Nigerian Journal of Tropical Engineering
Vol. 15 No. 1 | ISSN: 1595-5397 | Dec. 2021

BIODIESEL PRODUCTION FROM *PARINARIUM MACROPHYLUM* SEED OIL USING SODIUM HYDROXIDE AS HOMOGENEOUS CATALYST

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ABSTRACT

*Biodiesel has gained support and recognition as a fuel to replace and blending agent with fossil diesel. In search of non-edible seed oil feed stock that can be used for biodiesel production. In this context, non-edible seed oil (*P. macrophylum*) was used for biodiesel production using sodium hydroxide (NaOH) as homogeneous catalyst. An investigation was carried out with P. macrophylum seed oil present in Bida, Niger State. The leaf of this seed is used for medicinal purpose by Bida people for treatment of scorpion and snake bite. The seed yielded 40.0% oil by solvent extraction. The oil was transesterified with methanol using homogeneous catalyst sodium hydroxide (NaOH) with optimize parameters; methanol to oil ratio (6:1), temperature (55°C), catalyst concentration (1.6 wt%), reaction time (60 min), and agitation speed (300 rpm). The cloud point and pour of the produced biodiesel falls between (-11.2 and -4.5) which is within ASTM and EU Standards. The biodiesel yield of 74.2, 75.3, 80.2 and 83.2 were also recorded with NaOH catalyst which fasting transesterification reaction than heterogeneous catalyst (CaO). P. macrophylum oil can be a potential feedstock for biodiesel production. Since the oil is non-edible and it will not interfere with food chain.*

Keyword: *Biodiesel, P. macrophylum oil, potential, transeterification, production*

INTRODUCTION

The use of petroleum for various activities has led to the depletion of petroleum stocks. Therefore another alternative must be sought as a substitute for petroleum. One of the alternative fuels that have been developed over the years is biodiesel. Biodiesel is one of the attractive alternative fuels that can be produced from renewable sources. The standard process for biodiesel processing is by transesterification process. The synthesis of biodiesel by transesterification reaction will not take place without a catalyst. One type of catalyst used to synthesize biodiesel from triglycerides with alcohol is the base catalyst (Verma *et al.*, 2016). Alkaline catalysts often used as NaOH, KOH, and calcium hydroxide ($Ca(OH)_2$) is a homogeneous alkaline catalyst. The advantage of these homogeneous catalysts is that they are very fast during transesterification process.

Biodiesel is a non-toxic, biodegradable, renewable fuel that can be produced from a range of organic and renewable raw material including fresh or waste vegetable oils, animal fats, and oilseed plants. Biodiesel has significantly lower emissions than petroleum-based diesel when it is burned, whether used in its pure form or blended with petroleum diesel (Hasibuan *et al.*, 2019). It does not contribute to a net rise in the level of carbon dioxide in the atmosphere and leads to minimize the intensity of greenhouse effect. In addition, biodiesel is better than diesel fuel in terms of sulphur content, flash point, aromatic content and biodegradability (Aransiola *et al.*, 2012).

Developing countries have a comparative advantage for biodiesel production because of greater availability of land, favourable climatic conditions for agriculture and lower labor costs (Hasibuan *et al.*, 2019). In developed countries there is a growing trend towards employing modern technologies and efficient bioenergy conversion using a range of biofuels, which are becoming cost-wise competitive with fossil fuels. Many studies have investigated the environmental

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benefits and impacts of biodiesel (Agbro and Ogie, 2012).

The successful introduction and commercialization of biodiesel in many countries around the world has been accompanied by the development of standards to ensure high product quality and user confidence. Some biodiesel standards are ASTM D6751 (American Society for Testing and Materials) and EN 14214 (European norm) (Dzida and Prusakiewicz, 2014). Biodiesel fuel is attractive and recently increasing attention worldwide as a blending component or a direct replacement for diesel fuel in vehicle engines. For example, B5 used in Europe contains 5% of biodiesel and 95 % of petro diesel. Biodiesel blends up to B20 can be used in nearly all diesel equipment and are compatible with most storage and distribution equipment source. These low-level blends generally do not require any engine modifications. There are different potential raw materials for biodiesel production. Currently, edible oils are the main resources for world biodiesel production. However, non-edible seed oil of Ginger Bread (P. macrophylum) is used for biodiesel production using sodium hydroxide (NaOH) as homogeneous catalyst (Galadima *et al.*, 2015).

MATERIALS AND METHODS

The plant seeds (*P. macrophylum*) were collected from different places within Bida town in Niger State.

