



Standardization of non-edible pongamia pinnata(karanja) oil methyl ester conversion using GC-MS analysis

B Venu Gopal^{1,*}, D Swathi¹, P A Satynarayana¹, V Sridevi¹ and P V Rao²

¹Department of Chemical Engineering, Andhra University, Visakhapatnam-530003.

²Department of Mechanical Engineering, Andhra University, Visakhapatnam-530003.

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ABSTRACT

Production of Pongamia Pinnata (Karanja) oil methyl ester (biodiesel) from non-edible vegetable oils for diesel substitute is particularly important because of the decreasing trend of economical oil reserves, environmental problems caused due to fossil fuel use and the volatile prices of petroleum products in the international market. Present work reports an optimized protocol for the production of methyl ester through alkaline catalyzed transesterification of Karanja Oil. Three principal variables, molar ratio of methanol to oil, amount of catalyst, and reaction temperature affecting the yield of alkaline catalyzed production of methyl ester from Karanja oil were investigated. The methyl ester with best yield and quality was produced with karanja methyl ester at 1:9 mole ratio and 1 wt% of catalyst (NaOH). The rate of transesterification in a batch reactor increased with temperature upto 60 °C the yield was 91%. It was noted that greater or lower the concentration of NaOH or methanol than the optimal values, the reaction either fully occur or lead to soap formation. Physical and chemical properties of Karanja methyl ester are compared to that of petroleum diesel. Karanja oil to methyl ester conversion determined by GC-MS analysis. The produced methyl ester was found to exhibit fuel properties within the limits prescribed by the American Standards for Testing Material (ASTM D6751) and European EN standards.

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Introduction

Presently the world's energy needs are met through non-renewable resources such as petrochemicals, natural gas and coal. Since the demand and the cost of petroleum based fuel is growing rapidly, and if the present pattern continues these resources will be depleted in few years. Hence, efforts are being made to explore for alternative source of energy [1-2]. An alternative fuel must be technically feasible, economically competitive, environmentally acceptable and readily available. Fatty acid methyl ester (biodiesel) is extracted from renewable sources such as vegetable oils has gained importance as an alternative fuel for diesel engines, which is biodegradable and non-toxic fuel[3-4]. The problems of high viscosity and low volatility have limited the direct use of vegetable oils and animal fats as combustible fuel and their prolonged use would pose serious threats such as deposition of fats, ring sticking and injection choking in engine[5]. In order to overcome these difficulties, the triglycerides in vegetable and animal fats has to be subjected to transesterification, involving the conversion into fatty acid methyl ester (FAME), in the presence of short chain alcohols, such as methanol or ethanol and a catalyst such as alkali or acid with glycerol as a by-product [6]. It is an alternative diesel fuel composed of triglycerides with different fatty acids attached to the glycerol. The composition of fatty acids attached to glycerol. The composition of fatty acid will directly influence the properties of biodiesel [7]. In Indian context, the use of edible oils for engine fuel is not feasible. However, there are several non-edible oilseed species such as karanja (pongamiapinnata), jatropha (jatropha curcas), neem (azadirachta indica), mahua (madhuca indica), simarouba (simarouba indica) etc., which would be utilized as a source for production of oil [8].

Among these, karanja an oil seed bearing tree, which is non-edible and does not find any suitable application with only 6% being utilized out of 200 million tons per annum. The recent studies evaluated the potential of utilizing the waste cooking oils, renewable feed stock like vegetable oils and animal fats to produce biodiesel[9-11]. The composition of biodiesel varies with the reactant employed for transesterification and the products obtained are methanol and ethanol, respectively. but methanol is generally employed as a reactant because of their low cost and availability [12]. The freshly extracted karanja oil is yellowish orange to brown and rapidly darkens on storage. It has a disagreeable odour and bitter taste. The oil contains several furanoflavones such as karanjin, pongapin and pongaglabrin.

The presence of toxic flavonoids makes the oil non edible[10]. Vegetable oils and fats are chemically triglyceride molecules, in which three fatty acid groups are ester bound to one glycerol molecule. The triglyceride molecules differ by nature of the alkyl chain bounded to glycerol. Transesterification is a process of reacting a triglyceride such as one of the vegetable oil, with alcohol in the presence of catalyst to produce fatty acid esters and glycerol[13]. In this process there is the displacement of alcohol part by a monohydric alcohol that yields three alkyl esters from one triglyceride molecule. The molecular weight of a typical ester molecule is roughly one-third of a straight vegetable oil molecule and has viscosity approximately twice that of diesel fuel instead of a 10 to 20 times as in case of neat vegetable oils[14]. There is decrease in viscosity and improvement of fuel properties of product fatty acid alkyl ester in the process of transesterification[15]. The analytical methods used for the evaluation of methyl ester in the transesterification

of vegetable oils using GC-MS and Elemental analysis. These analytical techniques are more accurate and sensitive.

