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Production and characterizationof biodiesel from Acacia nilotica seeds

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Abstract: This paper reports the production of biodiesel from Acacia nilotica (karuvel) seed oil for the first time in literature. The karuvel oil has high free fatty acid (FFA) content; hence a two step process (esterification of FFA followed by transesterification) has been carried out to produce biodiesel. Sulphuric acid and KOH are used as catalyst for esterification and transesterification respectively. The biodiesel produced has been characterized using gas chromatography and physiochemical properties. It is found that karuvel biodiesel has high amount of unsaturated fatty acid methyl esters. For the transesterification process, the effect of Catalyst concentration and reaction time on biodiesel yield have been studied and reported. It has been found that optimum values of catalyst concentration and reaction time are 1% w/w and 1 hour respectively.
Keywords— Acacia nilotica, karuvel, biodiesel, high FFA, GC.

1. Introduction

The world's current petroleum resources are draining out alarmingly fast and every country is looking for alternative sources. Biodiesel is one such renewable source. The usage of some percentage of biodiesel blended with petroleum diesel vastly saves the exchequer on import constrains in developing nations like India. For example, recent statistics[1] shows that blending 5% biodiesel with petroleum diesel can save up to 4000 crore rupees. Furthermore, production of biodiesel may also be viewed as a potential alternative to speed up rural development and create employment opportunities. Developed countries like USA and European countries uses the edible sources like soybean and rapeseed for the biodiesel production. While in country like India, where the population is huge, biodiesel production from non ediblesources are viable from the view point of food versus energy conflict. Jatropha curcas, Pongamiapinnata (Karanj), Ricinuscommunis (Castor), Cerberaodullam (Sea Mango), Heveabrasiliensis (Rubber tree), Simmondsiachinensis (Jojoba), Azadirachtaindica (Neem) and Madhucaindica (Mahua) etc. are some of the non edible sources that have been tried in the past to produce biodiesel[1].

The objective of this study is to evaluate,non edible Acacia nilotica (Karuvel) seed oil for bioidiesel production. Acacia nilotica (family Leguminosae) generally grows to a height of about 15 - 18 m with a 2 - 3 m diameter (see Fig. 1a and 1b). The bark is slate green in young trees and nearly black in mature trees. The pods are normally 7 – 15 cm long, green and tomentose when immature and greenish black when mature. The pods are indehiscent and deeply constricted between the seed giving a necklace appearance[2]. 8 to 12 Seeds are present per pod. The seeds are compressed, ovoid, dark brown shinning with hard testa (see Fig. 1c). Acacia nilotica is naturally widespread in drier areas of Africa (Senegal, Egypt) and Asia (India, Burma and Srilanka). In India it is distributed in forest areas, road sides, farm lands, tank foreshores, wastelands etc. Acacia nilotica grows under climatic conditions ranging from sub tropical to tropical. It can withstand extreme temperatures (> 50^{o} C) and conditions of drought. It can also grow at any type of soil; saline (soluble salt content below 3%) or alkaline (up to PH 9).

In this work, the process to produce biodiesel from oil extracted from Karuvel seeds through tranesterification process is discussed. In addition to this, the effect of different process parameters like; reaction time and catalyst concentration on biodiesel yield are investigated. The physical properties of the biodiesels are measured and reported. Biodiesel is characterised using the measured physical properties and gas chromatography. To the best of our knowledge we are reporting the production of biodiesel from Acacia Nilotica (Karuvel) for the first time in literature.

