Production and Characterization of Biodiesel from *Allamanda Cathertica* Oil

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Abstract: The gradual depletion of world petroleum reserves and the impact of environmental pollution due to increasing exhaust emissions have necessitated the urgent need to develop alternative energy resources, such as biodiesel fuel. Vegetable oil is a promising feedstock because it has several advantages; it is renewable and environmental friendly. The present study involves extraction of oil from Allamanda cathertica seed (Allamanda), Azadarachta indica and Jatropha caucus; conversion of the oil into biodiesel and the characterization of the methyl ester. Transesterification of the different feed stocks was conducted using sodium methaoxide (NaMt), sodium ethaoxide(NaEt), potassium methaoxide (PMt) and potassiumethaoxide (PEt) as catalysts, using a range of reaction temperatures (45, 50, 55, 60 and 65^{O}C) and different rates of stirring. Result showed that Allamanda seed produced 54% oil yield using mechanical extraction. The biodiesel yield was 97% using NaMt and NaEt as catalysts, while azadarachta oil gave 95% yield with PEt catalyst alone. Jatropha oil gave a yield of 70% biodiesel with all the catalysts used. The yield of biodiesel from Allamanda oil with respect to temperature were 63, 88, 94, 46 and 20% respectively. Characterization of the biodiesel produced from Allamanda oil compared favorably with the ASTM standards, viscosity 5.4, flash point 115^{O}C, refractive index 1.4756 and energy value 35.0MJ/L. The GCMS analysis of Allamanda methyl ester showed a range of 10 different methyl esters which includes hexadecanoic acid (24%), linoleic acid (14.8%), 13-Decosenoic acid (35.3%), 9-Octadecanoic acid (13.5%). The work concludes that allamanda oil could be a good and alternative feedstock to the edible feedstocks currently in use for biodiesel production.

Keywords: Biodiesel, non-edible feed stock, allamanda oil, environmental friendly.

1. INTRODUCTION

Environmental issues are the driving forces for the development of alternative energy sources, since the burning of fossil fuels causes various environmental problems including global warming, air pollution, ozone depletion, acid precipitation, forest destruction and emission of radioactive substances [1] The alternative energy sources of fossil fuels includes: hydro, wind, geothermal, hydrogen, solar, nuclear and biomass [2]. Among these alternative energy sources, biofuels derived from biomass are considered as the most promising alternative fuel sources because they are renewable and environmental friendly. Biodiesel is a mix of monoalkyl esters of long chain fatty acids derived from renewable feedstock like vegetable oils and animal fats mainly made of fatty acid glycerides. It is produced by transesterification processes in which oil or fat are reacted with a monohydric alcohol in the presence of a catalyst. The transesterification process is affected by reaction conditions, alcohol to oil molar ratio, type of alcohol, type and quantity of catalyst, temperature and purity of reactants [3]. The alkaline catalysts show high performance, providing biodiesel fuel of high quality, but the oils often contain significant amounts of free fatty acids, which are turned into soap by reacting with the alkali catalyst. In addition, the outflow of the alkaline catalysts with the biodiesel fuel product is a serious problem that required the addition of further washing and separation steps to the process [4]. Fossil fuel has been a widely used source of energy since the industrial Revolution just before the dawn of the 20th century. Fossil fuels are relatively easy to use to generate energy because they only require a simple direct combustion. Energy generation and utilization is a key factor to the development of any nation. The growing concern due to energy depletion, environmental pollution caused by the conventional fossil fuels and the realization that they are non-renewable have led to search for more environment friendly renewable fuels. Among various options investigated for diesel fuel, biodiesel obtained from vegetable oils has been recognized worldwide as one of the strong contenders for reductions in exhaust emissions. Worldwide biodiesel production is from edible oils such as soybean, sunflower and canola oils [2]. Since, Nigeria like any developing country is not self sufficient in edible oil production and the fear of food crisis (biodiesel competing with food), some non-edible oil seeds available in the country are required to be tapped for biodiesel production. With abundance of forest and plant based non-edible oils available in the country such as *Jatrophacurcas* (Jatropha), *Azadirachtaindica* (Neem) and *Allamanda cathertica*