Sample Preparation and Oil Extraction

The seeds collected were cleaned by removing foreign materials such as insects, stains, leaves, sand and dirts. After cleaning, the seeds were dried in the oven at 300°C for 72 hours until constant masses were obtained. The dried seeds were then mechanically dehulled to remove the seed coat.

Removal of the seed coat is important because the seed coat contains little or no oil and more importantly, inclusion would make extraction less efficient. The dehulled seeds were further dried at 400^{0}C for another 48 hours and ground to powder using pestle and mortar. The oil was extracted from *P. macrophylum* seed using soxhlet extractor with petroleum ether as solvent. The percentage oil yield were determined. The physicochemical properties of the oil extracted was carried out according to AOAC (2009). Standard methods were used to analyze the oil.

Refining of P. macrophylum Seed Oil

Prior to refining of the seed oil by esterification, its free fatty acid was determined. In order to do this, 10.0g of the seed oil was dissolved in 25ml propanol and the solution was stirred., Thereafter, two drops of phenolphthalein were added. The solution was titrated against 2.0M sodium hydroxide to pink colour. The acid value (free fatty acid) was calculated from the titre value. The oil was esterified with a mixture of hydrochloric acid and methanol. The mass of methanol used was calculated as 2.25 x % FFA x mass of oil and that of hydrochloric acid as 0.02 x % FFA x mass of oil (AOAC, 2009). These were mixed and added to the oil at 60°C. The temperature was maintained at 60°C for 55 minutes. The product was transferred into separating funnel and left to settle. The organic layer was collected at the bottom and tested for acid value again. The process was repeated until the acid value reduced to 0.58 (AOAC, 2009).

Transesterification

100ml of the refined oil was heated to 60°C, a mixture of 15.5g methanol and 0.8g sodium dydroxide catalyst were added and the temperature was maintained at 60°C for 55 minutes. The procedure was repeated with 1.0, 1.2 and 1.4g of the catalyst keeping other parameters constant. The products were filtered poured into separating funnel to settle. The biodiesel was dried on hot plate to remove residual methanol (AOAC, 2009).

Determination of peroxide value

The sample (1 g) was weighed into a conical flask. 1g of powered potassium iodide (KI) and 20cm^3 of solvent mixture (2 volume of glacial acetic acid + 1 volume chloroform) was subsequently added to the conical flask. The mixture was shaken vigorously and allowed to stand in the boiling water for 30sec; and immediately poured into another flask containing 30cm^3 freshly prepared 5% potassium iodide solution. The previous conical flask was rinsed twice with the 25cm^3 of distilled water and poured into the flask. The mixture was titrated with 0.005M sodium thiosulphate solution using starch indicator. The

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production of biodiesel which are all accepted by Codex Standard for biodiesel production.

Iodine value is a measure of the degree of unsaturation and it is an identity characteristic of oil seed making it an excellent raw material for biodiesel production. The iodine value for *P. macrophylum* oil is (102 g/100g). Oils with iodine values less than ($100I_2$/100g) of oil are non-drying oils. Aremu *et al.*, (2015) reported that oil with low iodine value would have low number of unsaturated bond.

Effect of Transesterification Factors on the Biodiesel Yield given in Tables 2-7 are the various results obtained when various transesterifcation factors were varied to evaluate their effects on the system.

Table 2: Methanol to Oil ratio Effect on the Biodiesel Yield

Mole ratio	Yield (%)
1.1	20
1.2	35
1.3	40
1.4	50
1.5	65
1.6	75
1.7	80
1.8	65
1.9	60

Table 2 shows the result obtained when methanol to oil ratio was varied out. It can be observed that the more preferable ratio for Sodium hydroxide, methanol to oil ratio was 7:1 which gave the maximum biodiesel yield 80.0%; with constant temperature (55^0C), catalyst concentration (1.6 wt), reaction time (60min); and agitation speed (300rpm)

Table 3: Temperature Effect on the Yield of Biodiesel

Temperature (^{0}C)	Yield (%)
15	20
25	40
40	60
55	75
70	72
85	68
90	61

The reaction and yield of biodiesel were both strongly influenced by the reaction temperature used. The effect of varying the temperature from 15–90°C was studied. From Table 3, the maximum percentage yield of biodiesel obtained at 55°C was 75.02% from sodium hydroxide.

