EXTRACTION AND CHARACTERIZATION OF ALLAMANDA SEED OIL AS FEED STOCK FOR BIODIESEL PRODUCTION

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ABSTRACT

Allamanda cathartica is regarded as an environmental weed and mostly planted as flowers for home beautification, allamanda seeds in most cases is underutilized. Research had shown several importance and uses of allamanda cathartica, it ability to cure colic, jaundice, diarrhea, malaria and vomiting. Allamanda cathartica contains nutrients such as alkaloids, fatty acid, carbohydrates, flavonoids and saponins (Satiah, 2016). The extracted oil from allamanda cathartica seeds has non edible property, this property makes allamanda seed oil a good substitute of palm oil, coconut oil and other edible oils as feedstock for biodiesel production. In this research, soxhlet extraction method was used to extract oil from the allamanda seed and characterized, hexane was used as the extraction solvent and the extracted allamanda oil is dark brown in colour with a percentage yield of 54 %. The saponification value of allamanda oil is 158.483 mgKOH/g which falls below the values given by ASTM, AOCS and Abdelaziz et al..,2012, this indicates the absence of unsaturated fatty acid and characteristics of foaming ability. The free fatty acid value of allamanda oil is 2.60 % which is in the range given by ASTMD 6751, this indicates that the allamanda oil will not be corrosive when used for biodiesel production. The peroxide value of allamanda oil is 5.36 meq/kg is slightly above that of ASTM but lesser than the sighted literature, this indicates that the oil has good oxidative stability. From the obtained result, it can be concluded that allamanda oil is a good substitute for edible oil as feed stock in the production of biodiesel.

Keywords: *Biodiesel, allamanda seed oil, soxhlet extraction and feed stock*

INTRODUCTION

Allamanda cathartica is commonly called golden trumpet, yellow bell,yellow allamanda, guinea herb or trumpetvine, it is a species of flowering plant of the genus allamanda in the family Apocynaceae (Petricevich and Abarca-Vergasa, 2019). Yellow allamanda (Allamanda cathartica) is regarded as an environmental weed in northern Queensland, it is one of the exotic ornamental vines that have become invasive in this region after escaping from garden plantings (Rodolfo, 2019).

This specie also grows along creeks and roadsides and in disturbed natural vegetation in northern Western Australia. It was recorded as naturalized in this state in 1993 and is locally naturalized on creeklines on Koolan Island (Rodolfo, 2019).

Allamanda cathartica can also be found in other parts of the world including Nigeria, it can be found at Ciromawa Estate along Bosso road, Minna, Niger State, Nigeria.

Yellow allamanda fruit is a seed capsule, round with soft spines 4 cm across, seeds are tan flat and slightly winged, yellow allamanda spreads via the dumping of garden refuse and plants climbing from gardens into adjoining areas, it seeds are spread on wind and water (Chaithra,2016).

One of the studies of allamanda carthatica has indicated the potential anti-inflammatory, laxative, antioxidant, antibacterial and antifungal properties from allamanda flower extracts (Petricevich and Abarca-Vergasa, 2019). Other studies had shown that allamanda carthatica cures colic, jaundice, diarrhea, malaria and vomiting, it also contains nutrients such as alkaloids, fatty acids, carbohydrate, flavonoids and saponins (S. Satiah, 2016).

Different methods can be used to obtain allamanda oil from its seeds, but the common methods used for the extraction of the oil includes mechanical pressing, supercritical fluid extraction and solvent extraction.

Mechanical extraction is the most widely used method. However, the oil produced with this method is not always pure and contains significant amount of water, metals and dust contents that make it less suitable for biodiesel production (Albert, 2008). The extraction using solvent has several advantages over mechanical pressing especially in obtaining higher yield of oil that is less turbid. The oil obtained using solvent extraction method has a very suitable viscosity compared to fossil fuel (Adewoye, 2012).

Extraction of oil using solvents is the most effective method for oil recovery of almost 98%, especially with materials having low oil content. Moreover, solvent extraction involves the use of chemicals referred to as the solvents in the extraction of oil from oilseeds. It is known for its high yielding of oil output, easiness and swiftness to carry out, and it is relatively cost effective (Adewoye, 2012). The use of this method requires a complete refining process to ensure that traces of the solvents are removed totally from the oil in order to avoid contamination. Hexane and petroleum-derived product had been extensively used as a solvent for oil extraction of some seeds because of its low vaporization temperature, high stability, low corrosiveness and low greasy residual effect (Rahul, 2013).

Soxhlet extraction method allows extraction of oil from the seed samples using the distillation extraction method. In the Soxhlet extractor, the sample soaks in hot solvent usually hexane that is periodically siphoned off, distilled and returned to the sample. This process continues until the siphoned-off solvent becomes clear. The advantage of soxhlet apparatus over hot water extraction is that, there is no filtration necessary and oil yield is better than hot water extraction process (Rahul, 2013).

