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POSSIBILITY OF BIODIESEL PRODUCTION FROM CAESALPINIA PULCHERRIMA (PRIDE OF BARBADOS) SEED OIL

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ABSTRACT

Reduction in fossil-fuel based resources is in the vast due to the growing concern to meet the rising global demand for energy and the need to reduce global warming caused by carbon dioxide emissions, mitigate environmental pollution and overcome the unpredictable movement in crude oil demand and fluctuation of prices. Biofuel's production is increasingly gaining global popularity as cleaner production technology and alternative energy sources to crude oil. However, research has not established the synthesis of Biodiesel from *Caesalpinia* (C.) *Pulcherrima* (Pride of Barbados) seed oil. The study is based the manufacturing of biodiesel using oil extracted from C. Pulcherrima seed. The production of biodiesel from C.Pulcherrima seed oil was due to factors such as inconsumable fruit, cannot bring about shortage of food production etc. The following important tests were carried out to ensure the good yield and quality of the biodiesel produced at the completion of chemical reaction. The tests are moisture content, Iodine value and free fatty acid. After these tests trans-esterification process then proceeds. Under standard conditions and using standard materials, the manufacturing of biodiesel from C. pulcherrima seed oil was done without hitch. The process was carried out when the extracted oil was heated at temperature of $50^{o}C$ with sodium methoxide at a temperature of $60^{o}C$ being added as solution. A magnetic stirrer was used for stirring until a homogeneous mixture was obtained. Settling was achieved for 24 hours after settling for 24 hours, a by-product known as glycerin was then decanted out. The main product, biodiesel was completely cleaned to remove both soap and methanol. The result shows that the produced biodiesel met the ASTM6751 limit for biodiesel. *Caesalpina Pulcherrima* seed oil has proven to be a valuable raw material for the production of biodiesel with its characteristics as follows; specific gravity (Kg/L) = 0.817, Pour point, (^{0}C) =14, Cloud point, (^{0}C) = 11, Sulphur content, (mg/L) =11.25, Carbon residue, (% wt) = 0.45, Kinematic viscosity, (mm^2s^{-1}) = 5.98, Cetane number = 66.7, Flash point, (^{0}F) = 152, Free glycerin, (% mass) = 0.03, Total glycerin (%mass) = 0.18

1.1 Introduction

Current energy demands are to a large extent dependent on fossil or petroleum-based fuels, which are non-renewable. However, there has been a gradual decrease in fossil-fuel based resources due to the growing concern to meet the rising

global demand for energy and the need to reduce global warming caused by carbon dioxide emissions, mitigate environmental pollution and overcome the unpredictable movement in crude oil demand and fluctuation of prices. The application of fossil fuels from times has been shown to worsen global warming and accelerate climate change. Therefore, to accelerate the pace of development of alternative non-renewable energy, economic feedstock production and processing are required to improve the commercialization aspects of renewable sources, including biofuels from microorganisms.

Biodiesel production is available to combats conventional fuels in recent years (Aransiola et al., 2014). Sources have shown that it can be renewed, non-toxic and biodegradable, and therefore does not constitute hazard to the environment. Biofuels production is increasingly gaining global popularity as cleaner production technology and alternative energy sources. Biofuels can be directly or indirectly derived from plants, oils or microalgae through the process of photosynthesis (Mondal et al., 2017; Ganesan et al., 2020; Yi-Feng & Quigyu, 2021)

Biodiesel is a fatty acid of methyl or ethyl ester (FAME or FAEE) which can be applied for as substitute for diesel engine fuel. Biodiesel is manufactured through the process of trans-esterification of vegetable oils extract and animal fat with catalyst in the form of methanol or ethanol. The increasing demand of biodiesel is due to the possession of the same properties in comparison with normal fosil fuel and other important as in emissions of low soot, independent on crude oil, etc. (Madaan & Suneja, 2018).

Over 350 plants that possessed oils have been discovered being important for the production of biodiesel. But some of these plants are considered viable for industrial and commercial manufacturing of biodiesel. These are soybean, rapeseed, sunflower seed, cottonseed, palm fruit, jatropha, etc.

However, considering the environmental factors and availability, various consumable oils seek application as sources biodiesel manufacturing by various nations across the world. Countries like Malaysia and Indonesia used palm fruit oil and coconut oil. In United State of America, U.S.A, soybean oil is mostly applied for the production of biodiesel. But for industrial scales, safflower and oil extracting from peanut is mostly applied for manufacturing.

The manufacturing of biodiesel from inconsumable oils is currently undergoing sustained development. The reason being that consumable oils are used for food and production of energy for human consumptions and there will be scarcity if continually used for biodiesel production. To decrease the costs of manufacturing and diverse from the use of edible oil for fuel production, non-edible oils are then applied mostly as sources for the production of biodiesel. Comparing with comsumable oils, non-edible oils are affordable and readily available. Inconsumable oils that consist high value of mono-unsaturation for manufacturing of biodiesel are Neem oil, Jatorpha curcas oil, Honge oil, Caper spurge oil, Putranjiva oil, Rice bran seed oil, Castor oil, Yellow Oleander oil, Crambe oil, and Tamnuoil (Aransiola *et al.,* 2014). Oil from soybeans, *Jatropha curcas* (Adeniyi *et al.,* 2018; Kamel *et al.,* 2018), *Euphorbia lathyris*, *Brassica napus* and *Ricinus communis* (Zapataa *et al.,* 2012) was proposed to be in abundant all over the world and possesses significant quality for the production of biodiesel that can operates diesel engines with maximum efficiency.

