Abstract

Biodiesel is an alternative bio fuel for transportation which is renewable and environment friendly. Biodiesel can be produced from animal fat, vegetable oil (edible or non edible) or waste cooking oil. To avoid the food vs. fuel problem, non-edible oils can be the best way to use to produce the biodiesel and they are the focus of this thesis.

The main objective of the PhD research is to check the feasibility of producing biodiesel (methyl ester) from castor seeds directly via reactive extraction technique. Before preceding the reactive extraction, the performance of seed pre-treatment on the oil yield and the suitability of possible extracting and reactive solvent for biodiesel production was also investigated. Further objective includes an investigation on engine performance, emulsification of prepared castor oil biodiesel in order to reduce the emission of pollutants. Further includes storage stability and biodegradability of castor oil biodiesel, the estimation of various properties of the castor oil biodiesel and emulsions.

Initially, pre-treatment of castor seed on oil yield and properties was investigated in this research. Pre-treatment of castor seed was carried out by heating the cleaned seed for 24 h at 50 °C. Extraction of castor oil from castor seed was carried out by Soxhlet method using polar and non- polar commercial solvents at optimum conditions obtained during preliminary oil extraction study. The solvents used were hexane, pentane, petroleum ether, cyclohexane, ethyla cetate, methanol and isopropanol. The effect of different process parameters such as temperature, solute to solvent ratio and extraction time were studied to optimize and compare the extraction efficiency of different solvents. The highest oil yield of 56.07% and 55.22% were obtained with polar solvents ethyl acetate and methanol respectively. The oil was also extracted by vial method using

hexane for the successive extraction from a single castor seed. The yield obtained from this method was comparable to the yield obtained from the Soxhlet method. Physicochemical properties of the oil extracted using different solvents were also estimated to determine its quality potential using ASTM methods. Similarly the performance of seed pre-treatment on oil yield and the suitability of methanol as a possible extracting and reactive solvent for biodiesel production was also investigated. For castor seed, after pre-treatment slight increased in extraction yield was noticed, with significant decrease in both acid value (3.92 to 0.925 mg KOH/g) and pour point (-15 to -21 °C). Apart from that thermal and oxidative stability analysis of oil was estimated using thermo gravimetric analysis (TGA) and differential scanning calorimetry under nitrogen and air atmosphere respectively. The fatty acid profile of castor oil was determined by gas chromatography (GC). The obtained physico-chemical properties indicated that oil meets the prescribed biodiesel feedstock quality standards, further justifying methanol as a capable solvent for simultaneous extraction and transesterification. Therefore, methanol was considered as desirable solvent for further reactive extraction of castor seed in a single step.

Among non-edible feed stocks, castor seed is a cheap feed stock for the production of biodiesel. In this research, reactive extraction was carried out in two approaches i.e. integrated and non-integrated. Integrated reactive extraction includes no direct contact of the seed material with the catalyst. Whereas non-integrated includes the direct contact of the seed material with the catalyst and alcohol. As an optimization of reaction conditions has the capacity to decrease reagent use and raise yields, reactive extraction was optimized by RSM (Response Surface Methodology) design technique based on the preliminary studies in both the approaches. Initially, optimization of

integrated reactive extraction of castor seed was carried out using KOH as a catalyst and methanol as alcohol. Since an alkali catalyst is favourable than acid catalyst due to its higher reaction rates at lower temperatures, same was used in the reactive extraction. The optimum COME conversion of 95% was achieved with oil/methanol molar ratio of 1:400, catalyst concentration of 1.5 wt % and 6.3 h reaction time. The results showed insignificant effect of co-solvent on the conversion but on the properties such as thermal and oxidative stability are slightly inferior compared to that of COME-without co-solvent (hexane). Similarly optimization of reactive extraction of castor seed by non-integrated approach was carried out by using NaOH as a catalyst. A biodiesel conversion of 97% was achieved with oil/methanol molar ratio (1: 200) using NaOH as catalyst (1.19 wt %) within 3 h reaction time at 30 °C temperature. An estimated properties of COME and its blends are within ASTM standards and comparable to the reported literature data. This study suggests that reactive extraction by integrated or non-integrated approach is an effective process for methyl ester production in single step and COME can be a good alternate fuel for petro-diesel.

