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SYNTHESIS OF BIODIESEL FROM TROPICAL ALMOND (*TERMINALIA CATAPPA*) SE OIL

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ABSTRACT
The objective of this study is extraction and characterization of oil from tropical almond seed, trans-esterification and characterization of tropical almond seed oil biodiesel. All experiments were replicated and average results were evaluated. The moisture content of the seed was 2.04 %; the oil was extracted using solvent method and the percentage of oil yield was 50.33 %. The physicochemical properties of the oil obtained during the experiment were; density (0.90 g/cm^3), specific gravity (0.89), kinematic viscosity at 40 °C (14.1 mPa.s), cloud point (16.0 °C), pour point (11.5 °C), smoke point (173.0 °C), flash point (208.0 °C), fire point (271.0 °C), saponification value (199.19 mgKOH/g), acid value (3.37mgKOH/g), FFA (1.68 mgKOH/g), Peroxide value (5.0 meq/kg), and Iodine value (98.0 gI$_2$/100g). The oil was trans-esterified to biodiesel using oil to alcohol ratio of 4:1 and KOH as catalyst. The percentage of biodiesel yield was 75.0 % averagely. The physicochemical properties of the biodiesel obtained during the experiment were; density (0.96g/cm^3), specific gravity (0.90), kinematic viscosity at 40 °C (5.20 mPa.s), kinematic viscosity at 100 °C (4.30 mPa.s) cloud point (7.0 °C), pour point (6.0 °C), smoke point (161.0 °C), flash point (186.0 °C), fire point (216.0 °C), saponification value (182.4 mgKOH/g), acid value (0.84 mgKOH/g), FFA (0.42 mgKOH/g), Peroxide value (8.0 meq/kg), and Iodine value (109.0 gI$_2$/100g, the calculated cetane number was 51.70. The result obtained for the physicochemical properties of the biodiesel were compared with the ASTM standard and it was concluded that tropical almond seed oil is a good feedstock for biodiesel production since the result is within ASTM specification standard.

Keywords: Almond seed, Biodiesel, Physicochemical properties, Cetane number, Pour point, Oil yield, Iodine value, ASTM specification standard.

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Contribution/ Originality

This study is one of very few studies which have investigated new sources or avenue of novel underutilized sources. Biodiesel production from tropical almond seed oil will be a reasonable alternative to petroleum diesel since the available petroleum based fuels are exhaustive. Biodiesel will be of great advantage as this will reduce the adverse effect caused by the petroleum diesel, which include global warming, air pollution and emission of sulphuric compound. This study will also ensure there is good utilization of tropical almond seed.

1. INTRODUCTION

Tropical Almond (*Terminalia catappa*) is a tropical tree of the *Combretaceae* family that grows mainly in the tropical region of Asia, Africa and Australia. The tree grows up to a height of 20 – 45m and it is tolerant of salt, drought and wind. It produces fruits with a thin flesh surrounding a large fibrous nut which encloses the seed. The

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fruit of *Terminalia catappa* is classified as a drupe with fleshy mesocarp and stone-like stiffened endocarp, where the seed is. The plant is believed to have originated in Malaysia. *Terminalia catappa* is native to tropical Asia. It was introduced to Cote d'Ivoire during colonization for urban ornamentation [1]. The fruit is large (3.05 – 5.84 cm in length), it is fleshy and edible, and the unripe fruit is greenish in colour and yellow or red when it is ripe containing a single seed. The fruit has a husk, a porous and fibrous pericarp, an exocarp which is relatively thin and smooth while the hard endocarp encloses an edible kernel [2].

The seeds are often of small size and difficult to extract and these factors may have contributed to its lack of use in many areas. The sun-dried kernel yield 38-54% of a bland, yellow oil that is edible but becomes turbid on standing. The oil is used for cooking in some parts of South America and the nuts may be consumed fresh after extraction from the shell or preserved by drying or smoking and consumed up to a year later. Tropical almond is rich in vitamin E and high in unsaturated fat. Other parts of the plant such as bark, leaves, fruit shell, roots and trunks are used for medicinal and other non- food purposes [3].

Under-utilized seeds, such as tropical almond seed can be used for the production of biodiesel, the seed of tropical almond are edible, and has considerable amount of oil, this oil can be converted to biodiesel as an alternative to petroleum based diesel. The percentage of the oil yield from tropical almond seed is about 51.80% [4]. Generally, oil obtained from some seeds or vegetables generate fuels with lower carbon emissions and lower sulfur compared with conventional petroleum-based fuels, biofuel are nontoxic and biodegradable renewable fuel that comprised mono-alkyl esters of long chain fatty acids, which are derived from vegetable oils or animal fat. The most commonly used oils for the production of biodiesel are from soyabean, sunflower, palm kernel, rapeseed, cotton seed and jatropha. However, there are good numbers of seed-oils that are presently under-utilized for biodiesel production among this is tropical almond (*Terminalia catappa*) seed oil [5].

