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Biodiesel Production from Seed Oil Obtained from *Pongamia pinnata* L.

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

At the present time biodiesel are the most promising source of energy as it is renewable and can accomplished the rising energy demand. *Pongamia pinnata* L. (commonly known as Karanj) is an evergreen tree of family *Fabaceae* sub family *Papilioneaceae*, has been recognized as a potential source of biodiesel prepared from the oil obtained from its seeds. In the present work, biodiesel fuel was prepared by alkaline-catalyzed esterification of high free fatty acids present in Karanj oil. The transestrification reaction was performed by varying practical parameters such as NaOH percentage (0.50%, 0.75%, 1%), methanol to oil ratio (3:1, 6:1, 9:1), and reaction temperature and time (40°C for 2h, 60°C for 2h, room temperature for 24h) at constant stirring at 150 rpm. Optimum alkaline-catalyzed transesterification was achieved using 1% NaOH as a solid alkaline catalyst with a methanol-to-oil ratio of 1:6, temperature at 60^0C. The yield of methyl esters from Karanja oil under the optimal condition was 92%. The biodiesel and oil contents were analysed using Gas Chromatography and Mass Spectroscopy (GC-MS) analyser. Fuel properties of the biodiesel obtained by transesterification were tested and found to meet the ASTM (American Society for Testing and Material) specifications.

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1. INTRODUCTION

Energy is a crucial component of a country's economic success. The majority of energy needs are met by fossil fuels. Increasing energy consumption and population pressure have put increasing strain on the available fossil fuels [1]. Fossil fuels are currently in short supply, and their widespread use causes significant environmental effects [2]. When a replacement for fossil fuels is needed, renewable energy sources, which are more environmentally friendly and can take the place of current energy sources, should be considered. This has spurred an effort to discover new, sustainable, and renewable energy sources during the past few decades. In addition, the use of fossil fuels increases the greenhouse gas emissions that cause global warming. Because of this, researchers are becoming increasingly interested in using alternative energy sources, such as biofuels. On the basis of biofuel sources of biomass, their limitations as a renewable source of energy, and their technological progress, generally biofuels can be categorised in three generations (1st, 2nd and 3rd generation). Depending upon climate and soil conditions, different nations are looking into different vegetable oils for diesel fuels. For example, soya bean oil in the United States, rapeseed and sunflower oils in Europe, palm oil in Southeast Asia (mainly Malaysia and Indonesia), and coconut oil in The Philippines are being considered as substitutes for diesel fuels [3]. European Union had already banned first generation biofuel made up of fermentation of consumable food like soybean and rapeseed oils to secure the food supply. Some studies also carried out on how these biodiesels affect engine performance and emissions [4]. Second generation biofuel includes cellulosic ethanol, non-food feed stock, waste vegetable oil [5], forest residues, industry residue and sustainable biomass. Third generation includes Algal fuel, generally obtained from microalgae [6].

Biodiesel obtained from non-food feed stock is one of the finest possibilities for today's vehicle fuel due to price increases and the non-renewable nature of fossil fuels. Transesterification reaction is key reaction for the conversion of oil into biodiesel. It is a process of reacting triglyceride (the main component of oil) with an alcohol (methanol) in presence of a catalyst (mainly use NaOH or KOH). According to technical definitions, biodiesel is a fatty acid alkyl ester produced by transesterification of animal or plant fat with short-chain alcohols like methanol or ethanol. Biodegradability, low toxicity, low sulphur content, high flammability, and high cetane number are the distinctive characteristics of biodiesel that make it special [7].

Pongamia pinnata L. (Family: *Leguminosae* family, subfamily *Papilionaceae* , commonly known as Karanj) is one of the sources of non-edible oils [8]. It is mostly found in the Western Ghats of India and can grow on a variety of soil types, from clayey to sandy. *P. pinnata* kernel contains between 30 and 40 present oil, it is thought to be a viable source for making biodiesel [9]. It is a medium-sized glabrous tree with a trunk diameter of less than 50cm and a height of about 18m. Karanj thrives in humid and subtropical conditions with annual rainfall ranging from 500 to 2500mm. It is producing flat, elliptic fruits that are nearly 7.5cm long. Each fruit has 1-2 brownish red kernels shaped like a kidney. The oil can be extracted from the kernels by oil expeller or soxhlet method. The kernel yield per tree ranges from 9 to 90 kg. The colour of the freshly extracted oil ranges from yellowish-orange to brown. It has an unpleasant odour and a bitter flavour. But, presence of toxic furanoflavones, such as Karenin, Pongapin, Kanjone, and Pongagalabrin makes it nonedible. The Karanj oil is rich in fatty acids such as palmitic, stearic, oleic, linoleic, logoceric, eicosenoic, arachidic, and behenic. The saturated acids, palmitic (hexadecenoic acid) and stearic (octadecanoic acid), as well as the unsaturated acids oleic (octadic-9-enoic acid) and linoleic (9,12-octadecadienoic acid), are found in maximum concentration. In the present study, we focus on the optimum yield of oil via Soxhlet method with polar solvents and further transesterification reaction performed for biodiesel production.