METHODOLOGY

SEED PREPARATION

The allamanda seeds were cracked manually to obtain the kernels, the kernels were covered with hulls, the hulls were blown off with air. The dehulled allamanda kernels was kept under the sun for 6 hours, the kernels were oven dried at a temperature of 85^{o} C to 100^{o} C for 2 hours, the dried kernels were crushed for size reduction to increase the interfacial area for proper extraction of oil. The crushed allamanda seeds was kept in an air tight container to prevent intake of moisture into the crushed seeds (Nadia, 2013).

EXTRACTION PROCEDURE

50 g of the crushed allamanda seeds was placed into the center of the extractor through the thimble, the round bottom flask was filled with 250 ml of hexane, the heating mantle was set at a temperature of 68 ^{0}C and the time for each batch of extraction was 6 hours (K. Karmalakar, 2003). The round bottom flask containing the hexane was heated until the hexane boils, during the steady

extraction, the extract seeped through the pore of the thimble and filled the siphon tube, where it flows back into the round bottom flask. This process was repeated for several batches until the needed quantity of oil was extracted from the crushed allamanda kernels, the extracted oil was heated with rotary evaporator to separate the little amount of hexane and water from the oil (J. Blin, 2013).

Determination of chemical properties of allamanda seed oil

Determination of saponification value

Saponification value is the measure of the molecular weight of the fatty acid. 2g of the allamanda oil was weighed and transferred into a 250 ml conical flask, 50 cm^3 of 0.5 ethanolic KOH was added to the sample and mixture was heated to saponify the oil. The unreacted KOH was back titrated with 0.5 N HCl acid using 2-3 drops of phenolphthalein indicator (Gunstone, 2004). The saponification value was determine using the equation below.

The saponification value (S.V.) is given by: $S.V = \frac{(V0-V1)\times 0.5\times 56.10}{M}$ (mgKOH/g) 1.0

Where V0 = the volume of the solution used for blank test

VI = the volume of the solution used for determination

N = Actual normality of the HCl used

M = Mass of the oil used.

Determination of free fatty acid value

Percentage free fatty acid is the percentage by weight of the specified fatty acid in the oil, the method employed for this analysis is the American Oil Chemists Society (AOCS) method, 1g of allamanda oil was weighed and poured into conical flask, 25 ml of isopropyl alcohol and 3 drops of phenolphthalein indicator solution was added. The mixture was titrated against 0.1 N sodium hydroxide shaken constantly until a pink colour persisted for 30 seconds (Gunstone, 2004). The acid value was determined using the equation below

$$\%FFA = \frac{(mL\ of\ titrant)(Normality\ of\ NaOH)+ 28.2}{sample\ weight}\ X\ 100 \qquad 2.0$$

Determination of acid value

1g of allamanda oil was weighed and poured into a conical flask and the weight was recorded. 25 ml of isopropyl alcohol and 3 drops of the phenolphthalein indicator solution was added. it was titrated with 0.1 N potassium hydroxide solution with constant stirring until a faint pink end point appears and persists 30 seconds (Cradle, 2001). The volume of the titrant used to reach this endpoint was recorded and from the value obtained, the acid value is evaluated using the equation

$$\text{Acid value} = \frac{56.10 \times V \times C}{Y} \qquad 3.0$$

Where V = Volume of potassium hydroxide used for titration (ml),
C = Concentration of potassium hydroxide used for titration (mol/l) and
Y = mass of oil sample used for analysis (g)

Determination of peroxide value

This was carried out in accordance to the method specified by AOCS official method Cd 8-53. 1g of the oil sample was weighed and transferred into the flask and 20ml of the acetic acid – chloroform (2:1) solution was then added to the oil. The flask was gently warmed using water bath and swirled until the sample was completely dissolved. This was followed by the addition of 0.5ml of saturated potassium iodide solution and 30ml of distilled water. The flask was shaken vigorously to liberate the iodine from the chloroform layer. The resulting solution was titrated with 0.002N sodium thiosulphate using starch indicator until the blue gray colour disappeared in the aqueous upper layer (Kumar, 2008). This same procedure was followed for the blank test. The volume of titrant used for determination and blank test were recorded.

