

Methanolysis of *Pongamia pinnata* (karanja) oil for production of biodiesel

L C Meher, S N Naik* and L M Das[#]

Centre for Rural Development and Technology, Indian Institute of Technology, New Delhi 110 016

Received 05 April 2004; accepted 06 August 2004

The present study deals with the transesterification of *Pongamia pinnata* oil by means of methanol to study the feasibility of methanolysis process by using potassium hydroxide catalysts. The yield of biodiesel obtained was >97 per cent by using oil/methanol molar ratio 12:1, potassium hydroxide as catalyst, at 65°C and stirring at 360 rpm in 3 h. The biodiesel was characterized by TLC and HPLC analysis to determine the fatty acid methyl esters, mono-, di- and triglycerides and glycerol. The properties like viscosity, flash point, cloud point, and pour point have been determined for accessing the fuel quality of karanja based biodiesel.

Keywords: Karanja oil, Biodiesel, Transesterification

IPC Code: Int. Cl.⁷: C 12 P 7/02

Introduction

Karanja belongs to the family *Leguminaceae*. It is a medium sized glabrous tree that generally attains a height of about 18 m and a trunk diam > 50 cm. It can grow under a wide range of agroclimatic condition and is a common sight around coastal areas, riverbanks tidal forests and roadsides. Karanja is a native to humid and subtropical environments having annual rainfall between 500-2500 mm in its natural habitat, the maximum temperature ranges from 27-38°C and the minimum 1-16°C. It can grow on most soil types ranging from stony to sandy to clayey, including verticals. It does not do well in dry sands. It is highly tolerant of salinity and can be propagated either by seeds or by root suckers¹.

The fruits and sprouts are used in folk remedies for abdominal remedies in India, the seeds for keloid tumors in Sri Lanka, and a powder derived from plants for tumors in Vietnam. In India, seeds were used for skin ailments and the oil is used as an ointment for rheumatism. Leaves are active against *Micrococcus* and their juice is used for colds, coughs, diarrhea, etc. Juices from the plant as well as the oil are antiseptic. It is said to be an excellent remedy for

itch and herpes. Flowers are used for diabetes. The bark is known to be the remedy for beriberi. The oil has been known for its curative effect for skin problems such as, leucoderma, scabies and skin itches¹.

The tree bears green pods, which after 10 to 11 months gets matured and changes to a tan colour in the month of May-June. The pods are flat to elliptic, 5-7 cm long and contain one to two kidney shaped brownish red kernels. The dried pods usually split with a hammer and the kernels are obtained. The seed collection is basically a rural activity. The oil is extracted from kernels in small oil mills or village ghanis. The yield of kernels per tree is between 8-24 kg.

The fresh extracted 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, kanjone and pongaglabrin. Karanja oil is mainly used as a raw material for soap, but the main constraints for its more usage are the colour and odour². The oil is used as lubricant, water-paint binder, and also as a fuel for cooking and lamps in rural areas of India.

Biodiesel

Methyl esters obtained by transesterification of vegetable oil are an attractive fuel *i.e.* biodiesel, and has gained more importance in the past few decades

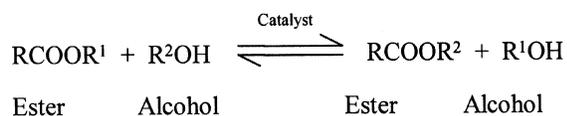
*Corresponding author
email: sn_naik@hotmail.com;
snn@rdat.iitd.ernet.in

[#]Engine and Unconventional Fuel Lab,
Centre for Energy Studies

due to the depletion of world petroleum reserves. Vegetable oil derived methyl esters may be considered as viable alternative diesel fuel and is derived from various sources. Country like India produces more than 100 varieties of oil seeds out of which only 10-12 varieties have been tapped so far. Only a few million tonnes have been utilized against the estimated potential of about 20 mt/y. Some of these oils have not been harvested to any noticeable extent due to lack of demand for industrial use in the country. Biodiesel is produced from the wild oilseeds crops/plants, which can easily be grown on wastelands. Among the oilseed plants, karanja is the promising one for sustained availability of raw materials feedstock for biodiesel production. Government of India is planning to grow suitable oilseed plants like, karanja and jatropha in the cultivable wasteland area of about 175 mha (ref. 3).