2. MATERIALS AND METHODS

2.1 Collection and Identification of Plant Material

Pongamia pinnata seeds were used as raw materials to produce biodiesel. These seeds were collected from different parts of Jaipur city. Specimen was submitted to Herbarium, Department of Botany, University of Rajasthan, Jaipur. Dry seeds were isolated from the kernel and sun-dried. Seeds were roasted for half and let cool. Then, it was crushed in mortar and pastel and fine powder was prepared with the help of a mixer grinder. Seed powder is weigh and collected in airtight jars and stored in a refrigerator for further extraction.

2.2 Extraction of Oil

The oil was obtained by the soxhlet extraction method. 50 gm seed powder was packed in a thimble and placed in the main chamber of the soxhlet extraction unit and 300 ml n-Hexane was added and run at 60^{o}C for 24 hours. Another experiment was run with petroleum ether at the same time and temperature. The oil was isolated and purified at rotary evaporator. Oil was further sent for GC-MS analysis.

2.3 Transesterification of Oil

Transesterification is the process by which a triglyceride (fat/oil) reacts with an alcohol in the presence of an acidic, alkaline, or lipase as a catalyst to produce mono alkyl ester, which is the base for biodiesel and glycerol. According to reports, alkaline catalyzed transesterification is the quickest and easiest to set up. Consequently, in the current investigation, the oil of *P. pinnata* was transesterified with methyl alcohol in the presence of a potent alkaline catalyst NaOH. In order to prepare biodiesel from *P. pinnata* crude oil, firstly Sodium methoxide was prepared by mixing NaOH, with 10 ml distilled methanol at constant stirring at 150 rpm at room temperature [10]. 10 ml of Karanj crude oil was warmed at 60^{0}C and stirred concurrently in a different vessel of the transesterification reactor. Then Sodium-methoxide was added. The reaction was repeated by varying practical parameters such as NaOH percentage (0.50%, 0.75%, 1%), methanol to oil ratio (3:1, 6:1, 9:1), and reaction temperature and time (40°C for 2h, 60°C for 2h, room temperature for 24h) at constant stirring at 150 rpm. Optimum alkaline-catalyzed transesterification was achieved using 1% NaOH as a solid alkaline catalyst with a methanol-to-oil ratio of 1:6, temperature at 60^{0}C. This process was continued until the separation between biodiesel and oil was observed. After completion of the reaction, the mixture was transferred to a separating funnel and allowed to settle for 24 hours. After settling, distinguished lower glycerol, water solubilized the soap, catalyst, and other impurities, and upper methyl ester (Biodiesel) layers were separated manually, settled at the bottom of the funnel, which was eventually drained out. After each wash, the pH of the water was checked. The washing was continued until the pH of the separated water reaches the range of 7-8. The final product obtained is biodiesel. *P. pinnata* biodiesel is amber yellow. Then, passed over anhydrous Sodium sulphate for removal of moisture and after filtration placed on rotary evaporator for complete clearance of biodiesel. The biodiesel and oil contents were analysed using Gas Chromatography and Mass Spectroscopy (GC-MS) analyser.

2.4 Quantitative and Qualitative Analysis of Biodiesel

Biodiesel Yield: The total yield of biodiesel was obtained by following formula:-

Yield of Biodiesel (%) = (Grams of Biodiesel Produced x100) / Grams of the oil used

2.5 Qualitative Analysis of Biodiesel

The physio-chemical characteristics of biodiesel obtained from *P. pinnata* oil, such as its density, kinematic viscosity, acid value, iodine value, saponification value and moisture content, were used to describe its quality. These oil characteristics were established by ASTM standards.