Soybeans, mainly grown to feed people and livestock, are the richest source of oils for the biodiesel industry. However, the energy and cost needed to grow them, extract their oils and make fuel are high. Using waste cooking oils from commercial kitchens lowers the cost, but not enough to make production pay off (Nightingale, 2020).

Among the over 75 plant species which have more than 29% oil in their seed/kernel; palm, *Jatropha curcas*, and *Pongamia pinnata* (Karanja) were found to be the most suitable for biodiesel production. It has been shown that biodiesel produced from palm and Jatropha have physical properties in the right balance; conferring it with adequate

oxidation stability and cold performance. Most of the strict requirements set by the American and European biodiesel standards for biodiesel have been achieved.

It is maintained that there are maximum opportunities for the manufacturing of biodiesel using inconsumable oil sources that can enhance the next generation biodiesel manufacturing (Atabani et al., 2013).

1.2 Statement of Problem

The use of fossil fuels over the years has been shown to worsen global warming and accelerate climate change. There has been an intensive search for non-edible plant oils for biodiesel production. The use of edible oils as raw materials for biodiesel production impacts on food resources hence, the need for increased search for acceptable non-edible oils for biodiesel production. This work therefore is carried out to determine the suitability of *C. Pulcherrima* plant seed oil as a source of biodiesel production. The biodiesel produced will help mitigate environmental pollution by reducing global warming caused by carbondioxide emissions.

1.3 Aim of study

The aim of this project is to determine the possibility of extraction and the transesterification of *Caesalpina Pulcherrima* seed oil to produce biodiesel which would serve as an alternative fuel to conventional diesel engines. This will reduce the dependence on crude oil thereby mitigating environmental hazards like acid rain, global warming and greenhouse emissions

1.4 Objectives of the Study

The following objectives are highlighted to achieve the stated aims;
  (i) To obtain and extract oil from *C. pulcherrima* seeds for transesterification.
  (ii) Analyze the oil extracted from *C. Pulcherrima* seeds.
  (iii) Transesterification of the extracted oil and characterization of the biodiesel
  (iv) To compare the produced biodiesel with petro-diesel and ASTM6751 (2017) standard of acceptable biodiesel.

1.5 Scope of the study

This work is experimental, plant seed was obtained and the oil extracted to produce biodiesel by transesterification. The produced biodiesel was then characterized and compared to ASTM D975 standard for Petro-diesel and the ASTM6751 (2017) standard acceptable range of biodiesel.

1.6   Significance of the Study

  i.   *Caesalpinia Pulcherrima* plant seed oil which does not compete with human consumption will be a standard raw material for manufacturing the biodiesel.
  ii.   The laboratory manufactured biodiesel will reduce the dependence on crude oil thereby mitigating environmental hazards like acid rain, global warming and greenhouse emissions.

2.0 *Caesalpinia pulcherrima*

Caesalpinia pulcherrimma is the family Fabaceae which contains Pride of Barbados as a member. Another names given to the members consisting this family are Flower fence, Dwarf flamboyant, peacock flower, Dwarf poiciana, Caesalpinia and Mexican bird of paradise. Pulcherrimma is a species name which usually signifies "very pretty" and the flower has importantly proved the name. The species flower consisted of five shadowed petals and some significant stamens of

about six-inch long red color. Therefore, Pride of Barbados is useful for heating shade by insects and thus mostly insects pollinated flower.

In climates without frost, Pride of Barbados is always but small green shrub plant. But in tropical climates, the height is about 15 – 20m tall with its branches reaching and spreading about the same with in length. Both the branches, the petioles and stems are fused and contains sharp spines, the leaves look like fern compounding with numerous smaller oval leaflets. The color of Pride of Barbados are mixtures of both orange and red of the flowers. The length of Pride of Barbados flowers is about 2-3cm which are bowel shaped across and have five crinkled petals of orange and red color that are not equal in size. But the stamens are ten in number and completely red throughout and grow above the corolla. In tropical climates, the flowers are 8-10cm tall and in terminal clusters during the summer and winter fall when there is frost, the flowers also borne in clusters. The plant consists of both yellow and dark red color flowers. The flowers produced flat fruits that are typically legume and is about 3-4cm long. When dried they split and explode with sounds and the small brown beanlike seeds are collected. (Rodriguez, 2006).