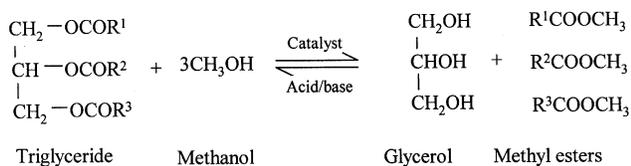
Transesterification Kinetics and Mechanism

Transesterification or alcoholysis is the displacement of alcohol from an ester by another in a process similar to hydrolysis, except than an alcohol is used instead of water⁴. This process has been widely used to reduce the high viscosity of triglycerides. The transesterification reaction is represented by Scheme 1.



Scheme 1—General equation of transesterification

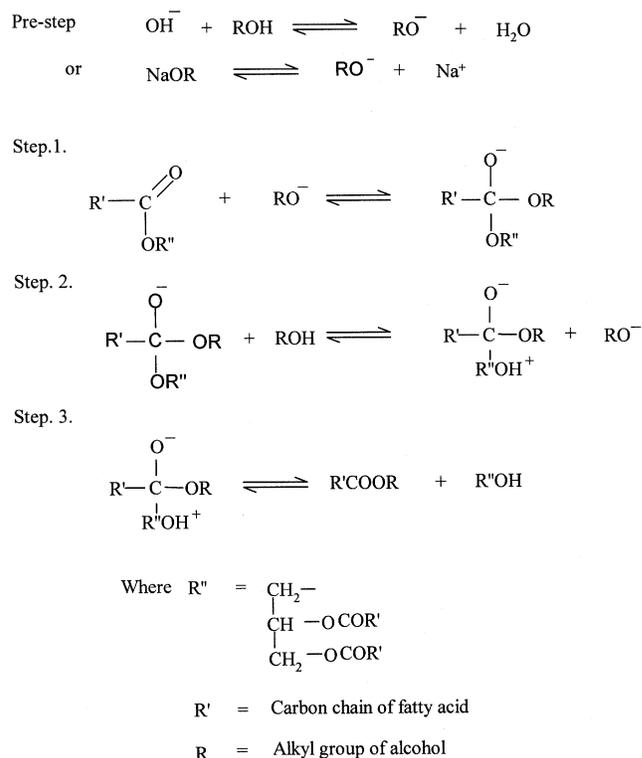
If methanol is used in this process then it is called methanolysis. Scheme 2 represents the methanolysis of triglyceride.



Scheme 2—General equation for methanolysis of triglycerides

Transesterification is one of the reversible reactions and proceeds essentially by mixing the reactants. However the presence of a catalyst (a strong acid or base) accelerates the conversion. In the present work the reaction is conducted in the presence of base

catalyst. The mechanism of alkali-catalyzed transesterification is described⁵ in Scheme 3. The first step involves the attack of the alkoxide ion to the carbonyl carbon of the triglyceride molecule, which results in



Scheme 3—Mechanism of base catalyzed transesterification the formation of a tetrahedral intermediate. The reaction of this intermediate with an alcohol produces the alkoxide ion in the second step. In the last step the rearrangement of the tetrahedral intermediate gives rise to an ester and a diglyceride. The same mechanism is applicable to di-glyceride and mono-glyceride.

Materials and Experimental Procedure

Materials

Karanja oil was expelled from its kernel, which was obtained from Rajasthan and this oil after filtration was used for the experimental studies without further pretreatment. The physicochemical properties of the oil were determined as per BIS method. Gas Chromatographic method was used to determine the fatty acid composition of the oil. Potassium hydroxide flakes (Merck), methanol (99.8 per cent purity, BDH) were used in the present study. Reference standards such as, methyl esters of palmitic, stearic, oleic and

linoleic acids and glycerol, mono-olein, di-olein, tri-olein were purchased from Sigma-Aldrich (New Delhi) for chromatographic analysis.