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(Allamanda), no much attempt has been made to use esters of these non-edible oils as substitute for diesel except jatropha and neem. Moreover, there are plenty of waste lands available in Nigeria, which can be utilized for growing such oil seed crops. Various vegetable oils, including palm oil, soybean oil, sunflower oil, rapeseed oil, and canola oil have been used to produce biodiesel fuel and lubricants [2]. One way of reducing biodiesel production costs is to use the less expensive feedstock containing fatty acids such as non-edible oils, animal fats, waste food oil and by products of the refining vegetable oils.

Allamanda cathertica, also known as Yellow Bell, Golden Trumpet or Buttercup Flower, is a genus of tropical shrubs or vines belonging to the dogbane family (Apocynaceae). The genus Allamanda is native to South and Central America. The year-round production of large, bright flowers has made the Allamanda popular ornamentals. A woody, evergreen shrub with vigorous growth, Allamada may reach a free-standing height of 2 meters or more. The plant does not tolerate shade, salty or alkaline soils; they are highly sensitive to frost. *Allamanda cathertica* is also notable for its medicinal properties: all parts of the plant contain allamandin, a toxic iridoid lactone. The leaves, roots and flowers may be used in the preparation of cathartic; the milky sap is also known to possess antibacterial and possible anticancer properties (http://en.wikipedia.org/wiki/Allamanda 2009).

2. EXTRACTION PROCESS

Allamanda seeds were collected from Allamanda tree in G.R.A Kontagora, Niger State, Nigeria. The shells of dried seeds were removed by cracking using hammer and mill. The seeds were grounded to fine particles and expelled by hand press with intermittent addition of hot and cold water drop wise. The oil obtained was dried, measured using a measuring cylinder and stored. This extraction process was repeated for *Jatrophacacus* and neem (*Azadirachtaindica).*

Titration Procedure

The percentage of free fatty acid (FFA) content of the oil is one of the main factors that affect biodiesel yield during transesterification process, it wastherefore determine before transesterification. FFA content of the oil was determined according to the method of [5]. Oil sample (0.1g) was weighed and dissolved in 50ml of methanol. The mixture was heated gently to temperature of 55°C for 30mins after which a drop of indicator (phenolphthalein) was added. Then the solution was titrated with concentrated 2N NaOH. The amount of NaOH required, in milligram (mg), to neutralized the free fatty acid in one gram of oil is known as acid number. The acid number is calculated as follows: Acid value = $56.1 \times N \times V/M$ Where V is the number of ml of NaOH N is the normality of NaOH M is the mass in gram of the sample

Esterification Setup

A round bottom flask was used as a laboratory scale reactor for the experiments. A hot plate with magnetic stirrer (calibrated; low, medium and high) was used for heating the mixture in the flask. The mixture was stirred at different speed for all the test runs to observe the contact effect of the catalyst on oils [5]. The temperature range of (45,50,55,60 and 65°C) was maintained during the experiment. The biodiesel was produced using base catalyzed transesterification [6].

Preparation of Methoxide

Fresh lye of NaOH Pellets (0.13g) was measured using a digital weighing balance. 20ml of methanol was added into a 250ml conical flask. The mixture was agitated to ensure complete dissolution.

Mixing Alkoxide and Oil

Fresh oil stock of 250ml was poured into the beaker and gently warmed; 50ml of the oil wasmeasured and transferred into a biodiesel reactor (500ml conical flask). The catalyst/methanol mixture was vigorously stirred at a different temperature range (45, 50, 55, 60 and 65°C) using a magnetic stirrer for 20mins.

Collection of Biodiesel

After the reaction time, the mixture was allowed to settle producing two layers (phases) using a separating funnel. The crude glycerol (the heavier brownish liquid) was collected at the bottom while a clear amber yellow methyl ester or biodiesel was withdrawn (decanted) from the top as employed by Choo *et al.* [7].

Washing and Drying of Biodiesel

The methyl ester or biodiesel was washed twice using a water solution of which 28 percentage volume of a solution of 1g/liter of tannic acid and dried at 40oC with continues stirring.