The aim of this study was to develop a two step process for the production of biodiesel from karanja oil with high free fatty acid (FFA).

Pongamia pinnata(Karanja) oil

Pongamia, a medium sized glabrous tree grown in many parts of India and Australia [16]. Pongamia is popularly known as Karanja in India. Karanja belongs to the family Leguminaceae [17] and its botanical name is *P. Pinnata*. Karanja tree bears flowers and then pods, which after 10 to 11 months gets matured and changes to a tan color in the month of May to June [18-19]. The pods are flatto elliptic in shape and contain one (or two) kidney shaped brownish red seeds (or kernels) as shown in Fig 1 and Fig 2. The oil content of karanja seed is about 33% [20]. The fresh extracted oil is yellowish orange to brown and rapidly darkens on storage.



Fig 1. Pongamia pinnata pods



Fig 2. Pongamia pinnata seeds [21]

Materials and Methods

Chemicals

Methanol (99.5% purity) of E Merck India Ltd., potassium hydroxide of Indian drugs and pharmaceutical Ltd., pongamia oil purchased at vizianagaram, Sulfuric acid and Phosphoric acid were used in the experimental work [22].

Preconditioning of oil

Preconditioning of oil involved the removal of the moisture and neutralization of free fatty acids (FFA). Usually the present feed (Cotton seed oil) consist less than 5% of FFA but they need to be neutralized as they result in the formation of soap [23]. For determination of FFA present in the oil taken, we titrated the oil sample with 0.1N NaOH solution with Phenolphthalein as indicator. Volume in ml of 0.1N NaOH required to neutralize 1gram of oil is called acid value. And with this we determined the amount of NaOH needed to neutralize the FFA's in the oil. Thus by adding calculated amount of NaOH, FFA's are removed in the form of soap. Removal of moisture involved heating the oil sample up to 105-120°C and maintaining it there for few minutes so that all moisture gets evaporated. If required

vacuum pump arrangement is used to remove the moisture present.

Experimental procedure

First stage (Acid catalyzed stage)

The free fatty acids can be reduced to esters by two processes viz. hydrolysis, methanol with acid catalyst. The two reactions are depicted in the Fig 3. The treated oil is taken in liters and heated to 35 ° C to melt the solid fats presented in the oil. Methanol of 99% pure is added (0.1 liters/liter of oil) to the heated oil. It is stirred for five to ten minutes (methanol is a polar compound; oil is strongly non –polar; hence a suspension will form). One milliliter of 95% pure sulfuric acid (H₂SO₄) is added for each liter of oil using a graduated eye dropper. The compound is stirred for one hour maintaining the temperature at 35°C. Heating is stopped and the mixture is stirred for another hour. The mixture is allowed to settle for eight hours in a decanter to remove methanol and chemical water.

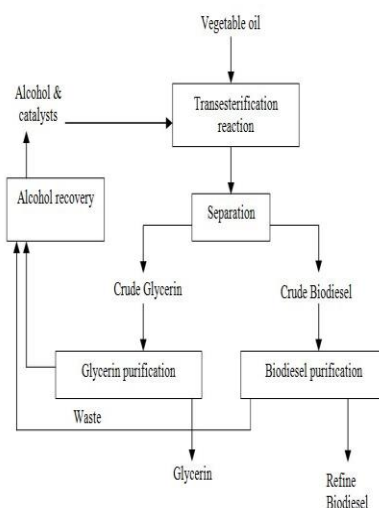
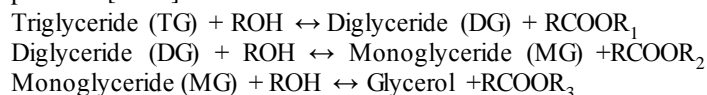


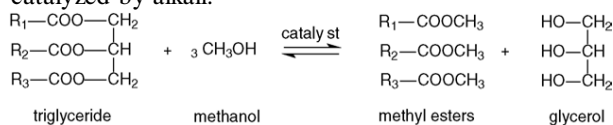
Fig 3. Outline of biodiesel production

Second stage (Base catalyzed stage)

Transesterification of triglycerides produce fatty acid alkyl esters and glycerol as shown in Figure 4. The glycerol layer settles down at the bottom of the reaction vessel. Though esters are the desired products of transesterification reactions, glycerol recovery is also important due to its numerous applications in daily products. The overall transesterification reaction is given by three consecutive and reversible equations as shown below. Diglycerides and monoglycerides are the intermediates in this process [24-25].