Global warming and other forms of pollution are few of the consequences emanating from over dependence on fossil fuels. Different forms of alternative energy are being exploited by researchers on daily basis to provide substitutes that are friendly to the environment. Biodiesel is one of the options that are very promising because of its lower carbon and sulfur emissions compared with conventional petroleum-based fuels. Basically, biodiesel fuels are generated from three sources namely: edible sugars and starches, non-edible plant materials, algae and other microbes [6-8].

Therefore, the objective of this study is extraction and characterization of oil from tropical almond seed, trans-esterification and characterization of tropical almond seed oil biodiesel.

2. MATERIALS AND METHODS

Tropical almond fruits were collected from various locations in Minna, Niger state, Nigeria, latitude 9.5836°N and longitude 6.5463°E having an annual precipitation of between 1100-1600mm. The outer flesh of the fruits was manually removed with a knife. The initial moisture present in the hard-shelled nuts was 6.74% averagely; they were sun-dried for 9 days at an average temperature of 35.5°C and relative humidity of 79.6%. The final moisture content at which the hard-shelled nuts were broken without the seed destroyed was 1.94% averagely. The seeds (Figure 1) were removed from the dried shell by manually breaking the dried shells with a hammer.

2. 2.1. Determination of Moisture Content of the Seed

A container where the almond seed is to be placed was weighed and recorded as W, samples of the almond seed were placed inside the container both the seed and the container was weighed and recorded as W_1, the sample was placed in an electric oven and dried for about 24 hours at a temperature of 105°C, the sample was removed after every 24hrs and the weight determined.

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Figure-1. Almond seeds used for the study

It was finally removed from the oven when it was observed that the weight does no longer change which means there is no moisture present, the final weight of the sample was measured recorded as W_2. The percentage of the moisture content present in the seed was calculated using the formula:

$$MC = \frac{\text{Weight of sample before drying} - \text{Weight of sample after drying}}{\text{Weight of sample before drying}} \times 100$$

$$MC = \frac{W_1 - W_2}{W_1 - W} \times 100\% \qquad 1$$

2.2.2. Oil Extraction

Almond seeds were gotten after breaking the hard part of the almond. The seeds were ground into fine particles with the aid of an electric blender. The weight of the filter paper to be used was taken and recorded as W_1. The ground sample of the almond seed was then poured into a filter paper, the sample was wrapped with the filter paper as much as possible and carefully stapled with the aid of a stapler. The weight of the filter paper containing the ground sample was taken and recorded as W_2. The samples were then carefully inserted in a thimble and placed inside a soxhlet extraction apparatus, about 300ml of the solvent (n-hexane) was carefully poured in the round bottom flask which was attached to the soxhlet apparatus, the round bottom flask which holds the thimble was seated on an electrically connected heating mantle, the heat regulator was adjusted in order to increase the temperature of the solvent and hence boil the solvent, immediately the solvent start boiling the regulator was adjusted to set the heating mantle temperature base on the boiling temperature of the solvent or the nature of the solvent. Plate V shows a soxhlet apparatus for extracting oil.

Heating was done for about 4 – 6 hours at a temperature of 40 – 60^{o}C at which the n-hexane would not escape. The sample was removed from the thimble and oven dried at 50^{o}C for about 4 hours in order to evaporate the solvent present in the oil. After oven drying the sample was placed in a digital weighing balance and weighed as W_3. The percentage of oil obtained from the sample was calculated using the relationship:

$$\%\ \text{of Oil} = \frac{W_2 - W_3}{W_2 - W_1} \times 100 \qquad 2$$

Where W_1 is the Weight of the filter paper; W_2 is the Weight of the filter paper + sample before extraction; W_3 is the Weight of the filter paper + sample after extraction and oven dried.

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2.2.3. Determination of Physical and Chemical Properties of the oil

The AOAC International [9] Methods of *analysis were u*sed in determining the physical and chemical properties of the oil extracted from almond seed. The properties are density, specific gravity, kinematic viscousity, acid value, free fatty acid value, saponification value, peroxide value and iodine value.

2.2.4. Production of Biodiesel Fuel

During the production of biodiesel production process, two phases were undergone, they are: Trans-esterification phase and Separation and washing phase

2.2.5. Trans-Esterification Phase

The reactions in the trans-esterification phase involve glyceride (oil) and alcohol in the presence of catalyst. 100ml of the oil was measured with a measuring cylinder, using oil to alcohol ratio of 4:1, 25ml of methanol (alcohol) was measured into a beaker and 0.7g of KOH (catalyst) was dissolved inside the methanol. 0.7g of KOH was used because for standard 7g of KOH is required for 1 litre of oil. The oil and the methanol and KOH were mixed inside a round bottom flask attached to a magnetic stirrer. The magnetic stirrer temperature was set to 50^{o}C and stirring was done for 30 minutes. Plate VII shows the mixture of oil, methanol and KOH on a magnetic stirrer.