Characterization of Biodiesel

The biodiesel produced were characterized to evaluate its quality as diesel fuel in terms of the following parameters.

Density

The density of the oil was calculated using pyknometer;

P = m_1-m_0/v_tWhere m_0 is the mass in gram of the pyknometer or density bottle. M_1 is the mass in gram of the pyknometer filled with water. $V_t$is the volume in ml of the oil in the pyknometer.

Energy Value

The energy value was determined using a bomb calorimeter (1281 automatic bomb calorimeter model). One gram of the biodiesel sample was poured into the bomb for complete combustion, and was calculated as follows:

$$C_B/C_S = \theta_B/\theta_S$$

Where C_B = Calorific value of the standard sample (dry pure benzoic acid) C_S = Calorific value of the test sample θ_B= Peak galv deflection per gram of benzoic acid θ_S= Peak galv deflection per gram of test sample.

Flash Point

The flash point was determined using Pensky-Martens method. The biodiesel (10ml) was poured into an evaporating dish. A thermometer was then suspended at the center of the dish, ensuring that the bulb just dips inside the oil without the bottom of the dish. The temperature of the oil was gradually raised using an electric stove, until the oil started flashing. The flash point is the temperature at which the flame application causes a distinct flash in the dish.

Refractive Index

Refractive index is the quotient of the sine of the incident angle of light in the air, and the sine of the angle of refraction of light in the substance. This is determined directly using a refractometer (BeerSmith).

Specific Gravity

The specific gravity of the biodiesel was determined according to the method of [6]. The specific gravity was determined by taking a known volume of thebiodiesel and weighed on the weighing balance; also the same volume of water was taken and weighed. The ratio of the weight of the fuel of same volume with water was calculated, this is the specific gravity of the biodiesel.

Viscosity Test

This was determined directly using a viscometer (Brookfield digital viscometer DV-E), and the viscosity was calculated by: Kinematic viscosity = Time of fall × stokes constant.

The Methyl ester was analyzed using GCMS-QP2010 PLUS, Shimazu Japan to determine the methyl ester profile of the biodiesel produced from Allamanda oil.

3. RESULTS

Comparison of the Oil Yield from Allamanda with other Non-Edible Feed Stocks

The result of oil yield from Allamanda, Azadarichta and Jatropha is shown in Figure **1**. Allamandacathetica gave higher oil yield than Jatropha and *Azadirachtaindica*.

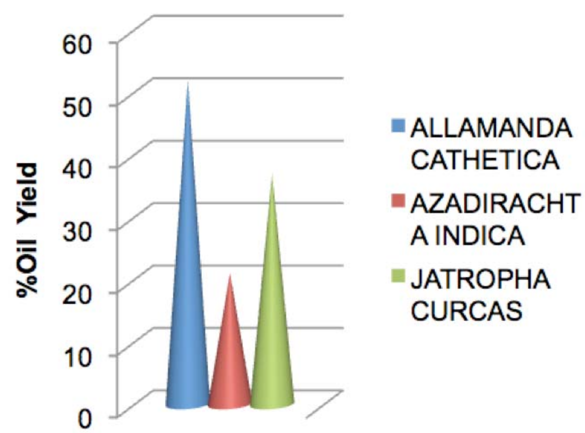

Figure 1: Oil yield of Allamanda. Azadirachta and Jatropha.

The effect of different catalysts on biodiesel yield from different feed stocks is shown in Figure **2**. The result showed that Allamanda oil gave a biodiesel yield of about 97% with sodium methaoxide and ethaoxide catalysts, while Azadirachta gave a yield of 95% with potassium ethaoxide alone. Jathrophamatained a yield of about 70% with all the catalysts used.

Effect of Temperature and Rate of Stirring on Allamanda Biodiesel Production

The effect of temperature and rate of stirring on allamanda biodiesel production is shown in Table **1**. It showed that the biodiesel yield was optimized at a temperature of 55^{O}C and at medium stirring.