Peroxide value was calculated from the expression

$$\text{Peroxide value} = \frac{(S-B) \times N\ of\ thiosulphate \times 1000}{weight\ of\ sample}\ (\text{meq/kg}) \qquad 5.0$$

S=titrant of sample, B= titrant of the blank,

Determination of iodine value

The iodine value was determined in accordance to the method specified by AOCS cd3-25. 0.5 g of oil sample was weighed and transferred into a flask. Carbon tetrachloride, 25ml was added to dissolve the oil and 25 mL of the wijs solution was added into the flask the stopper was inserted and the mixture was

shaken gently and kept in the dark for 1 hour. At the end of 1 hour, 20mL of potassium iodide KI, 10 % solution and 125 mL of water were added. The mixture was titrated with the 0.1 N sodium thiosulphate ($Na_2S_2O_3$) solution until the yellow colour due to the iodine had almost disappeared. 1mL of the starch, 1 % indicator solution was added, and the titration was continued with very vigorous shaking until the blue colour just disappeared (Akintayo, 2004). This same procedure was followed for the blank test.

The iodine value (I.V) is given by the expression:

$$I.V = \frac{(V1-V2.)\times 0.1269\times C\times 100}{M} (gl_2/100g\ oil) \quad 5.0$$

Where C = Concentration of sodium thiosulphate used

V_1 = Volume of sodium thiosulphate used for blank test

V_2 = Volume of sodium thiosulphate used for determination

M = Mass of the sample

Determination of specific gravity

Density bottle was used to determining the density of the oil. A clean and dry bottle was weighed (A) and then filled with water, stopper inserted and reweighed to give (B). the bottle was dried in an oven and the oil was substituted with water and weighed to give (C).

The expression for specific gravity (Sp.gr) is:

$$Sp.gr = = \frac{C-A}{B-A} = \text{Mass of the substance / Mass of an equal volume of water.} \quad 6.0$$

A=mass of empty bottle,

B= mass of bottle +mass of water,

C=mass of bottle + mass of oil

Determination of kinematic viscosity

An NDJ-5S Rotary Viscometer was used to determine the viscosity of the oil. The viscosities of the oil sample were determined at temperatures of 40 and 100 °C, following the procedure specified by the manufacturer. Rotor 2 and 1 with speed of 60 revolutions per minute (60 RPM) were selected for bio lubricant, crude oil and biodiesel respectively. The oil sample was then transferred into a 250 ml beaker and was heated to raise the temperature to the desired value using water bath heater. The rotor was attached to the upper coupling by holding the

coupling between the thumb and forefinger while cautiously rotating the rotor counter clockwise. The rotor was immersed in the centre of the sample up to the middle of the indentation in the shaft. The viscometer was then turned on and allowed to run until a constant reading was display; this reading was taken as the viscosity of the sample in mPas (Sharma, 2008).

Determination of PH value

The PH of the oil sample used was also determined and was obtained to be 5.96. This indicates that the acid level of the oil was very minimal. Higher or lower PH affects the activity of catalyst as reported by Dave *et al*.(2014).

Determination of physical properties of allamanda seed oil

Determination of cloud point

The cloud point is defined as the highest temperature at which an oil type begins to solidify. In order to determine this for the oil extracted in this work, a little quantity of it (the oil) was placed in a test tube and the entire content was put on an ice bath with a fixed thermometer. The temperature at which the oil began to condense was then recorded as the cloud point.

Determination of pour point

In determining the pour point of the extracted allamanda oil, a manual method was used by cooling the oil inside a bath to allow formation of paraffin wax crystals. At about 9°C above the expected pour point, and for every subsequent 3°C, the test tube was removed and tilted to check for surface movement. When the specimen did not flow when tilted, the test tube was held horizontally for 5 secs and 3°C was added to the corresponding temperature, and the result thereby obtained was recorded as the pour point temperature of the oil.

Determination of flash point

An improvised method was used to determine the flash point of the extracted oil. In doing this, a 50 ml conical flask was filled with 1 ml of the oil and heated at a low constant rate on a hot plate. The flash point was obtained when the application of a test flame caused the vapour above the oil to ignite.

Determination of kinematic viscosity

An NDJ-5S Rotary Viscometer was used to determine the viscosity of the oil. The viscosities of the oil sample were determined at temperatures of 40 and 100 °C, following the procedure specified by the manufacturer. Rotor 2 and 1 with speed of 60 revolutions per minute (60 RPM) were selected for bio lubricant, crude oil and biodiesel respectively. The oil sample was then transferred into a 250 ml beaker and was heated to raise the temperature to the desired value using water bath heater. The rotor was attached to the upper coupling by holding the coupling between the thumb and forefinger while cautiously rotating the rotor counter clockwise. The rotor was immersed in the centre of the sample up to the middle of the indentation in the shaft. The viscometer was then turned on and allowed to run until a constant reading was display; this reading was taken as the viscosity of the sample in mPas.