This step wise reactions are reversible and a little excess of alcohol is used to shift the equilibrium towards the formation of esters. In presence of excess alcohol, the forward reaction is pseudo-first order and the reverse reaction is found to be second order. It was also observed that transesterification is faster when catalyzed by alkali.



with R₁, R₂, R₃ = hydrocarbon chain from 15 to 21 carbon atoms

Fig 4. The chemical reaction involved in the transesterification

For each liter of oil/fat 0.12 liter of methanol (12% by volume) is measured to which it is added 6.5 grams / liter of lye

(Sodium hydroxide, NaOH). The mixture is stirred thoroughly until it forms sodium methoxide. Half of the prepared sodium methoxide is poured into the unheated mixture and the mixture is stirred for five minutes. This will neutralize the sulfuric acid. The mixture is heated to 55°C and the whole reaction is maintained. Remaining sodium methoxide is added to the heated mixture and stirred at low speed of not more than 500 to 600 rpm. After one hour the mixture is poured into a decanter and allowed it to settle for 8 hours. As glycerin is heavier than the biodiesel, it will settle at the bottom. The glycerin is separated from the biodiesel.

Purification of products

Bubble wash method is used, but there is no need to monitor pH value of the oil any more one milliliter of phosphoric acid (H_3PO_4) is added to the washing water first. One third water by volume to the oil is being used and the oil is bubble washed for twenty hours. The mixture is allowed to settle in a decanter for one hour and the water is drained off latter. The biodiesel is heated to 100°C to dispense with the traces of water and preserved. Samples obtained under optimum conditions, are characterized to know the physico-chemical properties of the cotton seed biodiesel, the characterization of biodiesel is also explained.



Fig 5. Karanja methyl ester (biodiesel)

Properties of Biodiesel

Density of Biodiesel

The density of biodiesel is slightly more compared to the conventional diesel, where the specific gravity of biodiesel is 0.88 while that of the diesel is 0.84. This property is well utilized in making the biodiesel blends; however, biodiesel should always be blended at the top of the diesel fuel.

Viscosity

Viscosity plays a significant role on the fuel. It has been claimed that biodiesel gives better lubricity and more complete combustion. It is important to control the viscosity from going up to the higher levels to avoid the negative impact on the fuel injection system performance. In general, the viscosity is specified close to that of the conventional diesel, which is around 1.9 centi Stokes.

Flash Point

The flash point of a fuel can be defined as the temperature at which it ignites and gives rise to a flame that burns only for a moment when exposed to a spark. For biodiesel, it is greater than 130°C that is significantly higher than that of the diesel obtained from crude, which has a flash point of only 64°C. This enables the safe storage of the biodiesel compared to the conventional diesel. However, the flash point can reduce drastically if the alcohol content of the biodiesel is not removed properly. It, as well, reduces the combustion quality of the fuel. A minimum flash point of 100°C is specified to ensure that the excess methanol used in the transesterification process is removed. The ASTM standards issued a flash point of min. 130°C.

Table 1. Fuel properties of Biodiesel

Property	Diesel	Biodiesel [26]
Standard	ASTM D975	ASTM D6751
Composition	HC (C10-C21)	FAME(C12-C22)
Kin. viscosity (cSt) at 40 °C	1.9-4.1	1.9-6.0
specific gravity (g/ml)	0.85	0.88
flash point (°C)	60-80	100-170
cloud point (°C)	-15 to 5	-3 to 12
pour point (°C)	-35 to -15	-15 to 16
Water (vol %)	0.05	0.05
Carbon (wt %)	87	77
Hydrogen (wt %)	13	12
cetane number	40-55	48-60

CloudPoint

When biodiesel is cooled below a certain point, some of the molecules aggregate and form crystals. The fuel starts appearing cloudy once the crystals become larger than one quarter of the wavelengths of visible light. This is the *Cloud Point*. As the fuel is cooled further these crystals become larger. The lowest temperature at which fuel can pass through a 45 micrometer filter is the *Cold Filter Plugging Point* (CFPP). As the biodiesel is cooled further it will gel and then solidify. The CFPP has a better correlation than cloud point for biodiesel as well as the conventional diesel.