Table 4: Catalyst Concentration (wt %) Effect on the Biodiesel Yield

Concentration (wt %)	Yield (%)
0.2	20
0.4	30
0.6	35
0.8	45
1.0	60
1.2	70
1.4	73
1.6	77
1.8	68
2.0	65

The concentration of the catalyst is an important parameter of the transesterification reaction and has a strong influence on the yield of biodiesel. Excess catalyst reacted with the oil, leading to the formation of soap, thus as the catalyst concentration increased, the separation of esters became difficult (Babajide *et al.*, 2013). The most suitable catalyst for this process proved to be sodium methoxide. The basic catalyst, sodium hydroxide, achieved similar results but its methyl esters contents were slightly lower. The optimum concentration of sodium methoxide catalyst is 1.6 wt. % as shown in Table 4. A catalyst is used to hasten up the process and Sodium hydroxide (NaOH) and potassium hydroxide (KOH) are the common catalyst used in the reaction process (Ojiego *et al.*, 2014). High concentrations of alkaline catalyst form soaps in the presence of large residues of fatty acids resulting in emulsion formation between soaps and water molecules, thus leading to low yields of methyl esters (Babajide *et al.*, 2013)

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above procedure was repeated for the blank in absence of the sample (AOAC, 2009).

The peroxide value (PV) is given by:

$$PV = \frac{2(a-b)}{\text{Weight of oil}}$$

Where a = titre value of sample; b = titre value of blank.

Determination of iodine value

0.5g of the sample was weighed into a conical flask and 15 of trichloro-methane was added to dissolve the oil. 25cm^3 of Wij solution was subsequently added to the conical cm^3 flask and covered tightly in the dark for 30min. 20cm^3 of potassium iodide solution (10%) and 150cm^3 of water was added to the flask and the solution turned to red colour. This was titrated using 0.1N solution of sodium thiosulphate until the reddish colour separates out of the solution. 5cm^3 of starch indicator was added and a blue coloration appeared. The titration was continued until the blue coloration disappeared. A blank was carried out and the Iodine value calculated according to the recommendation of AOAC (2009).

The Iodine value (IV) is given by the expression:

$$IV = \frac{12.69 \times M \times (v_2 - v_1)}{\text{Weight of Sample}}$$

v_2 = volume of sodium thiosulphate used for blank
v_1 = volume of sodium thiosulphate used for determination
M = Molarity of sodium thiosulphate solution
12.69 = atomic weight of iodine.

Viscosity

100ml beaker was filled to three-quarter of its capacity with biodiesel sample, heated to 40^{0}C and immediately placed on discometer and a spindle of a viscometer was adjusted until it submerged into the sample. The viscometer was switched on after spinning. The viscometer was switched on after spinning; reading was taken from the scale.

Transesterification is a process whereby alcohol or methanol react with triglyceride to produced biodiesel and water. This process is reversible and it is catalyzed with either homogeneous catalyst (NaOH) or heterogeneous catalyst (CaO). Transesterification of oil or fat to produce a high yield of biodiesel is typically investigated by optimizing the following reaction variables: alcohol/oil molar ratio, catalyst concentration, reaction temperature, and reaction time involved. These factors were determined by the methods described by Betiku and Adepoju, (2015).

CHARACTERIZATION OF BIODIESEL PROPERTIES

Biodiesel properties such as density, cetane number, cloud point, flash point, pour point, refractive index were determined by standard method described by ASTM D6751.

RESULT AND DISCUSSION

Result of Physicochemical Properties

Table 1: Physicochemical Properties of the Oil

S/No.	Properties	Values
1	Yield (%)	40.0
2	Moisture content	3.2
3	Specific gravity	0.86
4	pH	4.32
5	Iodine value	102
6	Saponification value	112
7	Colour	Brown

The result of the physicochemical properties of the oil seeds of *P. macrophylum* is presented in Table 1.0. The percent oil yield is 40.0% using soxhlet extractors with petroleum ether as solvent. The range of (25 – 55%) as reported by Oderinde *et al.* (2009) for *Piloswillgma thonmingi*. This results indicate that the oil seed of *P. macrophylum* contain appreciable quantity of oil that is enough to be extracted for the commercial production of biodiesel.

The pH value of the oil as presented in Table 1.0 is 4.32. This value is within the range according to Codex, (2011) for biodiesel production. The pH for this oil is less than seven is due to the presence of fatty acid content.

The colour of the extracted *P. macrophylum* oil is brown. This colour is acceptable for biodiesel production according to Codex, (2011). Singh and Singh, (2017) reported brown colour for Jatropha oil for the product of biodiesel, Sanjay (2013) reported brown yellow colour for neem oil for the

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Table 5: Reaction Time Effect on the Biodiesel Yield

Reaction Time (min)	Yield (%)
20	15
30	35
40	55
50	65
60	76
70	72
80	68
90	65

The methanol to oil molar ratio used was found to be the maximum yield in this study. The maximum biodiesel yield was obtained when the reaction time was 60min as it can be noticed from the result presented in Table 5. Generally, the formation of biodiesel increases with temperature. However, by increasing the temperature beyond the methanol boiling point may burn the methanol and may influence the saponification reaction of triglycerides and reduced the biodiesel yield (Vuppaladadiyam *et al.*, 2013).