3. RESULTS AND DISCUSSION

The *Pongamia* oil content about 42 wt %. GC-MS chromatogram of Karanj oil is shown in Fig. 1. GC-MS chromatogram of transesterified oil is shown in Fig. 2. The fatty acid composition of *Pongamia* oil is given in Table 1, which indicates the higher concentration of free fatty acids like Linoleic acid (46.08%), Oleic acid (28.56%), Palmitic acid (13.78%), Steric acid (11.07%) etc.

3.1 GC-MS Analysis of Karanj Oil

Pongamia pinnata seed oil is rich in the saturated acids, palmitic (hexadecanoic acid) and steric (Octadecanoic acid) and the unsaturated acids, oleic (octadecan-9-enoic acid) and linoleic acid (9.12-octadecadienoic acid). 2-[5-(2-Methyl-benzooxazol-7-yl)-1H-pyrazol(42.68%), 6-(2-Ethoxy-phenyl)-5-nitro-piperidin-2-one(21.08%), 3,5-Dimethoxyflavone(20.66%),1,4-Naphthalenediol(2.00%) were some major compounds identified via GC-MS.

GC-MS analysis of transesterified oil (FAME) is briefly mentioned in Table 1.

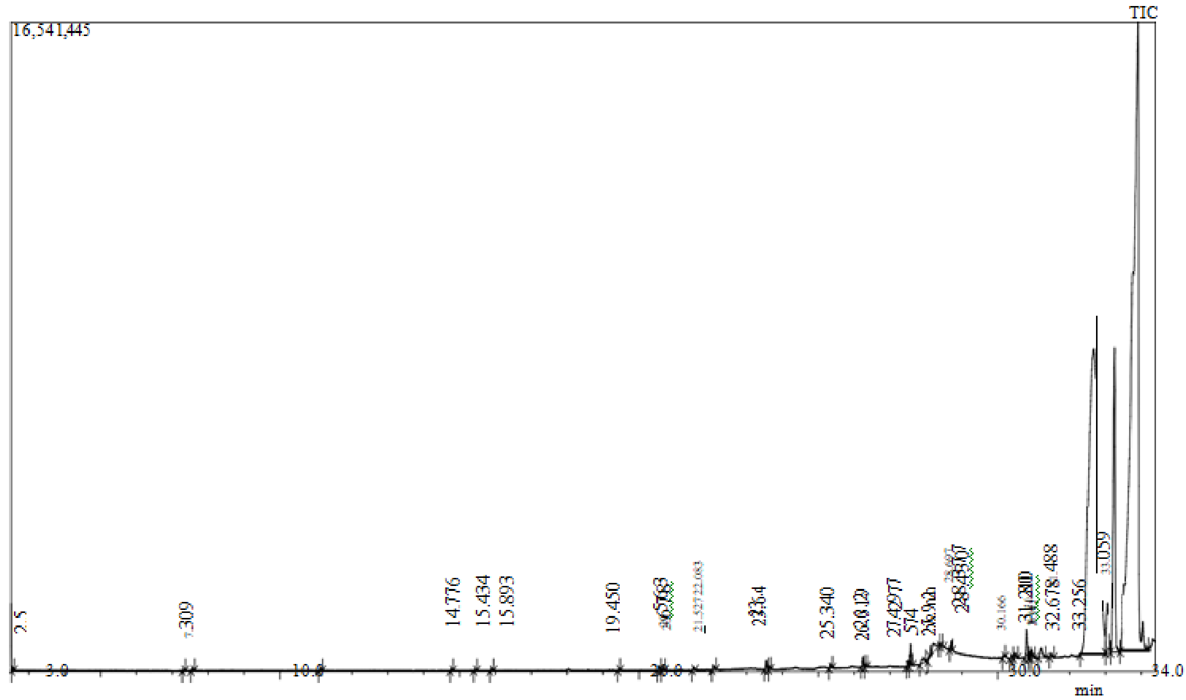

Fig. 1. GC-MS Chromatogram of Karanj oil

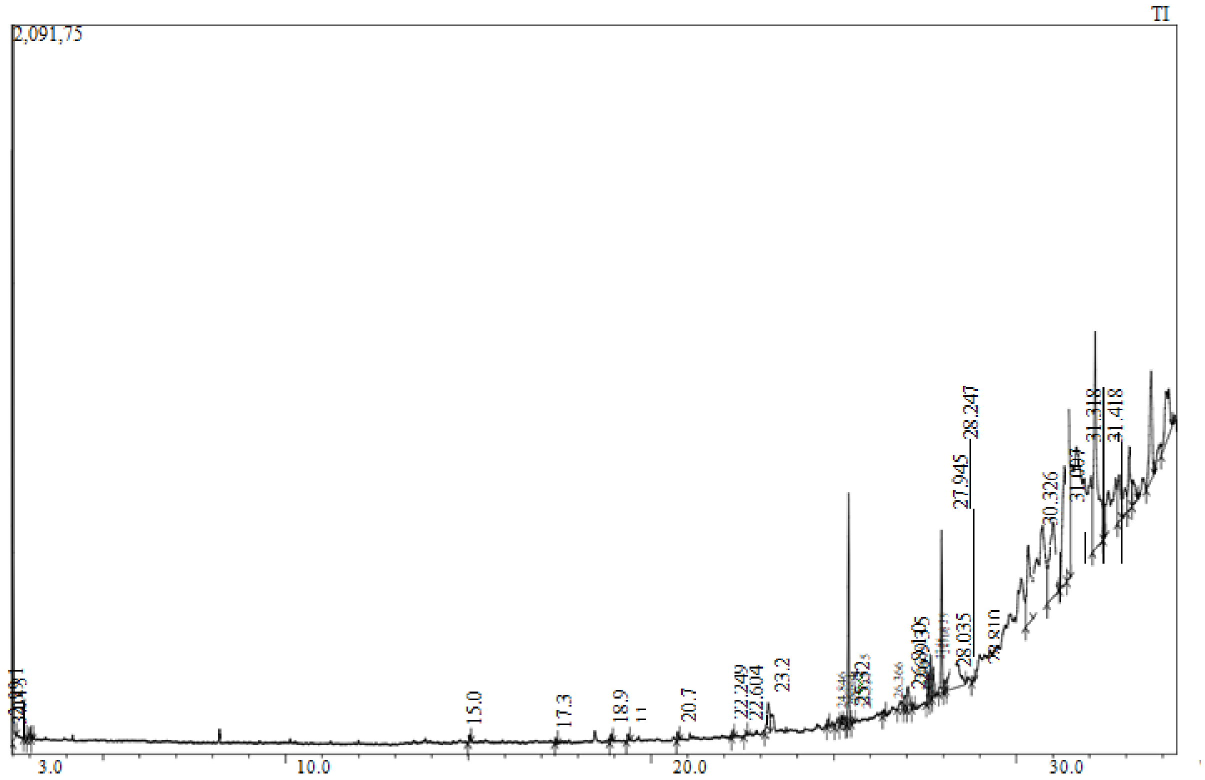

Fig. 2. GC-MS Chromatogram of transesterified oil (FAME)