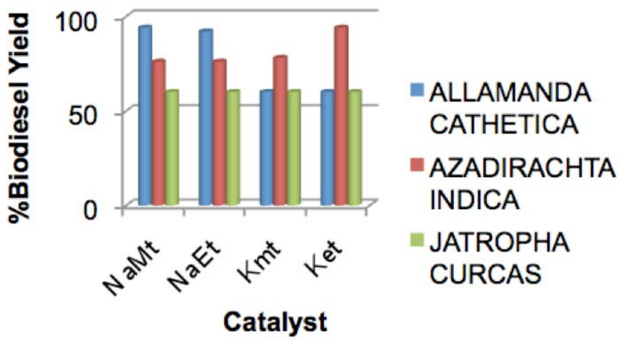

Figure 2: Effect of different catalysts on biodiesel yield.

while the methaoxides had no effect on biodiesel yield from *Jatrophacurcas*. This present result agrees with [10] who recorded highest biodiesel (98.4%) from waste sunflower cooking oil using sodium ethoxide as catalyst at 40^{o}C.

Furthermore, the methaoxide (sodiummethaoxide and potassium methaoxide) catalyst had the same effect with ethaoxides catalyst (sodium ethaoxide and potassium ethaoxide) in biodiesel yield from all the samples (*Allamandacathetica, Azadirachta*indica and *Jatrophacurcas*).

This result confirmed the study of [11] who reported that, Alkali-catalysed transesterification is much faster than acid-catalysedtransesterification and is less corrosive to industrial equipment, therefore is the most often used commercially. Also, [12] reported that ethanol is preferred alcohol for using in the transeterification process compared to methanol since it is derived from agricultural product and is renewable and biologically less offensive in

Table 1: Effect of Temperature and Rate of Stirring on Allamanda Biodiesel Production

Stirring rate Temp (OC) Biodiesel (% yield)	**Low**	**Med**	**High**
	45 50 55 60 65	45 50 55 60 65	45 50 55 60 65
	60 77 83 67 35	63 88 94 46 20	30 33 35 32 32

Table 2: Properties of Allamanda Biodiesel Produced at 55^{O}C, at 20mins Reaction Time and Medium Stirring

Parameters Determined	**Standard values for Fossildiesel Biodiesel**	**Experimental values Allamanda biodiesel**
Density (g/ml)	0.87 0.88	0.93
EnergyvalueMJ/L)	47 34.0	35.0
Refractive index	1.4613 1.4713	1.4756
Flash point	52 100	115
Specific gravity	0.86 0.88	0.87
Viscosity	1.7 4.7	5.4

DISCUSSION

The result of oil yield from Allamanda, Azadarichta and Jatropha is shown in Figure **1**. The result shows that Allamnda has a higher oil yield compared to Jatropha which is presently the most popular non-edible feed stock for biodiesel production. Previous studies have shown that Jatropha seed contains 30-40% oil [8,9]. The present study have shown that Allamnda with about 50% oil yield could be superior to Jathropha for biodiesel production. With higher oil yield, Allamanda may also be a cheaper feed stock for biodiesel production, there by driving the price of the finished product lower and more acceptable.

As shown in Figure **2**, sodium methaoxide catalyst had a better biodiesel yield from *Allamandacathetica* and *Azadirachtaindica* than potassium methaoxide

Table 3: Ethyl Ester Profile of Biodiesel from Allamanda Oil

Ethyl Ester	%yield
Hexadecanoic acid	24.29
Linoleic acid	18.31
13-Decosenoic acid	35.31
9-Octadecenoic acid	14.96
Octadecanoic acid	2.74

environment.Therefore, production of biodiesel could be greatly enhanced using sodium ethaoxide as catalyst.

The result in Table **1** revealed that temperature has a profound effect on the yield of biodiesel. The highest yield of biodiesel was obtained at 55^{O}C. At lower and higher temperatures above 55^{O}C, the yields were lower. The optimum temperature of 55^{O}C, agree with the finding of [13]. Table **1**, also showed that the production of biodiesel from allamanda oil using different rate of stirring or mixing has effect on the yield. The stirring intensity appears to be of particular importance for the transesterification process. The medium stirring rate gave the highest yield; this result is in accordance with the finding of [13]. This is because medium stirring increases the intact area between oils and sodium methoxide solution.

