) shows the ascorbic acid content of the seeds to be 5.16%. This value is low compared to 66.88% reported by Chinyere *et al.* (2009) for lagenaria seeds. This implies that, *Jatropha curcas* seed is not a good source of ascorbic acid compared to *Lagenaria sphaerica* seed (see Table 2).

The result of ascorbic acid content of *Jatropha curcas* seed (% w/w)

Parameter	Value (Percentage %)
Ascorbic Acid	5.16

The physiochemical properties of the biodiesel produced from *Jatropha curcas* seed oil presented in the Table 3 are discussed below.

Table 3: Physicochemical properties of biodiesel produced

Properties	Units	ASTM standard	EN standard	Tint & Mya (2009)	Nayak & Patel (2010)	This work
Specific gravity		0.81-0.90	0.86	0.87	0.86	0.87
Free fatty acid	mgKOH/g	0.8	-	22.6	-	18.06
Flash point	^{o}C	>130	>120	93	91	87
Viscosity at 40^{o}C	mm^2/s^{-1}	1.9-6.0	3.5-5.4	4.51	4.78	3.8
Iodine value	mg/I_2	-	-	100.1	-	110
Peroxide valve	mg/I_2	-	-	-	-	0.30
Saponification V	$mgKOH/g^{-1}$	-	-	208.27	-	189
Density	Kg/m^3	875-900	860-900	-	-	0.89

Specific gravity

In this study the specific gravity of the biodiesel produced was observed to be 0.87. This result shows that the effect of transesterification has reduced the specific gravity of Jatropha curcas oil from 0.921 to 0.812 making the biodiesel good enough to be run in diesel engine. This result was consistent with ASTM standard (0.88) and EN standard (0.86 min). The result compares favourably with the work of Tint and Mya (2009), and Patil, *et al.* (2009) showed in Table 1.

Free fatty acid

The acid value of oil measures the quality of the oil. It depends on the degree of rancidity which determines the index of freshness. The acid value for the oil was determined as 18.02. The value is compared favorably with Ojolo *et al*. (2011). This indicates that the Free Fatty Acid content of the oil is high and will probably cause high soap formation during transesterification resulting to low ester yield. However, this require heavy refining to reduce the FFA to as low as 1 % before alkaline transesterification (Knothe and Steidley, 2005).

Flash point

The flash point of a volatile material is the lowest temperature at which it can vaporize to form an ignition mixture in air. The flash point (87min.) shows a significant difference compared to the biodiesel flash point standard [ASTMD-93 (130min)]. This difference can be attributed to some factors; the prolong storage of the biodiesel produced before the analysis of the flash point was conducted and the container that was used for the storage of the biodiesel. This might have caused the loss of some volatiles. More so, this may be due to the presence of contaminants such as water molecules which may have not been completely removed during the washing and drying of the biodiesel.

Measuring flash point require an ignition source. At the flash point. The vapor may cease to burn when the source of ignition is removed. The flash point is often used as a descriptive characteristic of liquid fuel and it also help to characterize the fire hazards of liquids. There are various standards for defining each term. Liquid with a flash point less than 60.5 (140.9 F) or 37.8 (100.0 F) depending upon the standard being applied are considered flammable, while liquids with a flash point above those temperatures are combustible (Gerpen, 2005, Ma and Hanna 2008, Mike Benge 2008 and Knothe *et al.* 2006).

Viscosity

This is an important parameter used to determine the quality of biodiesel. The high viscosity of vegetable oil called for transesterification of the oil in order to reduce it to an appropriate level that will enable efficient functionality in the diesel engine. The result of this study was 3.8 mm^2/s at 40 ^0C. This was quite consistent with the ASTM standard (1.9-6.0 mm^2/s) and EN standard (5.4 max). This implies that the biodiesel produce sustained high quality. High viscosity of the oil has been reported to result in poor fuel atomization in internal combustion engines resulting in improper fuel-air mixture and inefficient combustion (Bari *et al*. 2002; Alamu *et al.* 2007). The result of this study clearly depict that the biodiesel sample can operate efficiently in a diesel engine.

Iodine Value

The Iodine value of oil is a measure of the degree of unsaturation of the oil. Higher iodine value or lower iodine value of oil indicate higher or lower unsaturation of oils (Veljkovic *et al.* 2006).The iodine value for this study was 110 mg/I_2 for the oil. This result shows agreement with the report of (Nakpong and Wootthikanokkhan 2010) which is low iodine value. The results generally show decrease in the average degree of unsaturation of the oil, compared to the possibility that some oils can absorb 200 g iodine and beyond. Then generally, low Iodine values imply that they are all non-drying oils.