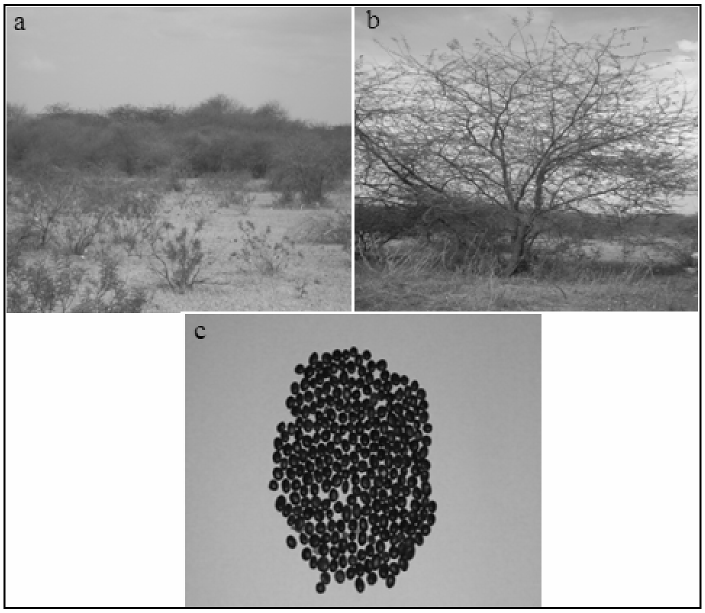


Figure 1a - 1c. Karuvel tree and seeds

2. Experimental Section

2.1 Materials

The Karuvel pods are collected from the Karuvel trees in and around Government College of Engineering, Tirunelveli, Tamilnadu. The seeds are then removed from the pods for further processing. Methanol, n-Hexane, Potassium hydroxide and Sodium sulphate used in the experiments are of AR grade. The fatty acid composition of karuvel seed oil taken from the literature[3] is given in Table 1.

Table 1. Fatty acid Composition of Karuvel Oil

Fatty acids	*Percentage*
Myristic acid (C14:0)	0.4
Palmitic acid (C16:0)	15.7
Stearic acid (C18:0)	9.0
Arachidic acid (C20:0)	1.2
Vaccenic acid (C18:1)	29.0
Linoleic acid (C18:2)	44.5

In CXX:Y, XX indicates the length of the carbon chain and Y indicates the number of double bonds

2.2 Oil Production by Solvent Extraction

Oil has been extracted from karuvel seeds through solvent extraction process. The apparatus consisted of a heating mantle which could hold a round bottomed flask of 1.5 L capacity. Soxhlet extraction chamber has been attached on top of the flask and on top of the extraction chamber a condenser has been fitted. 0.5 Kg of seed powder has been was used for the extraction each time. The seeds were finely powdered by a dry grinder and added to the extraction chamber. Anhydrous n-Hexane (organic solvent) has been added to the flask and the temperature of the flask has been maintained at 50^{o} C using a temperature controller mechanism. At this temperature, the hexane gets vaporized and reaches the condenser where it gets condensed and trickles in to the extraction chamber. The powdered seeds percolate in n-Hexane solvent thereby the oil content from the seeds gets dissolved in to the solvent. The extraction chamber has been designed in such a way that when the solvent reaches a certain level, it overflows and trickles back in to the flask. This process has been repeated till most of the oil from the seeds is extracted by the solvent. Then, distillation has been carried out to separate oil from n-Hexane. The oil thus produced has been filtered using Whatman No 1. filter paper. Then degumming process has been carried out in a centrifuge with water to remove water soluble phospholipids. The degummed oil has been then treated with sodium sulphate to remove any traces of moisture. The oil yield was about 20% by weight.

2.3 Biodiesel Production by Transesterification

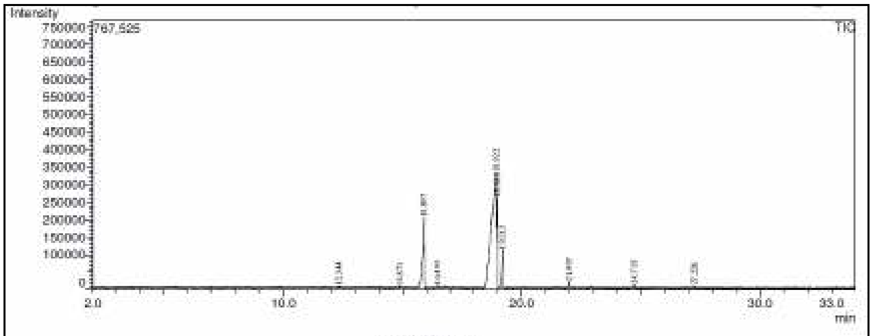
The experimental setup for production of methyl esters of Karuvel oil consisted of a heating plate with a magnetic stirrer and thermostat to control the temperature. A flat bottomed flask with three necks was placed on top of the heating plate. A reflux condenser has been attached to one neck of the flask. Another neck was used to add the reactants to the flask. A thermometer was attached to the third neck to monitor the temperature. The Karuvel oil produced had a high acid number of about 18.2mg KOH/g repectively. Therefore esterification of free fatty acids has been done first. Methanol to oil molar ratio used for esterification was 9:1. Sulphuric acid was used as catalyst at 1 % w/w of oil. Sulphuric acid has been slowly added to the methanol and mixed well. Then the mixture has been added to the preheated oil. The esterification has been carried out for about 2 hours. The reactant mixture has been allowed to stand in a separating funnel for 24 hours. The oil layer that got settled at the bottom has been separated and used for tranesterification. Transesterification reaction has been carried out in a similar experimental set up. The tranesterification parameters such as Methanol to oil ratio, reaction temperature and speed of the stirrer have been maintained as constant for all experiments at 6:1, 60^{o} C and 600 rpm respectively. The concentration of catalyst (potassium hydroxide) and reaction time have been varied and the biodiesel yield has been measured and compared.

