

Technology Systems Programme

6.) INTEGRATED PROJECT ON "DEVELOPMENT OF PROCESSES/TECHNOLOGIES FOR VALUE ADDED PRODUCTS FROM KARANJA OIL AND CAKE"

Implementing Institute: Indian Institute of Chemical Technology Hyderabad
Duration of the Project: November 2006 to June 2009
Total Financial Grant : Rs 186 lakhs

Karanja (*Pongamia glabra*), is projected to be one of the most important feed stocks along with jatropha for biodiesel production in India. In India organized cultivation of karanja crop is being done over 4 lakh acres of land (Fig 1). Eventhough, biodiesel has potential as an attractive alternative to diesel, the economic viability of biodiesel has not yet established in the country. Hence, exploitation of the by-products of biodiesel industry like oilseed cakes, glycerol is the need of the hour to improve the overall economics of the biodiesel industry. With this background, DST has sanctioned this integrated project for "Development of Processes/Technologies for Value-added Products from Karanja Oil and Cake" to Indian Institute of Chemical Technology, Hyderabad

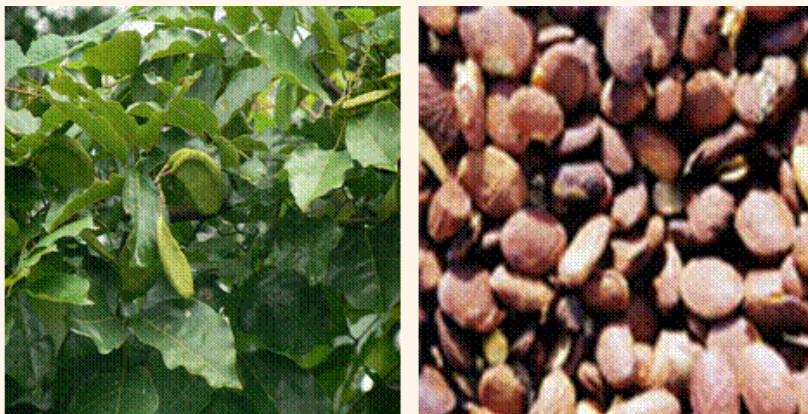


Fig 1. Karanja Tree and Seeds

The integrated project was divided into the following four activities: i) Isolation, Characterization and Evaluation of Bio-constituents from Karanja Oil and Cake; ii) Utilization of Karanja Cake for Value Addition with a Main Thrust to Protein and Starch Based Products; iii) Purification of Crude Glycerol Different Grades and its Utilization for the Preparation of Value Added Products giving main thrust to hydrogenolysis, oxidation reactions and preparation of crown ethers; iv) Development of Lubricant Base Stocks and Additives from Karanja Oil and their Characterization. The project was executed by six different teams of IICT consisting of 13 scientists and 8 research fellows.

The major achievements of the project are listed below:

Isolation, Characterization and Evaluation of Bio-active Constituents from Karanja oil and Cake: Every ton of biodiesel produces two tons of karanja cake and value addition to expelled cake

economically strengthens the biodiesel industry. Karanja cake contains several bioactive constituents and the major among them is the karanjin. Karanjin is known to exhibit insecticidal, pesticidal, nematocidal and piscicidal activities. Though there are many reports of extraction of karanjin from karanja oil, there were no reports of extraction methods from deoiled cake. A simple solvent partitioning approach was developed for the isolation of bioactive constituents-rich fractions followed by isolation of karanjin in high purity (~98%) from expelled and deoiled cakes. Crude extract containing 24% was evaluated for mosquito repellent activity employing two strains, namely *Aedes aegypti* and *Culex quinquefasciatus* strain over a period of 24 and 48 hr and excellent mortality was observed at very low concentrations. There is also huge scope on the outcome of this project for commercial exploitation of crude karanjin-rich extract for mosquito larvicidal activity and also of pure karanjin for different applications.

Utilization of Karanja Cake for Value Addition with a Main Thrust to Protein and Starch-based

Products: Karanja cake obtained after expelling the oilseeds for the extraction of oil is rich in protein, but the cake is unpalatable and toxic to cattle even at lower levels due to the presence of several toxic principles. The cake also contains nitrogen (N) 4-5%, phosphorous (P₂O₅) 1-1.5% and potash (K₂O) 1.8-2.0% and has potential as a useful organic manure for different crops. Hence, the major objective of this component of the project was to prepare surfactants from protein and carbohydrates of deoiled karanja cake and use expelled, de-oiled and de-proteinated karanja cake samples as organic manure for cultivation of selected crops. Methodologies were developed for the extraction of protein and carbohydrates in good yields from expelled cake at 5 kg scale. The protein isolated from the cake was utilized for the preparation of two types of surfactants, namely, diethanolamides and N-acyl amino acids/peptides, by reacting with diethanolamine and fatty acids respectively. The protein-based surfactants produced exhibited superior surfactant properties as far as surface tension and emulsion stability are concerned. The foaming properties were found to be inferior compared to standard surfactants. Based on the properties, these surfactants may be used in formulating industrial cleaning products where low foam is required. As protein based surfactants are highly biodegradable, these can replace petroleum based products in making eco-friendly products. Different types of karanja cakes (expelled cake, deoiled cake and deproteinated cake) were used as organic manure in IICT garden for cultivation of different crops including tomato (Fig 2); expelled and de-oiled karanja cake samples showed better growth and resistance towards pests as compared to control. These studies may have huge impact on economy of biodiesel industry, if the protein-based surfactants are commercialized.