2.1 Properties of *Caesalpinia* Seed

Caesalpinia pulcherrima plant *(*also popularly known as Pride of Barbados) seed oil is an ideal raw material for biofuel production. The plant is widely distributed all over Nigeria and is primarily planted as ornamental shed plant. In the physical and nutrient contents evaluation of PoB using standard analytical methods (gravimetric, Spectrophotometric and titrimetric), amino acid and fatty acid composition of the seeds flour were evaluated. The results of proximate composition (g/100 g sample) were: moisture (6 - 9 %), total ash (6 - 7 %), crude fibre (6 - 9%), crude protein (35 – 48 %), crude fat (5 - 6 %) and carbohydrate (39 – 46 %). Amino acid analysis revealed that leucine is the most concentrated essential amino acid (EAA) with value of 7.48 g/100 g crude protein while methionine was the least concentrated EAA (0.89 g/100 g crude protein). The predicted isoelectric point and protein efficiency ratio were 4.41 and 2.19, respectively. Result of fatty acid analysis showed that linoleic (C18:2) was the most predominant fatty acid with value of 51 – 53% while total saturated fatty acid was 21 - 24%. Generally, the studies revealed that seeds of *C. pulcherrima* are good sources of essential amino acids and unsaturated fatty acids (Yusuf et al. 2007; Aremu et al., 2012).

2.2 Use of *Caesalpinia* Oil for Biofuel Production

Ethanol and biodiesel are classified as biofuels used for transportation. These are produced from pyrolysis gasification of biomass materials and are mixed with gasoline as additive or diesel fuels, but can be used ordinarily in engines (US EIA, 2021). Biofuels can be characterized according to origin and type. Biofuels biomass can be sourced from the forest, or obtained from agro-industry waste, as by-product and agricultural waste. Categories of biofuels are bio-gas, bio-liquid and charcoal (Nigam & Singh, 2011; Williams et al., 2018). Ethanol and biodiesel are the common types of biofuels in use today and are both representatives of the first generation of biofuel technology. Both conventional diesel and biodiesel are blended and applied in ignition compression process in fuel engines. The blending can be 100% which is pure biodiesel or commonly 20and 80 percent's blending that are designated B20 and B80 respectively

Table 2.1: Physical Characteristics of Biodiesel (U.S Department of Energy, 2016)

Properties	Values
Specific gravity	0.88
Kinematic viscosity at 40°c	4.0 to 6.0

Cetane number	47 to 65
Higher heating value, Btu/gal	~127,960
Lower heating value, Btu/gal	~119,550
Density, Ib/gal at 15.5°c	7.3
Carbon, wt%	77
Hydrogen, wt%	12
Oxygen, by diff. wt%	11
Boiling point, °C	315-350
Flash Point, °c	100-170
Sulfur, wt%	0.0 to 0.0015
Cloud point, °c	-3 to 15
Pour point, °c	-5 to 10

3. Materials and Methods

3.1 Materials

The following materials and apparatuses were used in this study to investigate the manufacturing of the biodiesel on a laboratory scale. The materials are: *C. pulcherrimma* seed oil, methanol, sodium hydroxide NaOH, potassium hydroxide KOH, n-hexane, sulphuric acid H_2SO_4, distilled water, all chemicals and reagents used are of analytical standard. The apparatuses are: Soxhlet extractor, magnetic stirrer, hydrometer, hot plate, digital weighing balance, thermometer, stop watch, Oven, water bath, retort stand, conical flask, pipette, separating funnel.

3.2 Methods

3.2.1 Sample Preparation

C. pulcherrimma seeds were obtained from within Port Harcourt municipality in Rivers State, Nigeria. The C. pulcherrinma shells covering the seeds were allowed to dry in the sun for seven days, broken gently for the removal of seeds from the shells. The dried seeds were grinded using a blender and coffee grinder to obtain a fine consistency to maximize particle surface area by using 0.6 mm sieve plate. Determination of the optimum amount extractable oil from the meal was done following the method proposed by Jonas et al. (2020). Approximately 650 seeds per 1/4 the seed pod and seeds of *C. pulcherrima*

3.2.2   Oil Extraction from *C. Pulcherrima*

Oil from the seed of *C. pulcherrima* was extracted in this work using soxhlet extraction method. Fifty (50) grams of the grinded seeds (meal) was extracted with 350mL of the solvent, n-hexane of boiling point 68°C. The ground seeds were put into Soxhlet apparatus and hexane was added at a ratio of 6:1 (mL hexane to grams' meal). The mixture was given an initial stir to ensure that all meal was wetted with hexane. The extraction temperature was increased from 24°C (room temperature) to the boiling point of the hexane, and the meal size was fixed at 0.6 mm. Extraction time was 8 hours. When extraction was stopped, the hexane/oil mixture was taken, sieved and transferred into aluminum foil container for the evaporation of solvent, it is then kept in the fume cube board for 8 to 10 hours for safety reasons. A ratio of 1:1 hexane was poured into the Soxhlet for extraction 2, following the same method of extracting the oil. During discovering that the hexane has completely escaped from the mixture, the remaining biofuel in the apparatus was measured and reading was taken and then transferred into containers for analysis. The oil yield and the oil recovery were calculated with equation (3.1) and (3.2).

$$Oil\ yield, Y_O(\%) = \frac{M_o}{M_s} x100\ (\%) \qquad\qquad (3.1)$$

$$Oil\ recovery, Y_R(\%) = \frac{M_o}{M_s} x \frac{1}{S_O} \qquad\qquad (3.2)$$

Where,

M_O = mass of oil extracted in gram (g),

M_S = mass of solid (meal) used in gram (g), and

S_O = content of oil in the seed in (% sw/w).