Table 1. FAME composition (%) of Karanj oil

S.N.	Methyl esters of Fatty acid	Molecular formula	Percentage
1.	Heneicosanoic acid, methyl ester	$C_{16}H_{32}O_2$	36.73
2.	Stearic acid, methyl ester	$C_{18}H_{36}O_2$	23.7
3.	Linoleic acid, methyl ester	$C_{18}H_{32}O_2$	16.15
4.	Palmitic acid, methyl ester	$C_{17}H_{34}O_2$	12.33
5.	Oleic acid, methyl ester	$C_{18}H_{34}O_2$	5.84
6.	Tetracosanoic acid, methyl ester	$C_{24}H_{48}O_2$	4.06
7.	Eicosanoic acid, methyl ester	$C_{20}H_{40}O_2$	0.99
8.	Dosocasnoic acid, methyl ester	$C_{22}H_{44}O_2$	0.16

Table 2. Qualitative parameters of biodiesel obtained from Karanj oil

S. No.	Parameter	ASTM value	Biodiesel from Karanj oil
1.	Moisture content	0.05 max	0.04
2.	Density	820-860	867
3.	Kinematic Viscosity	1.9-6.0(40^0)	4.7
4.	Acid value	0.80 max	0.78
5.	Ester value	96.5 min	125
6.	Iodine value	1.0-6.0	1.15

The qualitative parameters of biodiesel obtained from *Pongamia* oil are given in Table 2. Moisture content (0.04), density (867), kinematic viscosity (4.7), acid value (0.78), ester value (125) and iodine value (1.15) are reported which are in the range of established by ASTM parameters.