Table 6: Agitation Speed

Agitation Speed (rpm)	Yield (%)
100	30
150	40
200	55
250	70
300	75
350	70
400	68
450	60

Most literature indicate that during the transesterification reaction, the reactants initially form a two-phase liquid system. The mixing effect has been found to play a significant role in the slow rate of the reaction. As phase separation ceases, mixing becomes insignificant. The effect of mixing on the kinetics of the transesterification process forms the basis for process scale-up and design (Kyari, 2015). In this study, the best agitation speed for the produced biodiesel was 300 rpm as shown in Table 6.

Table 7: Fuel Properties of Biodiesel Production

Biodiesel properties	*P. microphylum* seed oil	ASTM Standard
Density g/cm^3	0.83	0.75 – 0.84
Cetane number	46	48 – 65
Cloud point (^{0}C)	-11.2	-13 – 12
Flash point (^{0}C)	125	100 – 170
Pour point	-4.5	-1.5 – 10

Density is a key fuel property, which directly affects the engine performance characteristic. It affects the mass of fuel injected into the combustion chamber and thus, the air-fuel ratio. This is because fuel injection pumps meter fuel by volume not by mass and a denser fuel contains a greater mass in the same volume. Thus, the changes in the fuel density will influence engine output power due to a different mass of fuel injected. It is known that biodiesel density mainly depends on its esters content and the remained quantity of alcohol; hence this property is influenced primarily by the choice of vegetable oil (Encinar *et al.*, 2015). The density of diesel fuels is another important property of the fuels that affects the fuel injection system, density is usually measured at 15 °C (Alnuami *et al.*, 2014). Density of biodiesel is the weight of a unit volume of fluid while the specific gravity is the ratio of the density of a liquid to the density of water. The fuel injection equipment meters the fuel volumetrically and high densities translate into a high consumption of the fuel. It can be seen that the produced biodiesel had densities of 0.83g/-cm^3 which is within ASTM standard for biodiesel production (0.75g/cm^3 and 0.84g/cm^3) (Alnuami *et al.*, 2014).

Flash point Flash point of a fuel indicates the minimum temperature at which the fuel will ignite (flash) on application of an ignition source under specified conditions. Flash point varies inversely with the fuel's volatility. Flash point minimum temperatures are required for proper safety and handling of fuels. It is noted that the biodiesel component must meet a flash point criteria, prior to blending, for the purpose of assuring that the biodiesel component does not contain methanol. The flash point of biodiesel is higher than the petro diesel, which is safe for transport purpose. High values of flash point decreases the risk of fire

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(Sanjay, 2013; Vuppaladadiyam *et al.*, 2013). The flash point of the produced biodiesel was 125 °C which is within the ASTM standard.

Cloud point and Pour point; the two most important criteria are the cloud and pour points. The cloud point is the temperature at which is the fuel starts to form crystals, with further decrease in temperature these crystals increase in size and quantity until the fuel gels and does not move again. The pour point is the lowest temperature at which the oil specimen will flow. Both parameters are often used to specify cold temperature usability of fuel oils. The cloud and pour point of the produced biodiesel were -11.2 °C and -4.5 respectively. Which are within the ASTM standard for biodiesel production.

The cetane number of a fuel is a measure of the ignition quality of the fuel, the higher the cetane number the better the ignition quality, which is conceptually similar to the octane number used for gasoline. Generally, a compound that has a high octane number tends to have a low cetane number and vice versa. The cetane number measures how easily ignition occurs and the smoothness of combustion. Higher is the cetane number better it is in its ignition properties. For this study, the obtained cetane number was 46which is acceptable since is within the ASTM standard (Knothe *et al.*, 2013).

CONCLUSION

The non-edible vegetable oil of *P. macrophylum* seed, sodium hydroxide as homogeneous catalyst and fuel-quality of biodiesel produced were investigated with optimize biodiesel parameters in this study. Many other processes are used in the production of biodiesel, but transesterification process is most effective and very fast than other methods. The optimized parameters include methanol to oil ratio (6:1), temperature (55 °C), catalyst concentration (1.6 wt%), reaction time (60 min), and agitation speed (300 rpm). All the evaluated properties of *P. macrophylum* seed oil and biodiesel produced such as cloud point and pour point (-11.2 and -4.5) complied with the limits prescribed by AOAC, AOCS, ASTM and EU standards. The study has also enable us to confirm that *P. macerophylum* seed oil can be used as raw materials to obtain biodiesel fuel of high quality and could be suitable alternative to fossil diesel.

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