At the end of the process, a volume of *C.pulcherrima* oil was recovered, purification was carried out, and then characterized with the method of standard testing to prove whether the extracted oil is viable for the production of biodiesel.

3.2.3   Oil Refining

The refining of *C. pulcherrima* oil was done with the procedure of Santos (2009). The methods of purification of oil such as degumming, neutralization, dewaxing and bleaching are given below.

3.2.3.1 Degumming and Neutralization

The procedure of degumming means to separate oils from contaminants in the form of compounds of phosphorus, which are lecithin and cephalin and then conversion to produce biodiesel. The substance separated is known as gum. The process of de-ionization was carried after the decanted oil heated at temperature between 65 and 67°C and 2 percent by weight of oil was then added. Also, 2 percent phosphoric acid containing oil was mixed to facilitate the process of degumming. The mixture was stirred continuously for about 1 hour at a temperature of considered above. Then the mixture was subjected to centrifugation to separate out the hydrated gums by centrifugal force. Conclusively for this procedure, both the oil and gums were removed and determination of the weight was done and recorded.

After degumming, sodium hydroxide, NaOH was added to the oil for neutralizing in aqueous solution. The content of FFA

present in C. pulcherrinma determined the volume of sodium hydroxide to be added. The American Oil Chemists Society (AOCS) official method was employed to determine the amount of FFA. Centrifugal force was also applied to separate the mixture with a contact time of 30 minutes. The oil which was passed through the process of neutralization was the washed by de-ionized water in 2 times to remove any atoms of soap present. Oil water were separated by the application of centrifuge. But oil and soap separated were weighed and recorded.

3.2.3.2   Dewaxing and Bleaching

There is the presence of waxes in the extracted oil that can cause cloud during cooling. Color substances and oxidized substances were also separated from the oil by bleaching. There was no trace of peroxide in the oil. Dewaxing was carried out by heating the oil to a temperature of 100°C. The process was continuously stirred with the addition of 1 percent Fuller's earth containing oil for the process time of 30 minutes. Application of centrifuge was made to remove clay from oil. Then, weighing of oil and oxidized substance was done and record was taken.

3.2.4   Characterization of *C. pulcherrima* Oil
3.2.4.1 Determination of Viscosity

The procedure for determining viscosity of the extracted oils are done by the application of viscosity. The filtered sample of oil was put into the viscometer through the inversion of the tube thinner arm applying suction force. The viscometer was placed vertically to its normal position. Also, the viscometer was placed into a temperature bath at 30°C. The bath was then heated to a temperature rise of 300°C. Then force of suction was used to increase the oil sample above the marked point. Finally, recording was taken after the flow of the sample between the upper and lower timing mark.

3.2.4.2 Determination of Moisture Content

Moisture content was determined by weighing the sample of oil. Then the mass was recorded as (w_1). Then the weighed mass (w_1) was oven dried for time, t and mass (w_2) was recorded after drying. Finally, moisture content percentage was determined using equation (3.3)

$$\% \, moisture \, content = \frac{w_1 - w_2}{w_1} \, x \, 100 \qquad\qquad (3.3)$$

Where,
w_1 = mass of oil sample before Oven drying in grams (g);
w_2 = mass of oil sample left after Oven drying in grams (g).

3.2.4.3 Determination of Free Fatty Acid, FFA

The laboratory process of titration was used to determine the free fatty acid contained in the oil sample. This was carried out by using potassium hydroxide, KOH to titrate with the free fatty acid applying phenolphthalein for indicator. A conical flask of 250mLcontaining neutral solution of 50mL was dissolved into by 2g of oil sample, then 3 to 4 drops of indicator was added. Then the combination was titrated in 0.1 molar KOH. Continuous stirring was carried out until about 15 seconds when the mixture turned pink color.

3.2.4.4 Determination of Specific Gravity of the Oil

Determination of the oil density was carried out by the application of density bottle. An empty dried bottle was weighed at 25 mL and the weight was recorded as (w_0). Then the oil sample was transferred into it. After this a stopper was put

into the bottle and weigh again, and the weight (w_1) was recorded. Finally, water with cleaned and dried weight was used to replace the oil and it was weighed to obtain weight (w_2). The specific gravity was calculated as:

$$Specific\ gravity = \frac{w_1 - w_0}{w_2 - w_0} \qquad (3.4)$$

3.2.4.5 Determination of Saponification Number

Determination of saponification number was carried out by filtering off impurities and moisture remaining in the oil sample. Then 5g of oil sample was transferred into a conical flask containing 5mL of potassium hydroxide, KOH. The mixture was allowed to drain out of the burette for about 15 seconds. A heat reflux condenser connected to the flask was heated to a temperature for an hour. After cooling, the condenser and the flask were cleaned with distilled water. The titration was carried out against HCl of 9.5 molar with indicator of about 1mL and stirred continuously until a pink coloration was obtained. A blank method was carried out by applying a blank solution under the condition for the determination of blank solution using HCl solution. Finally, the saponification number was calculated after recording the amount of HC used with Eq(3.5) as;

$$SN = \frac{56.1 \times C \times (V_O - V_s)}{m} \qquad (3.5)$$

Where,

 VS = HCl volume used for the determination,

V0 = HCl volume used for the blank test,

C = normality factor of the HCl solution and

m = mass of the test portion (oil sample).