Biodiesel obtained from *Pongamia* seed oil studied by many researchers Suresh et al. [11] are either used directly or blended with conventional diesel and then used in the engine with minor or no modifications. Biodiesel oils obtained from non-edible oils such as *Pongamia* oil are environment-friendly and non-toxic Fazal et al. [12] compared to conventional diesel fuel. In the proposed work, Pongamia oil conversion rate is 92% into biodiesel with the molar ratio (1:6) which is quite higher with the previous work of Karmee and Chanda [10] who discovered maximal oil conversions of 80 and 83 percent at the 1:3 and 1:10 molar ratios of oil and methanol. Similar reports were carried out by Hosseinzadeh-bandbafha et al. [13] on a small and a large scale. When the molar ratio was 9:1 (with the catalyst NaOH kept fixed at 1 percent of Karanj oil), they discovered that the production of biodiesel went up to 85 percent on small scale and 86 percent on a big scale. They also tested the impact of varying catalyst concentration (NaOH) with constant wt. of oil and methanol (9:1). The greatest percent yield was determined to be 82 and 81 in small-scale and large-scale experiments, respectively, when the weight of NaOH 1 percent of Karanj oil was used as the catalyst, according to the research on the effects of changing catalyst concentration with constant weights of oil and methanol.

In our experiment, the kinematic viscosity is 4.7 CST which is quite similar with the finding of Karmee and Chadha [10]. They discovered 4.8 CST kinematic viscosity of the methyl esters of Karanj oil.

The fatty acid composition of Keranj oil revels that Oleic acid ($C_{18}H_{34}O_2$) is found maximum *i.e.* (51.59%), Linoleic acid($C_{18}H_{32}O_2$) (16.64%), Palmitic acid($C_{16}H_{32}O_6$) (11.65%), Stearic acid ($C_{18}H_{36}O_2$) (7.50%) and other fatty acids in minute concentrations [14]. For better transesterification, the fatty acids should be comprises C_{16} to C_{18}. Table 2 exhibits that methyl esters of Heneicosanoic acid (36.73%); Stearic acid (23.7%); Linoleic acid(16.15%); Palmitic acid(12.33%), Oleic acid (5.84%) which indicates desire composition of biodiesel. Earlier, the properties of the FAMEs (Fatty Acid Methyl Esters) were also reported by Azam et al. [15]. The iodine value (80.9) for *P. pinnata*, which is a measure of the total number of double bonds amongst the respective fatty acids, are quite different then our findings (1.15).

Fu et al. [16] reported the *Pongamia* oil content from seeds was found to range from 19 to 32.5% with younger trees producing higher oil concentrations. However, in our findings, the oil yield was 42% as we roasted seed for a particular time which coagulate protein and enhance yield of free fatty acids.

Another study on properties on biodiesel mixtures and blends of biodiesel was done by Sriharsha and Satyanarayana [17], which supports our research. Kinematic viscosity, acid value, ester value, iodine value etc. are compared with diesel fuel according to the ASTM standards which suggest the use of Karanja methyl ester or biodiesel from *Pongamia* oil in the engine as blend in petroleum fuel with or without modification can be a potential fuel option. Biodiesel was synthesized through single stage transesterification process using methanol (20:1 to 40:1) and Mg-Al hydrotalcite by continuously stirring for 1.5 – 3.5 hours at 80-160°C from waste cooking oil [18]. Further, the use of octanol on the emission and performance characteristics of biodiesel fuel was investigated by Rangabashiam and Jayaprakash [19] on a single-cylinder, biodiesel engine using various blends of Pongamia biodiesel and octanol (O10PBD90, and O20PBD20) and Pongamia Biodiesel (PBD).

4. CONCLUSION

The major fatty acids in *Pongamia pinnata* crude oil were Heneicosanoic acid, Stearic acid, Linoleic acid, Palmitic acid, Oleic acid observed. The soxhlet extraction of roasted seeds gives maximum oil yield, which after transesterification method convert into biodiesel and glycerin. Here, glycerin can be purified and can be commercially used. The seedcake which remains after oil extraction can be used as feedstock. Thus, we can reduce the cost of biodiesel production. Further, different bland can be prepared with the proper mixing of Petroleum diesel and can be tested for its better performance. It is required to work on reduction of *Pongamia* biodiesel friction and viscosity by using organic solvents, so that it can use directly into engine rather than bland. At the same time, plantation of this useful tree at barren lands should be supported.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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