2.4 Quantification of Biodiesel

The quantification of methyl esters in Karuvel biodiesel was done using Gas chromatography (GC). GC analysis was carried out at CSMCRI, Gujarat, India. Fatty acid profile is given in Table 2. The chromatograph for the biodiesel is given in Fig. 2. The percentage of saturated and unsaturated fatty acid methyl esters in the biodiesel is 19.83 and 79.55% respectively.

Table 2. Fatty acid methyl ester composition in biodiesel

Fatty acid methyl ester	***Composition (%)***
Palmitic acid methyl ester	13.8
Behenic acid methyl ester	0.26
Arachidic acid methyl ester	0.74
Iso Stearic acid methyl ester	4.88
Lignoceric acid methyl	0.15
Elaidic acid methyl ester	11.22
Linoleic acid methyl ester	68.33



Peak#	R.Time	Area	Area%	Name	Base m/z
1	12.344	7482	0.12	Heneicosanoic acid, methyl ester	74.05
2	14.871	6444	0.10	1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester	149.05
3	15.897	895363	13.80	Hexadecanoic acid, methyl ester	74.00
4	16.493	25867	0.40	1,2-Benzenedicarboxylic acid, dibutyl ester	149.05
5	18.922	4432256	68.33	9,12-Octadecadienoic acid	67.05
6	18.988	727602	11.22	9-Octadecenoic acid, methyl ester, (E)-	41.05
7	19.213	316860	4.88	Methyl isostearate	74.00
8	21.997	48031	0.74	Eicosanoic acid, methyl ester	74.00
9	24.715	16941	0.26	Docosanoic acid, methyl ester	74.00
10	27.226	9581	0.15	Tetracosanoic acid, methyl ester	74.00
		6486427	100.00		

Figure 2. Gas Chromatograph of Karuvel biodiesel

2.5 Determination of Properties of Biodiesel

Density, kinematic viscosity and ultrasonic speed of the biodiesel produced have been measured using a single stem pycnometer, ubbelohde suspended level viscometer and a single crystal variable path multi frequency ultrasonic interferometer(2MHz) respectively. The reproducibility of the measured values of density, viscosity and ultrasonic speed is ± $2.8x10^{-3}$g/cm^{-3}, ± $1.9x10^{-3}$ mm^2/s^{-1} and 0.03 % respectively. The details of the measurement procedures are given in literature[4]. The flash point of the biodiesel has been measured using the Cleveland open cup apparatus. The cetane number of the biodiesel has been estimated using the equation given in literature[5]. The measured physiochemical properties of biodiesel are given in Table 3 and compared with the biodiesel standards. The biodiesel produced from Karuvel oil had density, viscosity, acid number, flash point and cetane number values well within the limits specified by ASTM D6751 and EN 14214 standards.

Table 3. Physical and Chemical properties of biodiesel

Properties	*Karuvel biodiesel*	*Standards* *EN14214*	*ASTM D6751*
Density ^{a} (kg/m^3)	890.1	860 – 900	-
Kinematic viscosity ^{b} (mm^2/s)	4.2045	3.5 – 5	1.9 – 6
Acid number (mg KOH/g)	0.1923	0.5 max	0.80 max
Flash point (^{o}C)	160	>101	130 min
Cetane number*	51	51 min	47 min

^{a} measured at 288.15 K ^{b} measured at 313.15 K

3 Results and Discussion

It is observed from the Table 3 that amount of unsaturated fatty acids in Karuvel biodiesel is high. Biodiesel fuel with more unsaturated fatty acid composition has more density and iodine number but less viscosity, heating value and cetane number[6]. Density which is defined as the weight of a unit volume of the fuel is an important property of the biodiesel. Fuel injection equipment that operates on volume metering system is sensitive to density of the fuel. In case of biodiesel, slightly higher mass of fuel is injected compared to petroleum diesel due to higher density[7]. Viscosity is the measure of internal friction of the fuel to its flow. Viscosity of the fuel influences the fuel injection process and atomization of the fuel[7]. Biodiesel generally has higher viscosity than petroleum diesel. Viscosity and surface tension of the fuel together affects the spray characteristics of the fuel[8]. The amount of free fatty acids present in the biodiesel is indicated by the acid number. Higher the acid number, greater the free fatty acid content and hence higher corrosive behaviour of biodiesel[9]. Cetane number of the fuel relates to ignition quality of the fuel. Since biodiesel is largely composed of long chain hydro carbons, it has higher cetane number than petroleum diesel[10]. Higher cetane number of the biodiesel fuel generally leads to reduced ignition delay[11].