3.2.5 TRANSESTERIFICATION PROCESS

The process was carried out by heating 10.5mL of C. pulcherrinma oil to a temperature of about $50^{\circ}C$ after measuring. Using the apparatus Soxhlet containing sample of methanol, purification of methanol was done by heating the round bottom Soxhlet apparatus. 0.2g of NaOH was weighed. Preparation of the catalyst concentration was done by methoxide solution using 250mL beaker of 0.25g of sodium hydroxide pellet and 63mL methanol to obtain a molar ratio of methanol to oil as 6:1. A continuous stirring of the solution was done until a complete dissolution of the sodium hydroxide pellet. The temperature of methoxide was raised to $60\,^{\circ}C$ by heating in an oven.

Solution of methoxide was then transferred into slightly boil C. pulcheerinma oil the magnetic stirrer was applied for stirring for about 50 minutes. Settling of the mixed component takes place a separating funnel for 24 hours. A two layers component was observed in the separating funnel. The upper layer which is the biodiesel was carefully decanted into a beaker, and the bottom layer containing soap and glycerol remain in the separating funnel. The separated biodiesel obtained was then washed with warm water to separate soap and glycerol out to obtain pure biodiesel. A hot plate was then applied to dry up any water content remaining in the biodiesel produced. The product from transesterification process was weighed and the record was taking.

The process of transesterification was carried out repeatedly by varying the molar ratio of methanol to C. pulcherrinma oil with constant time, temperature and the concentration of catatlyst.

3.2.6   Analytical Tests for the produced Biodiesel

3.2.6.1 Determination of biodiesel yield

An estimation of percentage yield of biodiesel per batch was done using:

$$\text{Biodiesel Yield} = \frac{mass\ of\ biodiesel\ yield}{mass\ of\ C.Pulc\ herrima\ oil\ used} \times 100 \qquad\qquad 3.5$$

3.2.6.2 Cetane Number (CN)

Diesel fuel cetane number is defined as a substitute of the gasoline number and is the index quality characterization for diesel fuel. During ignition of the of the engine combustion chamber, cetane number is used to indicate the preparation of fuel in the engine. However, high cetane number gives faster or easier ignition of engine.

Fuel diesels was early attributed to consumable commodities as evaluations were done. It is postulated that for instance, smooth operation is observed in some engine than the others because fuels comparison have been done using the quantitative approaches and processes. Determination of the quality of engine diesel fuel ignition in similarity with octane ratio was done by Boerlage and Broeze of the department of laboratory in Netherlands in 1930s by the application of 1-hexadecane and α-methylnaphthalene. 1-hexadecene as the cetane or ketene is the reference fuel that completely burns in air easily. It is characterized by straight chain structure and desinated100 cetane number. α-methylnaphthalene as the 1-methylnaphthalene is the second reference fuel that is difficult to ignite, and is designated 0 cetane number. It is characterized by two aromatic rings. Fuel cetane number was assumed to be blended 100% by mass with cetane and α-methylnaphthalene that can ignite efficiently in comparison with testing fuel (Ratcliff et al., 2014).

It was difficult for the United State of American researchers to obtain a double bond cetane or 1-hexadene in one position. However, cetane was easily oxidized when stored. As a results of difficulties in producing cetane or n-hexadecane with high purity, cetane was designated 100 rating number and primary reference fuel, PRF.

Definition of cetane Primary Reference Fuel number was given as:

CN = percent volume n-hexadecane + percent volume α-methylnaphthalene.   (3.6)

The approximation relating cetane and ketene (cetene) rating when compared was given as:

Cetane Rating = 0.875 × Cetene Rating   (3.7)

A replacement of the second reference fuel was 2,2,4,4,6,8,8-heptamethylnonane, HMN due to the impossibility of applying α-methylnaphthalene in the laboratory. The former was suspected to be carcinoid and a foul smell. The later was assigned cetane number 15.

The international method for measuring the cetane number is D613 based on ASTM international. It is the diesel fuel standard method of measurement. In 1941, there was the first publication of this method and a substitute was replaced as HMN, cetane number, CN is 15, and α-methylnaphthalene CN is 0 which is the lower scale and primary reference fuel, PRF.

The definition of the primary reference fuel blended cetane number is given as:

CN = percent volume n-hexadecane + 0.15 × (percent volume HMN)   (3.8)

3.2.6.3 Flash point

Flash point determination is carried out by the method of closed cup in which the vessel containing a sample is thermally jacketed from the surrounding or atmosphere. The vessel and content is then heated so that there will be ignition. This method is applicable to other chemical/gas or fuel storage facilities.

The closed cup method is also applicable for the specification and regulation of products in real situation. It is useful process for fuel testing. Due to the flammability of sample at the beginning of testing, the method gives low flash point. The method's application is basically for industrial standards because of the lower results provided. It is also applied for the testing flash point high than 79°C of fire and flash point of the general petroleum products.

3.2.6.4 Kinematic viscosity

Gravitational force of capillary orifice is used for measuring kinematic viscosity by recording the time taken for a particle to pass through the orifice. This orifice consists of constant flow resistance to oil. Capillary contained variable sizes that can carry several samples viscosity.