2.2.6. Biodiesel Separation and Washing Phase

After stirring the mixture for 30 minutes, it was then poured into a separating funnel. A 2-phase solution was obtained in which the biodiesel is below while the residual catalyst (glycerol) as the by-product is above, the biodiesel was removed and washed to purify it, while the glycerol i.e. the byproduct was not utilized. Finally, the biodiesel was then dried in an oven for 30 minutes.

2.2.7. Biodiesel Characterization

In order to test the quality of biodiesel as a diesel fuel substitute, the American Society of Testing Materials (ASTM) has set a standard for biodiesel as fuel for use in diesel engines. Numerous properties are included in the standard, such as specific gravity, kinematic viscosity, flash point, cloud point and so on. It is important to control the quality of biodiesel to meet the ASTM standards before using it in a diesel engine. The samples of biodiesel produced were tested for their fuel properties, the flash point was determined in a pensky-martens closed cup method; testing using ASTM D93; cloud point and pour point were determined using ASTM D2500 and ASTM D97.

3. RESULTS AND DISCUSSION

3.1. Results

The results obtained from the study are presented in Tables 1 and 2.

Table-1. Physicochemical properties of Tropical Almond Seed oil

S/No	Properties	Result
1	Moisture content of seed (%)	2.04
2	Percentage of oil yield (%)	50.33
3	Colour	Yellow
4	Odour	-
5	Density (g/cm^3)	0.90
6	Specific gravity	0.89
7	Kinematic viscosity at room temperature (33^{o}C)	18.2
8	Kinematic viscosity at 40^{o}C (mPa.s)	14.1
		Continue

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9	Cloud point (°C)	16.0
10	Pour point (°C)	11.5
11	Smoke point (°C)	173.0
12	Flash point (°C)	208.0
13	Fire point (°C)	271.0
14	Saponification value (mgKOH/g)	199.19
15	Acid value (mgKOH/g)	3.37
16	Free Fatty Acid (mgKOH/g)	1.68
17	Peroxide value (meq/kg)	5.0
18	Iodine value (gI_2/100g)	98.0

Table-2. Physicochemical properties of the Biodiesel from Tropical almond seed oil

S/No	Properties	Result	ASTM Standard for Biodiesel
1	Colour	Light yellow	-
2	Odour	-	-
3	Density (g/cm³)	0.96	0.86 – 0.90
4	Specific gravity	0.90	0.88
5	Kinematic viscosity at 40°C (mPa.s)	5.20	1.9 – 6.0
6	Kinematic viscosity at 100°C (mPa.s)	4.30	-
7	Cloud point (°C)	7.0	– 3 – 12
8	Pour point (°C)	6.0	– 15 – 10
9	Smoke point (°C)	161	-
10	Flash point (°C)	186	130 – 170
11	Fire point (°C)	216	-
12	Cetane number	51.70	47 – 65
13	Saponification value (mgKOH/g)	182.4	-
14	Acid value (mgKOH/g)	0.84	0 – 0.8
15	Free Fatty Acid value (mgKOH/g)	0.42	-
16	Peroxide value (meq/kg)	8.0	-
17	Iodine value (gI_2/100g)	109	≥ 130

3.2. Discussion of Results

The moisture content of tropical almond seed was 2.04%, this value is lower than that was reported by Matos, et al. [4] this may be because before the fruit were gathered sun has naturally remove some of the moisture. The percentage of oil yield from tropical almond seed obtained during the experiment was 50.33%, this value is within the range specified by Adu, et al. [3] i.e. 38 – 54%. Though the value obtained for the oil yield was slightly lower than 51.80% reported by Matos, et al. [4] and 52.11% reported by Barku, et al. [10]. The lower yield may be attributed to the duration of oil extraction, differences in variety of plant, cultivation climate, ripening stage, the harvesting time of the seeds and the extraction method used, the extracted oil were liquid at room temperature, this property makes it good for biodiesel production. The percentage yield of the biodiesel was 75.0 % averagely.

The density of the oil is 0.90 g/cm³ while that of the biodiesel is 0.96 g/cm³. The value of biodiesel obtained for the biodiesel is slightly higher than the range specified in the ASTM standard; this may be due to contamination. The density of biodiesel affects the performance of pumps and atomizers. The specific gravity of the oil is 0.89 this value is slightly lower than 0.92 reported by Barku, et al. [10] for tropical almond seed oil. While that of the biodiesel is 0.90. The density determines the specific gravity of both the oil and the biodiesel. The Kinematic viscosity of the oil at 40 °C was 14.1 mPa.s while that of biodiesel was 5.2 mPa.s. This value is within the range specified by ASTM D445. The Kinematic viscosity of the biodiesel at 100 °C was 4.30 mPa.s, the higher the temperature the lower the kinematic viscosity. The viscosity at 40 °C and 100 °C can be used to compute the viscosity index of the biodiesel, viscosity is an important property of biodiesel since it affects the operation of fuel injection equipment, particularly at low temperatures when the increase in viscosity affects the fluidity of the fuel or leakage at high temperature when too thin [11].