Apparatus

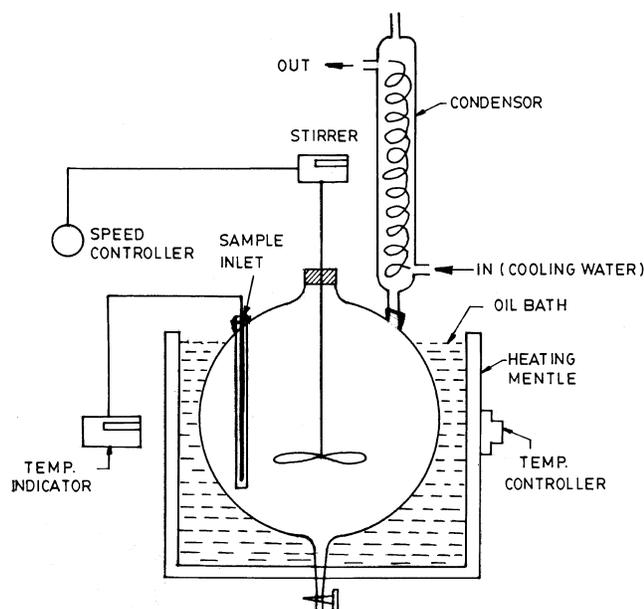
The apparatus used for transesterification was designed and fabricated locally at IIT Delhi as given in Fig. 1. The apparatus consisted of oil bath, reaction flask with condenser and digital rpm controller mechanical stirrer. The volume of glass reactor capacity was 1 L and consisted of three necks, one for stirrer, and the others for condenser and inlet of reactant. A digital temperature indicator was used to measure the reaction temperature. The batch reactor had an opening valve at the bottom for collection of the final product.

Preparation of Potassium Hydroxide-methanol Solution

Methanol was distilled to remove moisture. The moisture free methanol was used to prepare potassium hydroxide-methanol solution. The alcohol-catalyst solution was prepared freshly in order to maintain the catalytic activity and to prevent moisture absorbance. The reaction was conducted at different catalytic concentrations of KOH.

Process of Transesterification Reaction

A 200 mL of karanja oil was measured and charged



SCHEMATIC DIAGRAM OF TRANSESTERIFICATION REACTOR .

Fig. 1—Schematic diagram of transesterification reactor

into the reactor. The KOH-MeOH solution was added to the closed reaction vessel. The system from here on was totally closed to the atmosphere to prevent the loss of alcohol as well as to prevent moisture.

Once the reaction was complete, two major products exist, i.e., glycerin and biodiesel. Each layer had substantial amount of the excess methanol that was used in the reaction. After completion of the reaction the products were transferred to a separating funnel and allowed to stand for 1d. The glycerin layer was much more dense than biodiesel layer and the two could be gravity separated with glycerin simply drawn off from the bottom of the separating funnel. The excess methanol was recovered by using rotary evaporator from both the layers separately. The final biodiesel layer required washing with tap water in order to remove the excess catalyst and the methanol. After washing, the final product was heated to remove moisture from biodiesel.

Analyses

The transesterification reaction was monitored by using thin layer chromatography (Fig. 2) to check the completion of the reaction. The composition of the transesterified product was analyzed using high performance liquid chromatography (HPLC) (PerkinElmer Series 200) equipped with refractive index detector (PerkinElmer Series 200). A Spheri-5 C-18 column (PerkinElmer Brownlee column) (220×4.6 mm with 5 μ m particle size) was used for separation with 1 mL/min flow rate of methanol as a carrier solvent. The sample injection was 20 μ L and peak identification was made by comparing that of the standards of methyl esters, mono-glycerides, di-glycerides and tri-glycerides. The HPLC chromatogram of transesterified product is given in Fig. 3.

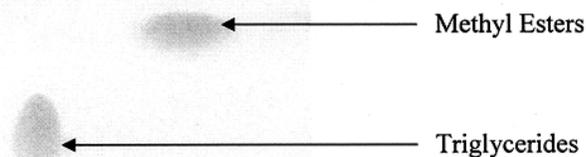


Fig. 2—Thin layer chromatographic analysis of karanja oil (triglycerides) (A) and karanja oil methyl esters (B)