A calibration constant is assigned for each tube of the capillary to be measured for the time taken by the fluid to pass through the capillary tube. This can be converted to kinematic viscosity. The international standard for measuring kinematic viscosity is the ASTMD445 in which modification in the analysis of laboratory oil for the conservation of time and efficient measurement (Drew, 2022).

3.2.6.5 Calorific Value (Cole, 2022)

The calorific value is determined experimentally using the specific heat test published in some article, and the procedure is discussed briefly as follows;

Experimental Set-Up

The procedure is done by measuring percentage by mass of water and transferred into the calorimeter. The sample is allowed to stay in the calorimeter until the temperature rises to room temperature. To obtain accurate results, there should be complete the same and enough volume of water in the calorimeter.

An approximately 300mL of water in a beaker was heated by a hot plate. A test tube containing the sample stainless-steel was carefully immersed in the beaker containing water placed on the hot plate, but was not allowed to touch the bottom or the side of the beaker.

Initially, a solid containing 316sample of 25.22g cylindrical stainless-steel was used. Accurate results were not obtained because of the test tube used for holding the sample. This is due to the fact that the test radius is bigger than the sample's radius, which led to the deficient experimental results.

Making changes in the experiment could completely destroy the sample. An insulated tong should be used to hold the sample and not test tube to obtain accurate results.

Wait

For evenly heated sample to produce good results, the beaker containing water should be heated to a temperature of 100°C and wait for approximately 10 minutes.

Transfer of Material

The sample was immediately transferred into the calorimeter after 10 minutes of heating. The transferred procedure should be immediately and quickly so as to reduce the heat lost to the surrounding environment. Ensure no amount of water enters the calorimeter so that it will not alter the mass of water calculated.

Subsequently, a metal thermols was used to substitute the Styroform cup calorimeter which was initially used for the experiment. This was done to determine how the conduction difference in the materials affect results.

Experimental Calculation

In the experiment, the application of the first law of thermodynamic was used. During cooling of the sample, there was lost energy to the surrounding in form of heat. In relation with the experiment, energy does not just lose raises the temperature of the water. Thus, the quantity of gain by water equals the heat lost by the stainless-steel sample is determined. This is expressed mathematically as;

Qw = -Qs   Where **Q** is the change in heat.   (3.9)

Applying the mass and specific heat of water used, the equation above can be expressed as;

Qw = cwmw (Tpeak – Tinitial) w = -Qs = csms(Tpeak – Tinitial)s   (3.10)

The formula can then be rearranged for determining the specific heat of the sample.

cs = cwmwΔTw / msΔTs   (3.11)

4   Results and Discusssions
4.2   Oil Content of *C. pulcherrima* Seeds

The quantity of oil determined from 1000g of the solid meal was obtained as 45.7% w/w. *C. pulcherrima* plant has many species, not named in this work, that are likely to develop maximum oil yield seeds. Applying the principle of mass balance, the amount of oil from the seed species need to be estimated based on Eqn (3.2) for the calculation of the amount of oil recovered. But several publications do not report the procedure of how to determine the amount of oil recover from seeds, thus results in difficulties to determine the actual amount of oil that can be recovered.

4.3   Effect of Temperature on Oil Extraction

From figure 4.1, the oil yield was 45.7%w/w at the boiling point of the solvent (68 ^{0}C). Applying hexane solvent, the maximum oil extracted was found to increase as the extraction temperature increases. Beyond the boiling point of the solvent, there was no significant oil yield.

When the boiling point was at 68°C, the extracted oil produced 45.7% w/w yield. Applying equation (3.2) and S_O of 0.468, the 45.7% w/w oil yield is calculated to be amount of oil recovered is 97.6% w/w, which shows a suitable yield for the chosen parameters. Between 95and 99% w/w oil from Jatropha seed applying hexane solvent was recovered (Atabani et al., 2012). The results show that at higher temperature, the oil is more soluble in the solvent that resulted in the increase of extraction of oil. But at maximum temperature above 68°C, there was no observable increase in the amount of oil extracted, thus 68°C was assumed to be the actual boiling point. This is premised on the fact that the solvent certainly will
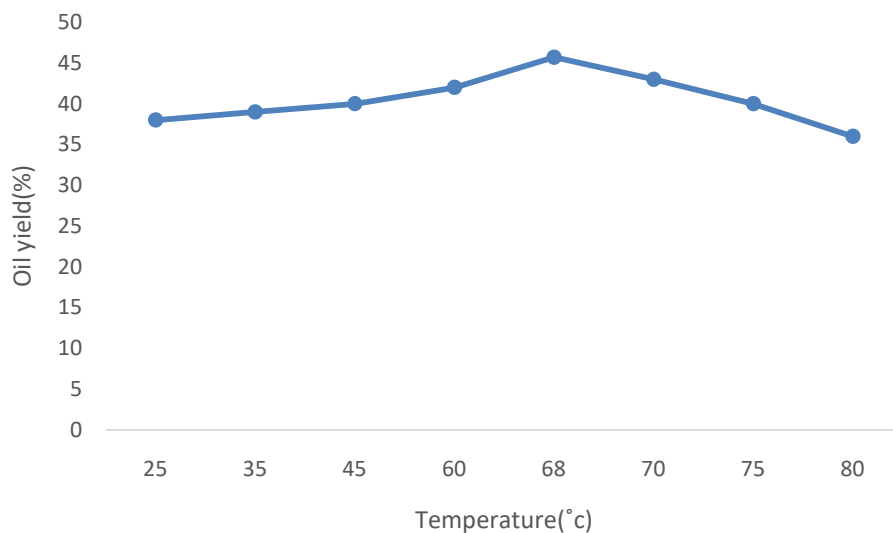
start boiling off.