Determination of density

An empty beaker was weighed and the weight was recorded, 50 cm^3 of the sample (allamanda oil) was transferred into the beaker and weighed. From the sample weight recorded, the density was determined by taking the ratio of the weight of the oil to the known volume (50 cm^3) in SI units according to the equation below.

$$\text{Density} = \frac{weight\ of\ sample}{volume\ of\ sample} \qquad 7.0$$

RESULT AND DISCUSSION

CHARACTERIZATION OF THE EXTRACTED ALLAMANDA OIL

Table 1: Physiochemical properties of allamanda oil, compared with physiochemical properties of crude castor oil, ASTM and AOCS.

S/N	Property	Units	Test Method	Castor oil value	ASTM	AOCS	Allamanda oil Value
1	Specific gravity	-	ASTM D1250	0.948	0.957-0.968	0.88-0.915	0.928
2	Saponification value	mgKOH/g	ASTM D558-95	178.72	175-187	174-184	158.483
3	Iodine value	gI_2/100g oil	AOCS cd 3.25	81.47	82-88	83-88	40.659
4	Acid value	mgKOH/g	ASTM D664	12.90	0.4-4.0	2.0	5.20
6	Viscosities at 40°C	Cst	ASTM D445	6.6	35max	-	20.5
7	Viscosity at 100°C	Cst	ASTM446	2.00	-	-	1.45
8	Viscosity @RT	Cst	ASTM2270	87.13	-21.7	-	48.9
9	Pour point	°C	ASTM D97	+5	-21.7	-	-5.6
10	Refractive index	-	AOCS cc7.75	1.440	-	1.467-1.470	-

11 Peroxide value	meq/kg	AOCS cd8.53	6.00	5.00		5.36	
12 PH value	-		-	6.50		-	
		5.96					
13 %FFA	%	ASTMD6751		6.45	25 max	<1	2.60
14 Density	g/cm^3	ASTM DM6710	-	0.7-0.95	-	0.924	
15 Percentage oil yield	%					54	
16 Smoke point	^0C	ASTMD97	-	-	-	149.0	
17 Flash point	^0C	ASTMD94	-	-	-	215	
18 Fire point	^0C	ASTMD901	-	-	-	270	

The extracted allamanda oil is dark brown in color with a yield of 54%, the physiochemical properties of the oil can be seen as shown on table 1, the physiochemical properties of allamanda oil was compared with castor oil (Abdelaziz et al..,2012), American standard for testing material (ASTM) and American oil chemists' society (AOCS) standard values. From the experimental result obtained, the saponification value of allamanda oil is 158.483 mgKOH/g, the value falls below the range of values given by ASTM, AOCS and lesser than the sited literature (Abdelaziz et al.., 2012), which indicates the absence of unsaturated fatty acid characteristics of foaming ability (Modestus et al.., 2008). The free fatty acid value of allamanda oil is 2.60 %, this is in the range of value given by ASTMD6751, this indicates that the allamanda oil will not be corrosive when used for biodiesel production, which can affect fuel pumps (Chigoziri, 2008). According to (Crabbe et al..,2001) oils with high fatty acid value are liable to form soap and difficult to separate during biodiesel production which will result to low biodiesel yield.

The viscosity of allamanda oil at 40^0C is greater than the sited literature but falls within that of ASTM value, which indicate that allamanda oil is suitable for the production of biodiesel (Chigoziri, 2008), viscosity increases with molecular weight and decreases with increasing unsaturated level and temperature (Nouredini et al, 1992). The iodine value of allamanda oil falls below the cited literature, ASTM and AOCS standard, this indicates that the oil has a low degree of unsaturation (Modestus et al..,2008), according to (Mittelbach, 1996) oils with low iodine value are better for biodiesel production due to the fact that heating oil of higher degree of unsaturation will lead to polymerization of glycerides and causes formation of deposit or deterioration of the biodiesel.

The peroxide value of allamanda oil (5.36 meq/kg) is slightly above that of ASTM but lesser than the sighted literature, this proves that the extracted allamanda oil has a good oxidative stability (Eromosele et al.., 1997).

The density of allamanda oil (0.924 g/cm^3) falls within the range given by ASTM6710 but lesser than the density of water, generally oils have density lesser than that of water. According to (Gunstone, 2004), the density of oil decreases with molecular weight but increases with unsaturation level.

CONCLUSION

This study was aimed at extraction and characterization of allamanda seed oil for biodiesel production, the soxhlet extraction method was used in the course of this work, it gives a better amount of oil yield but the time consumption is the major drawback of this method of extraction. The saponification value of allamanda seed oil is 158.483 mgKOH/g which is less than ASTM and AOCS values, this indicates the absence of unsaturated fatty acid characteristics of foaming ability. The free fatty acid value of the oil is 2.60 %, it was within the range given by ASTM, this indicates that when used for biodiesel production it will not form a corrosive biodiesel. From the result obtained, it showed that the extracted allamanda oil seed is a good potential feed stock and can serve as substitute for edible oil in biodiesel production.

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