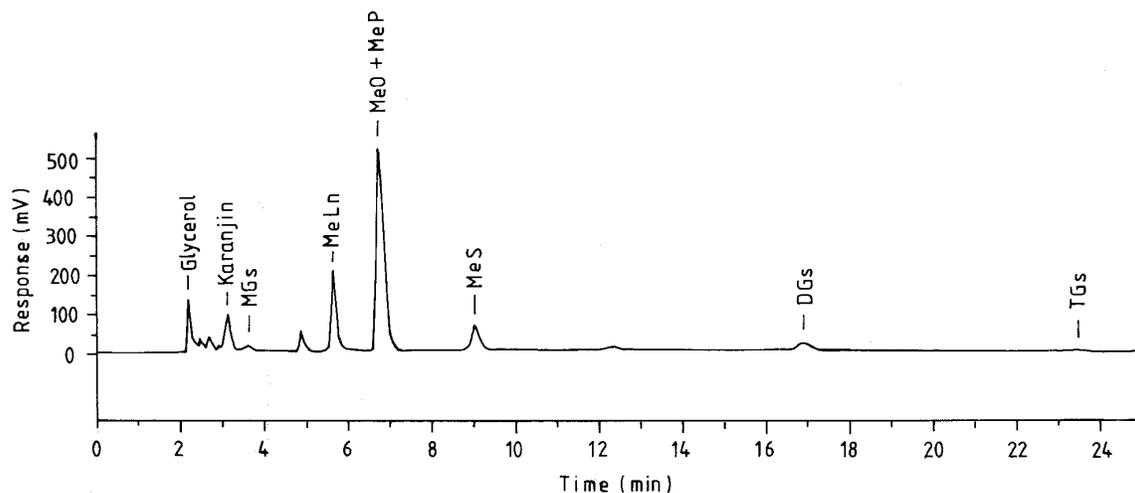


Fig. 3—HPLC chromatogram of product of transesterified karanja oil methyl esters [TGs: triglycerides, DGs: diglycerides, MGs: monoglycerides, and methyl esters, MeLn: methyl linolate, MeO: methyl oleate, MeP: methyl palmitate, MeS: methyl stearate]

Table 1—Percentage yield of oil from karanja kernel

Extraction method	Yield in per cent
Mechanical expeller	22
Cold percolation	21
Soxhlet extraction	32

Table 2—The physicochemical properties of karanja oil (determined as per BIS method)

Chemical properties	Value
Acid value (mg KOH/g)	5.06
Saponification value (mg KOH/g)	187
Unsaponifiable matter (w/w per cent)	2.6
Iodine value (g/100g)	86.5

Table 3—The fatty acid composition of karanja oil determined by gas chromatography (in which the first number of the subscript in the fatty acid is that of carbon in the alkyl chain and the second is that of the double bond)

Fatty acid	Percentage
Palmitic acid (C ₁₆)	11.65
Stearic acid (C ₁₈)	7.50
Oleic acid (C _{18:1})	51.59
Linoleic acid (C _{18:2})	16.64
Eicosanoic acid (C ₂₀)	1.35
Docosanoic acid (C ₂₂)	4.45
Tetracosanoic acid (C ₂₄)	1.09

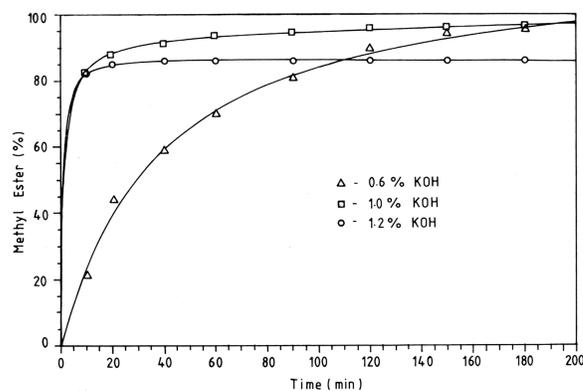


Fig. 4—Ester concentration vs time (Influence of KOH conc in the yield of methyl esters)

Results and Discussion

The extraction of oil from karanja seed was done by using different methods, i.e. mechanical expression, solvent extraction and cold percolation using *n*-hexane as solvent and their yields are given in Table 1. The percentage composition of fatty acids present in karanja oil was determined by gas chromatographic analysis and is represented in Table 2. Extracted karanja oil consisted of 94.09 per cent pure triglyceride esters and the rest were free fatty acids and lipid associates, particularly flavonoids, which is the measure of unsaponifiable matter. The physicochemical properties were determined as per BIS method and the results are reported in Table 3.