Figure 4.1 Effect of extraction temperature on oil recovery

4.4 Effect of Extraction Time

From figure 4.2, the oil yield of 45.7%w/w was obtained within 7 hours of oil extraction. The higher the time of extraction the more the yield of oil. The yield decreases for after 7 hours and no observable rise in oil yield after 6hrs of extraction. This suggests that almost all of the oil is extracted after 7 hours.
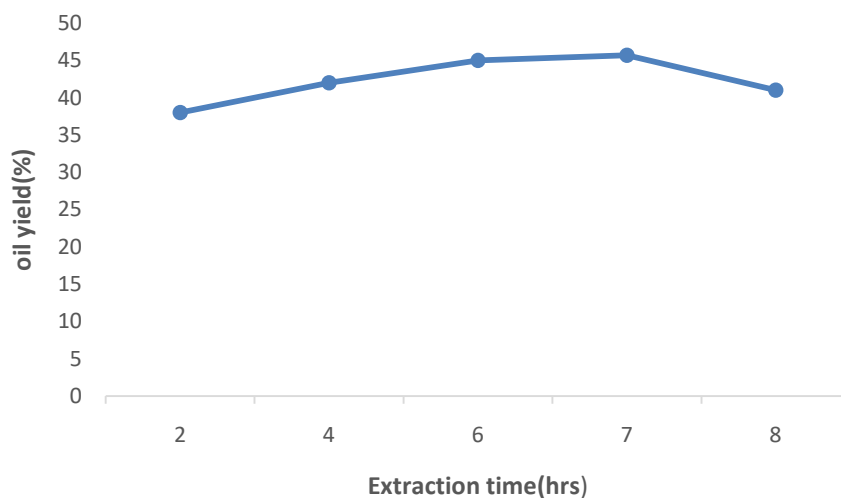
Figure 4.2 Effect of extraction time on oil recovery.

4.5   Effect of Solvent-to-Solid Ratio

Result of experiment shows that the effect of solvent-to-solid ratio on the oil yield is high, indicating that the amount of solvent used is possibly adequate and that hexane appears to provide a good yield in the extraction of oil from *C. pulcherrima* seeds. Molar ratio of solvent/solid that was taken to be 6:1, produces 45.7% w/w yield of oil for hexane. Yusuff (2018) reported oil yield of 56.69% w/w in his study applying n-hexane for Jatropha plant seed. This high yield attributed to the several species of Jatropha plant. It is assumed, 6:1 molar ratio of solvent/solid is adequate for the scope of the work. It is therefore deduced from the results that the molar ratio of 6:1 when increased, causes rise in the yield of oil extraction and it is also attributed to the increase in the concentration gradient existed and resulted in efficient performance of mass transfer between liquid and solid phases.

4.5   Analysis of the *C. pulcherrima* Seed Oil as compared to *Jatropha oil.*

Table 4.1 shows various properties of the *C. pulcherrima* oil used for the production of biodiesel. It shows that properties of the oil are within acceptable range for transesterification process.

Table 4.1: Properties of the *C. pulcherrima* oil extracted compared to *Jatropha* to be used for biodiesel production

Property	*C.Pulcherrima* Oil Value	*Jatropha Oil*
Specific gravity	0.885	0.9186
P^H	4.92	5.62
Free Fatty Acid	28.2	18.4
Saponification number, (mgKOH/g)	196	188-198
Moisture content	0.24	0.20
Viscosity, (cp)	56.2	50.73
Acid value, %	42.0	38.1

It was observed that, the saponification value of the *C. pulcherrima* oil is 196; and is between the acceptable limit. The value of saponification is significant because the production of high value resulted in higher amount of soap than the required percentage of biodiesel. Moisture content is also considered paramount in this study because high moisture content produces high amount of soap which leads to difficulties in the separation of glycerin from the produced biodiesel as observed form Table 4.1 with 0.24 moisture content during transesterification reaction. Other properties affecting this process are the free fatty acid and PH which are of paramount concerned, because high PH formed high value of glycerin. Thes properties of *C. Pulcherrima* oil are within the range of the acceptable standard as compared to *Jatropha* oil which is a standard oil for biodiesel production.

4.6   Characterization of the Biodiesel Produced from *C. Pulcherrima* as compared to Petrol diesel, the Biodiesel from *Jatropha* oil and ASTM 6751 (2008) standard for biodiesel.