Biodiesel has virtually low sulfur content, and it is often used as an additive to Ultra-Low Sulfur Diesel (ULSD) fuel to aid with lubrication, as the sulfur compounds in petroleum diesel provide much of the lubricity. It contains less than around 15 ppm sulfur. Biodiesel has better lubricating properties and much higher cetane ratings than today's low sulfur diesel fuels. Biodiesel addition reduces fuel system wear and in low levels in high pressure systems increases the life of the fuel injection equipment that relies on the fuel for its lubrication. Depending on the engine this might include high pressure injection pumps, pump injectors and fuel injectors. When considering the calorific values, for biodiesel, it is about 37.27 MJ/L; which is about 9% lower than the regular petroleum diesel.

These variations in energy density commonly depend upon the nature of the feedstock used for the production of the biodiesel. It has also been claimed that biodiesel gives better lubricity and more complete combustion thus increasing engine energy output and partially compensating for the higher energy density of petroleum diesel. The main reason is the persistence of mono and diglycerides left in the compound due to an incomplete reaction, which act as emulsifiers allowing water to mix with biodiesel. In addition to this, there may be water that is residual to processing or resulting from storage tank condensation.

Results and discussion

Characterization of methyl ester

The physico-chemical properties of karanja methyl ester are different from fossil diesel. The physical properties of biodiesel will be influenced on combustion, flow, and storage behaviors. The independent effects of the biodiesel properties on various operational aspects of diesel engine when compared with fossil diesel are discussed. The building blocks of fatty esters, the fatty

acid chain and the alcohol moiety, influence fuel properties and varying either can lead to a change in fuel properties. The feed stock dependent fatty acid compositions (hydrocarbon chains) of karanja oil vary from C16 to C24, with the long chain oleic acid (C18:1), linoleic acid (C18:2), palmitic acid (C16:0), stearic acid (C18:0), and behenic acid (C22:0) are the highest. The amount of fatty acids present in karanja oil is oleic acid: 49.4%, linoleic acid: 19%, palmitic acid: 10.6%, stearic acid: 6.8%, behenic acid: 5.3%. This oil contains 29% saturated fatty acids (SFA), 52% of mono-unsaturated fatty acids (MUFA) and 19% of poly-unsaturated fatty acids (PUFA).

Table 2. Results obtained from GC Methyl ester of Pongamia Pinnata oil

Fatty acid composition	Mass (%)
Oleic C18:1	49.4
Linoleic C18:2	19.0
Stearic C18:0	6.80
Palmitic C16:0	10.6
Beheni C22:0	5.30

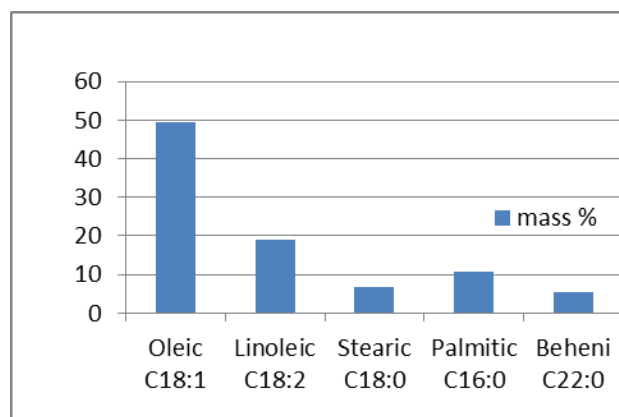


Fig 6. Fatty acids in karanja oil

Conclusion

The karanja oils can be used as a source of triglycerides in the manufacture of biodiesel by transesterification reaction. The production of biodiesel from edible oil is currently much more expensive than diesel fuels due to relatively high cost of edible oil. There is a need to explore non edible oils as alternative feed stock for the production of biodiesel non-edible oil like karanja. The oil extracts exhibited good physico chemical properties and could be used as a biodiesel feedstock. This study concludes the pongamia pinnata (karanja) oil to methyl ester conversions determined by GC-MS analysis was good.

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