The reaction was carried with different catalytic conc. of KOH and the yield of karanja oil methyl esters was plotted with respect to time as shown in

Table 4— The fuel properties of karanja oil methyl esters as determined by BIS method

Property	Experimental value of karanja oil methyl esters (KOME)	Test method	ASTM specification
Density at 15°C kg/m ³	889	IS 1448 P:16	-
Kinematic viscosity at 40°C cSt	5.431	IS 1448 P:25	1.9-6.0
Flash point°C	116	IS 1448 P:20	≤ 100
Cloud point°C	22	IS 1448 P:10	-
Pour point°C	15.8	IS 1448 P:10	-
Carbon residue per cent w/w	0.08	IS 1448 P:8	≤.05
Ash content per cent w/w	0.003	IS 1448 P:4	≤.01

Fig. 4. The reaction was completed to 85 per cent in 15 min and 97 per cent in 3 h using 1 per cent KOH. The results show that at catalytic conc. of 1 per cent KOH the reaction proceeded rapidly, while the yield of methyl esters after 3 h is nearly same as that of reaction with 0.6 per cent KOH. A highest yield of 97 per cent was obtained in the present work. Using 1.2 per cent of KOH as catalysts, the reaction proceeds rapidly but results in poor conversion, i.e. 87 per cent in 3 h. It was observed that the best yield was obtained with a catalytic concentration of 1 per cent of KOH. For higher value of catalyst concentration, the yields were lower. This fact seems to be related to the free fatty acid of the oil. It is found that when the oil contains large amount of free fatty acid the addition of potassium hydroxide compensates this acidity and avoids catalyst deactivation. Whereas for refined oil with free fatty acid less than 1 per cent the addition of excess amount of alkaline catalyst results in the formation of an emulsion, which increases the viscosity and leads to the formation of gels⁶.

Table 4 shows the fuel properties of biodiesel determined as per BIS method. Among the general parameters for biodiesel the viscosity controls the characteristics of the injection from the diesel injector. The viscosity of vegetable oil derived biodiesel can go to very high levels and hence it is important to control it within an acceptable level to avoid negative impacts on fuel injector system performance. Therefore the viscosity specifications proposed are nearly same as that of the diesel fuel.

Flash point of a fuel is the temperature at which it ignites when exposed to a flame or spark. The flash point of biodiesel is higher than the petrodiesel, which is safe for transport purpose.

Cold filter plugging point (CFPP) of a fuel reflects its cold weather performance. At low operating

temperature, fuel may thicken and might not flow properly thereby affecting the performance of fuel lines, fuel pumps, and injectors. CFPP defines the fuels limit of filterability, having a better correlation than cloud point for biodiesel as well as petrodiesel. Normally, either pour point or CFFP are specified. Pour point is the lowest temperature at which the oil specimen can still be moved. French and Italian biodiesel specifications specify pour point, whereas others specify CFPP.

The product of incomplete transesterification and separation may produce biodiesel of low quality. Thus the reaction should be completed and the glycerol and methyl ester layers should be separated completely and also the flavonoids are to be removed from the product. Thus the reaction condition needs to be optimized in order to get high yield of biodiesel and also complete reaction. Also the reaction depends upon the raw materials. For base catalyzed transesterification reaction, all the substances should be substantially anhydrous and the free fatty acid (FFA) content of the oil should be low.

The above listed fuel properties from experimental results indicate that the karanja oil methyl esters (KOME) is best suited as per ASTM norm for using as biodiesel. The properties are compared in Table 4.

Conclusions

Biodiesel has become more attractive to replace petroleum fuel. As per the reported literature, most of the transesterification studies have been done on edible oils like rapeseed, soybean, sunflower and canola by using methanol and NaOH/KOH as catalyst. There are very few studies reported on production of biodiesel by utilizing non-edible oils, among which, karanja is one of the most potential species to produce biodiesel in India, which could offer opportunities for generation of rural

employment, increasing income and improving environment. Presently, only 6 per cent of the total potential of the oilseed is being collected properly. The above experimental results reveal the alkaline catalyzed transesterification as the promising area of research for production of biodiesel in decentralized scale from economic point of view. Hence the process can be further improved to get high yield as well as fuel quality biodiesel.

Acknowledgement

The authors express their gratitude to Council of Scientific and Industrial Research (CSIR) India, for providing financial support to Mr Lekha Charan Meher in the form of Junior Research Fellowship.

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