3.1 Effect of Catalyst Concentration on Biodiesel Yield

The influence of catalyst concentration on the methyl ester conversion of the vegetable oil has been studied with catalytic loading of 0.5% to 2 % w/w at 60 ± 1^{o} C with methanol oil ratio as 6:1. From Fig. 3, it is observed that methyl ester yield has been less when the catalyst concentration was lower at 0.5% w/w. The optimal yield has been achieved with 1% w/w catalytic concentration. Any further increase in the catalytic concentration has adversely affecting the methyl ester yield that may be probably due to saponification process[12].

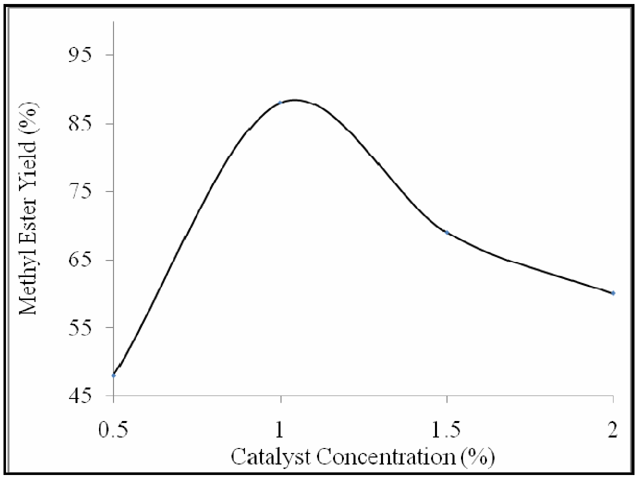


Figure 3. Effect of catalyst concentration on biodiesel yield

3.2 Effect of Reaction Time on Biodiesel Yield

The Transesterification process has been attempted with reaction time of 30 minutes to 2 hour keeping molar ratio 6:1 at 60 ± 0.1^{o} C with catalyst concentration of 1% w/w of oil. From Fig. 4, it is observed that the conversion of methyl ester has been lower at 30 min reaction time. However when the reaction time was increased to 1 hour, the yield has been maximum. Any further increase in reaction time has not drastically yielded more methyl ester. Similar observations have been reported in literature[12,13](Keera 2011 and Ma 1999).

The performance, combustion and emission characteristics of direct injection diesel engine operated with karuvel biodiesel blended with petroleum diesel at different proportions will be reported in detail elsewhere in literature.

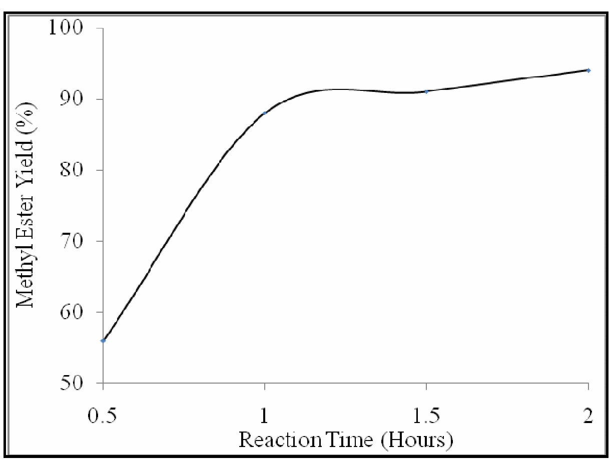


Figure 4. Effect of reaction time on biodiesel yield

4 Conclusion

From the experiments conducted we conclude that biodiesel has been successfully produced from non edible karuvel seeds for the first time in literature. From GC analysis, it is found that the amount of unsaturated fatty acids is high (79.55 %). The physiochemical properties of the biodiesel are well within the limits specified by international standards, there by indicating that this biodiesel may be used in diesel engine with proper blending with petrodiesel. Optimum catalyst concentration for maximum biodiesel yield is 1% w/w. Optimum reaction time for maximum yield of biodiesel is 1 hour.

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