TRANSESTERIFICATION OF KARANJA (*PONGAMIA PINNATA*) OIL FOR THE PRODUCTION OF BIODIESEL

BY

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To my parents

CERTIFICATE

This is to certify that the thesis entitled, **"TRANSESTERIFICATION OF KARANJA (*PONGAMIA PINNATA*) OIL FOR THE PRODUCTION OF BIODIESEL"** being submitted by **Mr. Lekha Charan Meher** to the Indian Institute of Technology, Delhi for the award of Doctor of Philosophy is a record of bonafide research work carried out by him under my guidance and supervision in confirmatory with the rules and regulations of Indian Institute of Technology, Delhi

The research report and results presented in this thesis have not been submitted, in part or in full, to any other university or institute for the award of any degree or diploma.

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ABSTRACT

The increased industrialization and the growing transport sectors in the developing countries face major challenges of the energy demand as well as the increased environmental concerns. The rising demand of fuel and limited availability of mineral oil provide incentives for the development of alternative fuels from renewable sources with less environmental impacts. One of the possible alternatives to the petroleum based fuels is the use of fuels derived from plant origins. Biodiesel is fatty acid alkyl esters derived from lipid feedstock such as vegetable oils and animal fats that can be used as diesel fuel substitute or extender. The conventional route of biodiesel preparation use alkali catalyst for transesterification of low free fatty acid oils with methanol or ethanol. Most of the research work has been done on the preparation of biodiesel from edible grade vegetable oils such as rapeseed, palm, soybean, sunflower etc. Since India is one of the largest importers of vegetable oil for food purpose, the use of edible oils for biodiesel production seems to be insignificant. India produces wide range of non-edible oilseeds like karanja (Pongamia pinnata), jatropha (Jatropha curcas), neem (Azadirachta indica), simarouba (Simarouba glauca), etc. Among these, karanja is one of the tree-borne plant having annual oilseed production potential of 2 lakh tons. The present study investigated the scope of karanja oil as an inexpensive feedstock for biodiesel production.

Fatty acid methyl/ethyl esters (biodiesel) were prepared by transesterification of karanja oil with methanol/ethanol catalyzed by a homogeneous alkali. The process conditions for transesterification of karanja oil with methanol and ethanol were optimized which

resulted 97-98% and 95% methyl and ethyl esters respectively. The initial rate of methyl ester formation was correlated with the process variables such as catalyst concentration, alcohol to oil molar ration, reaction temperature and rate of stirring.

The non-edible oils of Indian origin are often contaminated with high free fatty acids (FFA), which is problematic for alkali catalyzed transesterification. The acid value of karanja oil ranged from 0.6 to 11.5 mg KOH/g. The influence of FFA (0.3 to 5.8% w/w of oil) on karanja oil transesterification was studied. As the FFA level goes on increasing, the yield of methyl esters sharply decreases due to the predominating saponification reaction. In order to utilize the high FFA content oil, two-step process i.e. acid catalyzed esterification followed by alkali catalyzed transesterification was carried out for methanolysis to obtain methyl esters. Oil having 20% of FFA can be pretreated to reduce its acid value significantly, which will be suitable for alkali catalyzed second step. The overall yield of methyl esters was nearly same i.e. 96.7-97% from karanja oil containing FFA up to 20%.

The chemical kinetics of alkali catalyzed transesterification of karanja oil with methanol was studied. The reactants form two immiscible layers due to the differences in the polarities of methanol and oil and the reaction is mass transfer controlled and the reaction is initiated by vigorous mixing. The formation of methyl esters act as co-solvent since it is soluble in methanol and oil. As the reaction proceeds, a lower glycerol rich phase is separated from the ester-rich phase. The catalyst remains in the glycerol phase and again the reaction is mass transfer controlled. The reactions were studied at a *reaction temperature of 60°C and catalyst concentration 0.29-2.11% KOH (wt. of oil), methanol to oil molar ratio 1:1 to 6:1 with stirring at 600 rpm considering saponification of glycerides as competitive irreversible reaction.*