The transesterification process can occur at different temperature depending on the oil used. Generally the reaction is carried out close to the boiling point of methanol (60 - 70°C) at atmospheric pressure at molar ratio (alcohol to oil) of 6:1 [14].

In the present study, biodiesel yield was optimized at 55^{O}C. This lower temperature is of further advantage in using Allamanda oil as biodiesel feed stock. With lower temperature of production, energy input is reduced thereby lowering cost of production.

Previous researchers [15] have reported that soybean oil yielded 80% of biodiesel at 60^{O}C after 1min and 93-98% after 1hour. The present study has shown that the yield of 94% could be attained after 20mins reaction time at 55^{O}C

The physicochemical properties of the biodiesel produced showed a flash point of 115◦C and was quite high compared to 52^{O}C for the fossil diesel. Thus overall flammability hazard of biodiesel from this feedstock is much less than that of conventional fossil diesel, thereby making the biodiesel safe, this agrees with the standard in literature [16]. The density of allamanda biodiesel was observed to be 0.92 which is 5.5% higher than that of diesel. The higher densities of allamanda biodiesel as compared to diesel may be attributed to the higher molecularweights of triglyceride molecules present in them. This signifies that the biodiesel produced will have a better lubricating effect on the engine parts of compression ignition engine. This result is in accordance with postulation of Encinar *et al.* [17], who have shown that higher molecular triglycerides produce better biodiesel. The calorific value of allamanda biodiesel was found to be 35.0 which was 19% lower than 42.2 MJ/kg for fossil diesel. This could be due to the difference in the percentage of carbon and hydrogen content, or the presence of oxygen molecule in the molecular structure of allamanda oil. The energy value of biodiesel signifies it ability to power diesel engine. This agrees with the findings in literature [15]. The chromatogram of ethyl ester profile of biodiesel from Allamanda oil confirms that the ethyl ester contains high molecular weight triglycerides hence the higher viscosity of the ethyl ester. The chromatogram (Figure **3**) also shows the presence double bond triglycerides (Table **3**). This is an indication of reduced carbon to hydrogen ration, hence the lower energy value. The implication of this finding is that, allamnadabiodiediesel could be blended with other biosiesels with higher energy values but lower viscosity to improve on the performance and efficiency.

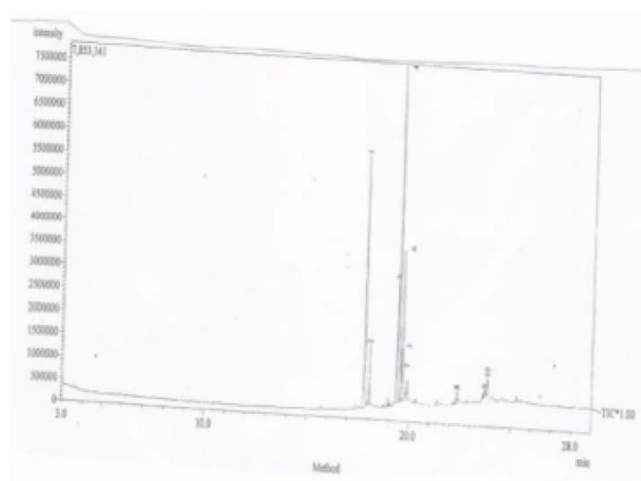

Figure 3: Chromatogram of Ethyl ester profile of biodiesel from Allamanda oil.

CONCLUSION

The present work has shown for the first time that allamanda oil could be a good alternative the production of biodiesel. The characterization of biodiesel from *allamanda catherticaoil* shows that it is essentially safe (higher flash point) than the fossil diesel, higher lubricating effect than the fossil diesel and will not cause corrosion of pipes. Thus, the biodiesel can effectively serve as an alternative to fossil diesel without modification to diesel engines Hence, reaction temperature of 55OC and medium stirring are two important factors in optimizing allamanda biodiesel yield.

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