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The cloud point and pour point of the oil were 16.0 °C and 11.5 °C respectively, this result shows that when the oil cool to a temperature of 16.0 °C a wax or cloud is formed, and that if the temperature keep reducing to about 11.5 °C the oil will seize to flow and become semi-solid. The cloud point and pour point of the biodiesel were 7.0 °C and 6.0 °C respectively, the result shows that at 7.0 °C a wax is formed and the biodiesel will seize to flow at 6.0 °C. The value obtained for the cloud point and the pour point is within the range specified by the ASTM standard, which means biodiesel from almond has a good cloud and pour point property. The cloud point and pour point are the two most important property of the biodiesel as frozen fuel may cause blockage of the fuel lines and filters and starve the engine of fuel. These results also show that the biodiesel cannot be used where the average temperature is lower than 7.0 °C, as this will cause the diesel to freeze during usage.

The smoke point, flash point, and fire point of the oil are 173.0 °C, 208 °C, and 271.0 °C respectively while that of biodiesel are 161 °C, 186 °C, and 216 °C respectively. The flash point is above the maximum value specified by ASTM for biodiesel. The flash point is a measure of the flammability of fuel and thus an important safety criterion in transport and storage. The flash point of pure biodiesels is usually higher than the ASTM limits, but fall rapidly with increasing amount of methanol [11]. The result also shows that at 216 °C the biodiesel will ignite on application of an ignition source.

The result obtained from the experiment indicates that the cetane number of the biodiesel from tropical almond is 51.70; this value is within the range specified by ASTM , the higher the cetane number the quicker the engine will start, less wear and improved fuel efficiency. The result obtained for Saponification value of the oil was 199.19 mgKOH/g, this result is higher than 168.27 mgKOH/g reported by Barku, et al. [10] for tropical almond this may be due to the method of extraction of the oil, and the method at which the saponification value was determined. These shows that more alkali would be required to enable it neutralize the available free fatty acid liberated by the oil. The higher the saponification value, the more easily the oil can be used for soap making, shampoos, and lathers shaving creams. The saponification value of the biodiesel was 182.4mgKOH/g, slightly lower than that of the oil, there is no specific standard value for saponification value of biodiesel and it is an insignificant property of biodiesel.

The acid value and free fatty acid of the oil are 3.37 mgKOH/g and 1.68 mgKOH/g respectively. This acid value is higher than 0.78mgKOH/g and FFA is higher than 0.38mgKOH/g reported by Barku, et al. [10] but the acid value of the oil is lower than 15.37 mgKOH/g reported by Bello and Agge [11] for groundnut oil. The acid value of the biodiesel is 0.84 mgKOH/g this value is slightly higher than 0.8mgKOH/g specified by ASTM but less than 3.366 mgKOH/g reported by Bello and Agge [11]. The FFA of the biodiesel is 0.42mgKOH/g. Jaichandar and Annamalai [12] reported that the nature of fatty acids can have influence on the characteristics of the biodiesel. Romano, et al. [13] reported that basic transesterification is viable if the value of free fatty acids (FFAs) is less than 2%, in the case of highly acidic raw materials.

The peroxide value obtained for the oil is 5.0meq/kg, this value is slightly higher than 4.073meq/kg reported by Barku, et al. [10] but lower than 18.0meq/kg reported by Bello and Agge [11] for groundnut oil and 8.33 meq/kg reported by Ofoefule, et al. [14] for tiger nut oil. The peroxide value of the biodiesel is 8.0 meq/kg there is no specific standard value for peroxide value of biodiesel.

The iodine value of the oil is 98.0 $gI_2/100g$; this value is lower than 121.19 $gI_2/100g$ reported by Barku, et al. [10]. While that of the biodiesel is 109.0 gI2/100g, this value is within the range specified in the ASTM standard.

4. CONCLUSION

Tropical almond seed oil was converted to biodiesel and characterized majority of the properties fall within the ASTM standard limits for biodiesel. The pour point is 6 °C which means it cannot be used when temperature fall below this value. The value of the flash point 186 °C is above the maximum specified by ASTM, though the flash point of pure biodiesel is usually higher than the ASTM standard limit. Hence, since the properties of biodiesel from tropical almond seed oil meet the standard for biodiesel, it can be used as alternative fuel in diesel engines.

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