The characterization of the biodiesel produced was shown in Table 4.2. The acceptable range of was compared with ASTM6751 allowable biodiesel standard. The results show cloud and pour points of the manufactured biodiesel higher

above the set conventional petro-diesel. At any temperature in which the fuel cannot flow is known as the pour point and high value above this point, the efficiency of the biodiesel is lower than the conventional fuel (Peterson & Reece, 1996). Flash point is the most significant properties of fuel. Biodiesel has a flash point temperature of 152oC above the conventional fuel with 50oC flash point. Thus, biodiesel is easily safe in its applications and storage. It is difficult for fuel with lower flash point temperature to ignite at that point thus resulting in high risk of ignition temperature.

Flash point is applied for the measurement of the quality of biodiesel combustion in the process of ignition compression in engine. The cetane number is assumed the determinant of the quality of ignition in its effects of the following processes in engine, hard starting, poor performance of engine, warm up and roughness of combustion in the engine.

Table 4.2: **Characteristics of the biodiesel produced from C.Pulcherrima oil compared to Petro-Diesel D975 (2017), ASTMD6751 (2017) and Biodiesel from Jatropha oil (Bahadori, 2012)**

Property	Bio-diesel Values from *C.Pulcherrima*	Bio-diesel Values from *Jathropha*	Petro-Diesel ASTM D975	ASTM D6751 Biodiesel Limit
Specific gravity(kg/L)	0.817	0.90	0.85	0.95 max
Pour point, (^{0}C)	14	2	-35 to -15	-
Cloud point, (^{0}C)	11	37	-15 to 5	40 max
Sulphur content, (mg/L)	11.25	-	-.05 max	10 max
Carbon residue, (% wt)	0.45	0.20	87	15 max
Kinematic viscosity, (mm^2s^{-1})	5.98	4.93	1.3 -4.1	1.9– 6.0
Cetane number	66.7	52	40-55	47 min
Flash point,(^{0}F)	152	138	60 -80	130 min
Calorific values(Jg-1)	39500	38450	45000	-
Free glycerin, (% mass)	0.03	0.05	-	0.02
Total glycerin, (% mass)	0.18	0.32	-	0.24

In relation to fuel volatility rating, the fuel with more volatility have high rating than the catane rating. The fuel will not burn completely if the cetane number is higher. Ignition of the fuel in engine should not immediate, it should be allowed to completely combine and form complete mixture with the air to produce combustion that is at maximum. It is recommended from literature that engines operating using diesel should have cetane number ranges from 45 to 67 with a require minimum of 40, the production of biodiesel in this study gave 66.7 cetane number that shows that the value is within the limit of specifications that can best operates the diesel engines.

The viscosity of the fuel is also significant because of its effects on the atomization process in the combustion chamber during diesel injection into the engine. This is due to the fact that minimal amount of fuel injected results in complete combustion. Incomplete combustion produces carbon in the piston and rings walls, valves and tip of injector which results in high viscosity that is liable to cause engine clogging parts. But the ASTM biodiesel produced viscosity standard is applicable within the limited specification.

To achieve maximum of engine, it is significant to consider the density of the bio-fuel, because high density causes the difficulties of pumping the fuel into the engine. But in this study, the density of the biodiesel produced is 0.817 that is

according to the specified limit in the ASTM standard.

Conclusion

It has been confirmed that *C. pulcherrima* seed oil may be used as resource for the production of biodiesel. Characterization of the properties of the oil extracted from the seeds shows that the oil is within the range of the acceptable standard as compared to *Jatropha* oil which is a standard oil for biodiesel production. The conditions used in this work yielded 97.6% of biodiesel. The produced biodiesel was characterized, using appropriate analytical methods.

From analysis the results of the characterization, the physical properties of biodiesel from *C. pulcherrima* oil (specific gravity (Kg/L) = 0.817, Pour point, (^{0}C) =14, Cloud point, (^{0}C) = 11, Sulphur content, (mg/L) =11.25, Carbon residue, (% wt) = 0.45, Kinematic viscosity, (mm^{2}s^{-1}) = 5.98, Cetane number = 66.7, Flash point, (^{0}F) = 152, Free glycerin, (% mass) = 0.03, Total glycerin (%mass) = 0.18). ASTMD6751 was applied to determine the contents of methanol according to the specification limits. It is also observed that biodiesel viscosity drops drastically from 56.8cp to 5.98 mm^{2}s^{-1} when compared with petro-diesel at end of the process of transesterification.

Recommendations

Based on the objectives and results of this study, the following recommendations are proposed;

(i)   There should be further experimental findings on how several variables in the of types of solvent, reaction temperature and time, molar ratios of reactant, types of catalyst types and concentration on the oil extraction from *C pulcherrima* seeds and biodiesel yield with a view to optimizing production.

(ii)   It is also recommended that Petroleum Ester, Ethanol should be applied as oil extraction solvent because of its low purchasing cost and minimized cost of production of *C. pulcherrima* oil biodiesel.

Contribution to Knowledge

There is no information in literature on the production of biodiesel from *Caesalpinia Pulcherrima* seed oil. Hence, this study has shown that Biodiesel production from *Caesalpinia Pulcherrima* (Pride of Barbados) seed oil is achievable. The study also reveals that the produced biodiesel characteristics are comparable to that of the petro-diesel in accordance to the ASTM standards for biodiesels.

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