Fig 2. Control Plant (Left) and Plant Grown using De-oiled Cake (Right)

Purification of Crude Glycerol into Different Grades: Crude glycerol is produced as a by-product of the transesterification reaction during the production of biodiesel and contains methanol, water, alkali, soap and organic matter. The reactive extraction process developed during execution of the project proved to be an alternate and an efficient recovery approach to get pure glycerol from crude glycerol. The recovery of pure glycerol from aqueous effluent streams via reversible reactions was achieved by an acid catalyzed condensation reaction of glycerol with aldehydes and ketones to form acetals that were hydrolyzed to recover the glycerol in purest form. Compared to evaporation and distillation, extraction process is advantageous as the energy requirement is lower. Based on the data generated during the course of this study, it is possible to adopt the methodology for the purification of glycerol obtained from different types of minor oils during biodiesel production.

Value Added Products from Glycerol Giving Main Thrust to Hydrogenolysis and Oxidation Reactions: As a part of this activity catalytic processes were developed for the glycerol hydrogenolysis and glycerol oxidation. Two types of catalysts were developed for glycerol hydrogenolysis; one was copper-based catalyst where the focus was on obtaining high selectivity towards 1,2-propanediol. The second one was on ruthenium-based noble metal catalyst system in which the attention was on high glycerol conversion and a combined high selectivity towards 1,2-propane diol and ethylene glycol. High glycerol conversion of about 60% with 1,2-propane diol selectivity upto 95% was achieved with Cu-MgO system. Hydrogenolysis of glycerol was carried over a series Cu - MO (M=Zn, Mg) based catalysts with varying Cu to MO ratio at low hydrogen pressures. Based on the knowledge generated in individual ruthenium and solid acid catalysts, a

single bifunctional supported Ru catalyst was developed. The important aspect of the present catalyst was that, it was active with crude glycerol, which contained some amount of impurities like alkali salts. Glycerol oxidation was carried over a number of carbon supported Pd, Pt and Au catalysts. The analyses of the products were standardized and the prepared catalysts were screened. The Pd and Au catalysts are near complete conversion of glycerol with considerable selectivity towards tartronic acid.

Utilization of Glycerol for the Preparation of Crown Ethers: Crown ethers are excellent host for alkali (M+) and alkaline earth (M+2) metal cations and they are widely applied in chemical technology and analytical chemistry as ion pair extractants, synergists, ion carriers, masking agents, sensors, MRI agents, ionic liquids, molecular switches, liposomal gene delivery systems and drug delivery systems. During the execution of this activity, novel crown ethers were prepared from glycerol using chemo-enzymatic methods. Highly polar crown ether mixture was prepared containing mono crown ethers and bis-crown ethers with or without tetra ethylene glycol side arms. The crown ether mixture was evaluated for the metal extraction ability using sodium/potassium metal picrate by UV-VIS absorption spectroscopy and the metal extraction efficiency of the crown ether fractions indicated that, Na⁺ exhibited better extraction efficiency compared to K⁺ metal, attributing to the effect of suitability of the 15-crown-5 size to the ionic size of Na⁺. The studies revealed that the extraction efficiency of crown mixture for Na⁺ and K⁺ metal is superior compared to that of pure mono crown ether and similar to that of polar crown ether mixture. This shows the separation of the crown mixture into individual components does not have any significance and hence the crown mixture as such can be used for the metal ion extraction studies thus avoiding the separation steps.

Development of Lubricant Base Stocks and Additives from Karanja Oil and their Characterization: In contrast to mineral oil, lubricants based on vegetable oils are rapidly and completely biodegradable and exhibit low ecotoxicity. During the execution of this activity, IICT has developed high performance lubricant base stocks namely i). alkyl and polyol esters based on karanja oil (11 candidates); ii) epoxidised karanja oil and its fatty acid alkyl esters (5 candidates); iii) epoxy oil/methyl ester derivatives by hydroxylation followed by acylation (10 candidates). Lubricant testing facility (Fig 3) was also established as a part of this project with the following instruments: i) Oxidation Stability (RBOT) Test Apparatus (ASTM D-2272), ii) Air Release Value Apparatus (ASTM D-3427); iii) Copper Strip Corrosion Bath (ASTM D-130); iv) Noack Volatility Apparatus (ASTM D-5800); v) Rust Prevention Characteristics Apparatus (ASTM D-665); vi) Demulsibility Characteristics Bath along with Centrifuge (ASTM D-2711) and vii) Hydrolytic Stability Apparatus (ASTM D-2619). All the synthesized iso alkyl and polyol esters exhibited good potential as lubricant base stocks. Despite their relatively higher pour points, the other lubrication properties like viscosity, VI, flash point and Cu corrosion values were exceptionally good. Based on viscosity index, all the products can be categorized into group III category of base fluids as per API classification. Based on viscosity index of epoxy karanja oil and epoxy alkyl esters (C1, C4 normal and iso, and C8 iso), these the products can be classified into group III category of base fluids as per API classification. However, the lubricant characteristics reveal that epoxy 2-ethyl hexyl esters is found suitable for IS: 3098 hydraulic fluids in ISO VG 15 category and the rest of the epoxy alkyl esters were found suitable for neat cutting oils. These products can also be used for hydraulic fluid applications in ISO VG 10 category after

formulating with antioxidants and pour point depressants. Epoxy oil exhibited very high viscosity and after formulating with suitable additives it can be used as a base stock for industrial gear oil.



Fig 3. Some Lubricant Testing Facilities Established

Outputs: About 36 products were prepared during the execution of the integrated project and all the products have potential for commercial exploitation. Based on the data generated during the execution of the project, about 6 patents (one filed and other 5 will be filed shortly) and 14 publications (4 published, and the rest are to be communicated) resulted.