Determination of Peroxide Value

Peroxide value indicate the level at which oxidation can occur in the oil. The peroxide value of the jatropha curcas seed oil was 0.30 meq/kg. The peroxide value in this study is low and this indicates that the oil is not oxidized. It is high it can becomes sour. The value ranges from 20.0-40.0meq/g, showing that the oil is not sour (Pramanik K. 2001)

Saponification Value

The saponification value of oil indicates the ability of the oil to be used to make soap. High saponification value implies

that oils are normal triglycerides and very useful in production of liquid soap and shampoo industries. The saponification values (SV) of the oils used was 189 mg KOH /g and is lower than the ranges of 194.0 to 208.22 reported by Ojolo *et al.* (2011) and (Nakpong and Wootthikanokkhan, 2010) respectively. These results indicate that the Oil has an index of high average molecular weight of tricylglycerol. Therefore these oils may be good raw material for soap making aside biodiesel production.

Density of Biodiesel

The density of the biodiesel ($0.89glcm^3$) is within the range of biodiesel density standard ($0.860 - 0.900glcm^3$). The dark brown colour of the biodiesel produced compare to the colour of other biodiesel obtained from conventional oil seed such as groundnut (yellow), cotton seed (brown) and can be attributed to the seeds that were used for the extraction of oil from the blended *Jatropha curcas* seeds and the catalyst used during the mixture.

Refractive Index

This involves the property of oil that enables it to be sorted easily from a mixture of oils and fats. It makes it possible to determine impurity present in the oils (Olaniyan *et al*. 2007). The refractive index for the oil used is 1.262 which is close to ASTM standard -93

Biodiesel Yield

Based on the variables affecting *Jatropha curcas* oil methanolysis was studied under laboratory conditions. There were two experiments each involved in the four investigated variables of temperature, time, methanol-to-oil molar ratio and catalysts ($CoMgFe_2O_4$ and $MgFe_2O_4$) concentration. The optimum values for temperature, time molar ratio and catalyst were 60^oC, 180mins, 5:1, 7.1, and 0.5g each for the two nano catalysts been used. These results give high ester yield for ($CoMgFe_2O_4$) of 88, 92%, while ($MgFe_2O_4$) yield 57, 71% respectively. This is higher than 50% for 5:1 and 70% for 7:1 reported by Joshua (2012) for KOH as catalyst. This percentage shows that ($CoMgFe_2O_4$) and ($MgFe_2O_4$) are good nanocatalysts for the production of biodiesel using *Jatropha curcas* seeds oil and methanol concentration. See Table 4.

Table 4: Biodiesel yield for various catalyst and Mole Ratio of the methanol to Jatropha seed oil

S/N	Catalyst used	Temperature (C)	Time (min)	Mole Ratio(%) methanol to oil	Catalyst Conc. (g)	Biodiesel yield (%)
1	$CoMgFe_2O_4$	60	180	7:1	0.5	92
2	$CoMgFe_2O_4$	60	180	5:1	0.5	88
3	$MgFe_2O_4$	60	180	7:1	0.5	71
4	$MgFe_2O_4$	60	180	5:1	0.5	57

Conclusion

The present study on the analysis of the biodiesel produced from the seed oil extracted from the seeds was carried out using standard analytical methods. the variables affecting Jatropha curcas oil methanolysis was studied under laboratory conditions. There were four experiments each involved in the four investigated variables of temperature, time, methanol-to-oil molar ratio and catalyst concentration ($CoMgFe_2O_4$

and $MgFe_2O_4$). The optimum values for temperature, time, molar ratio and catalysts were 60^oC, 180mins, 5:1, 7.1 and 0.5g for each of the two catalysts been used. These results give high ester yields for $CoMgFe_2O_4$ of 88, 92% and $MgFe_2O_4$ yield was 57, 71% respectively. Based on these results, it is concluded that for methanol and Calcium Magnesium Spinel Ferrites ($CoMgFe_2O_4$) 88, 92% are the best recipes for transesterification of *Jatropha curcas* oil compared to methanol and Magnesium Spinel Ferrites ($MgFe_2O_4$) 57, 71%. Thus, Calcium Magnesium Spinel Ferrites ($CoMgFe_2O_4$) 7:1 and 5.1 ratios are the best optimum ratio and concentration for this reaction. As methanol to oil ratio was increased, the unreacted oil settled at the bottom was significantly decreased.

The results of this investigation reveal that *J. curcas* seed oil can also be useful in human nutrition in form of dietary supplements and possibly for livestock feed production

Some physico-chemical parameters of the biodiesel produced from *Jatropha curcas* seed oil were analyzed. The results showed that the biodiesel has a flash point of 120min, density (0.899/cm^3) and dark brown and yellow in colour based on the catalyst concentration. The parameters analyzed fall within biodiesel standard range. This is an indication that *Jatropha curcas* seed is a good source of biodiesel which is engine worthy and environmentally friendly. It is recommended that the Nigerian Government should adopt biodiesel production as policy to provide a sustainable alternative to fossil fuel dependency in the country.

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