The soluble alkali catalysts cause side reaction such as saponification during biodiesel preparation from high FFA oils. Pre-treatment of high FFA oil is required before alkali catalyzed transesterification, which adds extra cost to biodiesel. Solid catalysts have the advantage of less possibility of saponification, easy separation of the products which do not need washing of biodiesel and the catalyst can be re-used. Solid basic catalysts such as $Ba(OH)_2$*, alkali metal (Li, Na, K) doped CaO and* K_2CO_3/Al_2O_3 *have been used for biodiesel preparation from high free fatty acid karanja oil. The alkali metal doped catalysts are effective for transesterification of oil containing 5.8% FFA.*

Transesterification of karanja oil with methanol and ethanol catalyzed by Thermomyces lanuginosus (TL IM) and Rhizomucor miehei (RM IM) were studied in liquid CO_2 *medium. The reaction proceeds slowly as compared to the conventional alkali catalyzed route, but faster as compared to enzymatic transesterification in solvent free medium. The ethanolysis of karanja oil catalyzed TL IM resulted 72% ethyl esters in 5 h when the reaction was conducted in liquid carbon dioxide medium. Using the silica gel 5% (w/w of oil) in the reaction medium promotes the acyl-migration during the ethanolysis of karanja oil where the yield of ethyl esters is improved up to 75.2%. The influence of FFA (up to 20% w/w of oil) on TL IM catalyzed ethanolysis of karanja oil was studied, where FFA has no negative influence on the yield of ethyl ester. The reusability of lipozyme TL*

IM was studied for karanja oil ethanolysis, the catalytic activity remained intact after five time reuse.

The fuel qualities of biodiesel prepared by alkali catalyzed route were evaluated and compared with the IS 15607:2005 biodiesel specification. The karanja methyl and ethyl esters have the fuel characteristics: acid value (mg KOH/g) 0.5, 0.5; cloud point (°C) 19, 23; pour point (°C) 6, 15; flash point (°C) 174, 148; density (g/cc @15°C) 0.88, 0.88; viscosity (cSt) 4.77, 5.56; heating value (MJ/kg) 40.8, 40.7, respectively. The cloud point and pour point of karanja based biodiesel are slightly higher which is problematic for cold climate when pure biodiesel is to be used in engines, but in Indian climate this problem doesn't arise. When blended with diesel, the pour point is lowered to a considerable extent i.e. 0 and -3°C for B20 blends (20% esters in diesel) of karanja methyl and ethyl esters respectively. The fuel qualities of karanja based biodiesel are in accordance with the IS 15607 biodiesel specification.

The storage stabilities of karanja methyl and ethyl esters were evaluated. In the recent Indian as well as European specifications of biodiesel, a minimum value of 6 h induction period at 110°C measured with a Rancimat instrument is specified. The Rancimat induction periods of karanja methyl and ethyl esters are less than 6h. In order to satisfy the IS 15607 and EN 14214 norms, the effects of commercial synthetic antioxidants were studied on the induction period of karanja based biodiesel. Pyrogallol when added as an antioxidant (50 ppm), increases the induction period of both methyl and ethyl esters up to 12 h satisfying the specification for oxidation stability.

The raw material i.e. karanja oil contains some unsaponifiable matters such as karanjin and pongamol. These components get separated from biodiesel after completion of the reaction and do not need any extra steps for their separation from biodiesel. Also these components contaminate the by-product glycerol.

The crude glycerol obtained as byproduct of karanja oil transesterification contains excess methanol, alkali catalyst, soap, unreacted partial glycerides, unsaponifiable matters, methyl esters and water. The crude glycerol layer obtained as byproduct contains 45-47% glycerol and the used excess alcohol. The purification of crude glycerol was carried out where the purity is improved to 90-91% that can be used as industrial grade glycerol.

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