Even though, the usage of biodiesel has several increasing ecological benefits, deterioration of biodiesel is more severe compared to commercial petro-diesel during storage. Storage stability is a major concern about the flourishing commercialization of biodiesel in the fuel market. Therefore, storage stability of prepared biodiesel was evaluated over a six-month storage period (180 days) under three different storage conditions. The results showed a sharp decrease in fuel stability over time in terms of increase in density from 0.888 to 0.984 g/cm^3, kinematic viscosity (10.59 to 16.18 cSt), acid value (0.52 to 5.15 mg KOH/g) respectively. While, iodine value significantly decreased from 82.5 to 54.57 g I_2/100 g oil over time. The storage stability study of

COME suggests that COME stored in a dark was more stable than other two conditions. Similarly biodegradability of biodiesel is the strongest point for its use at industrial level. Biodegradability means breakdown of complex and probably poisonous substance in to simple and regular forms. Biodegradability of fuels can be evaluated by methods using microorganisms or without using micro-organisms i.e. bio-kinetic model. In the present study, biodegradability was evaluated by method without using microorganisms. Biodegradability of COME test carried out using a model of bio-kinetics was given 51% degradation in 28 days. The lower biodegradation of castor oil biodiesel may be due to the higher viscosity of COME. Recently, biodiesel fuel has been attracting the world as a blending component or direct fuel in diesel vehicle engines. The low level blends do not need any engine modifications and also produce lower NOx emissions than that of higher blends. Engine performance tests were conducted for castor oil methyl ester and its blends of 5%, 10% and 15% with diesel fuel. Among three blends, B10 blend was given the best brake thermal efficiency of engine at maximum load. The exhaust gas emission was found with reduced CO (26-36%), NOx (14-20%) and HC (17.5-50%) gases. This result proves that COME can be an alternative fuel for conventional diesel.

Biodiesel is an oxygenated fuel as generally contains about 10 wt % of oxygen. The high oxygen content in biodiesel results in the enhancement of NOx formation particularly under an elevated temperature burning environment. NOx discharge is detrimental to both humans and the atmosphere. During past few decades, researchers around the world are trying several options to control NOx emissions. Emulsification might be one of the options to be considered. This technique enhances fuel efficiency and reduces emission of hazardous pollutants from diesel engines. Therefore, two phase emulsions were prepared using COME and water. The study used an ultra sonification

method to investigate the emulsion characteristics of two phase emulsion systems i.e. water in oil (W/ME) and oil in water (ME/W). The optimum conditions in terms of higher emulsion stability for both emulsions were found to be HLB 13, 15 vol % water content, 2 vol % surfactant, 10 min sonication, 10 min agitation time, 2500 rpm agitation speed for W/ME and HLB 7, 20 vol % oil content, 2 vol % surfactant and 10 min sonication time for ME/W emulsions respectively. W/ME emulsion showed superior results than ME/W w.r.t droplet size and properties. The effect of sonication time showed positive effect on the droplet size reduction in both emulsions. The findings of the study have demonstrated the feasibility to produce the stable emusified fuel with castor oil methylester as an alternate fuel in diesel engine to minimize the NOx emissions.

As increasing the growth of biodiesel industry, there will be huge amount of glycerol (by-product) obtained during transesterification. It was still increasing due to the increase in replacement of 5.75% petroleum fuels by bio fuel. Therefore, in order to intensify the reactive extraction process with an intention to make use of by-product glycerol, preliminary studies was carried out using synthetic glycerol using purolite resin catalyst. From the preliminary study, the combination of optimum process parameters obtained for the highest solketal yield (74.68%) were 3 h reaction time, 1 wt % catalyst concentration, 1:4 glycerol/acetone molar ratio, at which the glycerol conversion was 96.57%. Comparison of solketal yield obtained for the present system with the reporetd in literature (continuous reactor) using purolite catalyst reveals that the yield of solketal in the present study found to be lower (74.68%) due to the formation of by-product water during the reaction. Therefore, results of the study seggested that irrespective of the catalyst used, removal of water is necessary to achieve higher solketal yield

The outcomes of this study have been published in some scientific journals and presented at national and international conferences. The published articles and conference presentations are listed at the ending of this thesis.