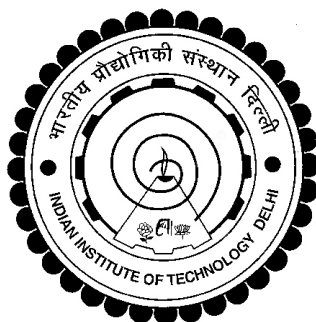


**DEVELOPMENT OF GREEN PROCESS FOR THE
PRODUCTION OF BIO-LUBRICANTS FROM CASTOR OIL**

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**DEVELOPMENT OF GREEN PROCESS FOR THE
PRODUCTION OF BIO-LUBRICANTS FROM CASTOR OIL**

by

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Submitted

in fulfillment of the requirements of the degree of

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Dedicated to

My parents for their love, endless support and encouragement

The Almighty who blessed me with the ability and strength to
accomplished it

CERTIFICATE

This is to certify that the thesis entitled, **“DEVELOPMENT OF GREEN PROCESS FOR THE PRODUCTION OF BIO-LUBRICANTS FROM CASTOR OIL”** being submitted by **Mr. Chandu Shankarrao Madankar** 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 conformity 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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(Chandu Shankarrao Madankar)

ABSTRACT

With increased industrialization and modernization, the world demand of lubricants is growing at a faster rate. The rising prices of petrochemical products, depletion of oil reserves, increased environmental concerns and strict regulations on environmental pollution are the major driving forces for the development of biolubricants from renewable resources with minimum environmental impact. One of the possible alternatives to the petroleum based lubricants is the use of lubricants derived from plant origins. Fatty acid alkyl esters derived from lipid feedstock such as vegetable oils can be used as biolubricants or additive for lubricity enhancement. Vegetable oil based lubricants are preferred over the petroleum based lubricants as they are ecofriendly, renewable, non toxic and biodegradable.

India produces wide ranges of non-edible oil seeds like Castor (*Ricinus communis L.*), Karanja (*Pongamia Pinnata*), Jatropha (*Jatropha Curcus*), Neem (*Azadirachta Indica*), Simarouba (*Simarouba Glauca*) etc. The production of castor seeds in India is 2.4 Million Tons annually and the castor seed oil has unique properties for the production of biolubricants.

Keeping above broad aspects, the present research work has been conducted on to utilize the renewable feedstock like castor by using green processes like reactive extraction and enzymatic transesterification for the production of fatty acid alkyl esters and its potential application as biolubricants.

The extraction and characterization of castor seed oil showed 45% oil content in castor seed and its fatty acid composition was ricinoleic acid 87%, linoleic acid 5%, oleic acid 3.4%, palmitic acid 1.3%, stearic acid 1.5% and linolenic acid 0.6% as determined by GC-FID.

Reactive extraction of castor seed with methanol yielded 96.1% of methyl esters in 3 h, and optimized process parameters were 1% KOH as catalyst, methanol/oil molar ratio of 250:1, temperature 65°C and stirring rate 600 rpm. The kinetic study of reactive extraction was carried out at different temperatures. The rate constants for the formation of methyl esters ranged from 0.0073 to 0.022 min⁻¹, and the activation energy for the reactive extraction of the castor seed was found to be 39 KJ/mol. Economic analysis of reactive extraction estimated the break-even price of methyl esters at \$3.71/gal, which is lower than the price from conventional transesterification. Reactive extraction is a simple process where oil extraction and transesterification proceed in single step reducing the production cost. The reactive extraction of castor seed with other alcohols like ethanol, n-propanol, n-butanol, n-hexanol and n-octanol were studied and optimized.

Enzymatic transesterification of castor oil and higher chain alcohol like n-hexanol catalyzed by *Thermomyces lanuginosus* (TL IM) was carried out in solvent free, hexane, and liquid CO₂ medium to study

its feasibility in various reaction media. The maximum yield of 70.2% was observed with 15% enzyme loading at 24 h in solvent free medium, 77.6% yield in hexane with 15% enzyme loading at 24 h and 88.3% yield in liquid CO₂ with 10% enzyme loading at 5 h. The rate of formation of alkyl esters in liquid CO₂ mediated enzymatic transesterification is higher than that of solvent and solvent free processes. The process parameters for enzymatic transesterification in liquid CO₂ were optimized. Kinetics of enzymatic transesterification in liquid CO₂ was investigated and the activation energy was found to be 22.5 KJ/mol.

Enzymatic transesterification of castor oil was carried out in packed bed reactor loaded with enzyme TL IM in supercritical CO₂. The optimized process parameters resulted in 94.3% of octyl esters were CO₂ pressure 100 bar, n-octanol to oil molar ratio 5:1, Temperature 60°C, substrate flow rate 2 ml/min and retention time of 20 min. Kinetics of transesterification in PBR was studied at different temperatures. The activation energy for the enzymatic transesterification of castor oil in PBR under SCCO₂ was found to be 32.7 KJ/mol. Economic analysis of enzymatic transesterification of castor oil in SCCO₂ estimated the break-even price of methyl esters at \$5.41/gal. The enzymatic transesterification of castor other alcohols like ethanol, n-propanol, n-butanol, n-hexanol and n-octanol were studied and optimized. Sub/supercritical CO₂ are green solvent and enzymatic transesterification in SCCO₂ are clean and green technology. The reusability of lipase enzyme was studied and it has been found that the catalytic activity of enzymes remain intact after five time use.

The other main objective of the research is to study tribological characteristics of fatty acid alkyl esters (biolubricants) prepared from castor seed oil. Lubricity study of castor oil alkyl esters have been carried out as alone and as an additive or blend with low lubricity diesel fuel on High frequency reciprocating rig (HFRR). Wear scar diameters of LLDF, COME, COEE, COPE, COBE, COHE and COOE on HFRR were 671, 221, 198, 186, 178, 174, 122 μm respectively. The effect of alkyl esters of castor oil as lubricity enhancer was tested by adding 0.5%, 1%, 2% and 5% (v/v) in low lubricity diesel fuel (LLDF). It shows that very little amount of alkyl ester is required (2%) to lower the wear scar diameter of LLDF by 75%.

The other important properties of the biolubricants are viscosity index, cloud point, pour point, thermal and oxidative stability. Viscosity index and oxidative stability of the castor oil alkyl esters increases with increase in the chain length. Castor oil alkyl esters have shown the improvement in low temperature properties as well as an effective antifriction and antiwear additive in terms of lubrication.

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