Synthesis of biodiesel using indigenous feedstocks and effect of co-solvent on biodiesel yield

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By

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Summary

The thesis entitled **"Synthesis of biodiesel using indigenous feedstocks and effect of co-solvent on biodiesel yield"** epitomized the synthesis of biodiesel from *Pongamia pinnata* oil as well as waste fish oil using the heterogeneous catalysts calcium oxide (CaO) and beta-tricalcium phosphate ($Ca_3(PO_4)_2$). World population growth led more energy consumption is but the energy producing resources are limited. Energy consumption increasing day by day since human life style has drastically changed with time. High energy consumption has posed significant effect on world fossil fuel reserves and at current usage rate, world fossil fuels will get exhausted shortly. By use of fossil fuels environmental pollution is increasing which will have effect on human health as well as on ecosystem also. An alternative fuel in the place of fossil fuel is needed to accomplish the world energy demand for coming generation. Biodiesel has potential to replace the petroleum diesel (petrodiesel) since biodiesel has many advantages like low or no sulfur content, no aromatics content, high flash point, natural lubricity, biodegradability, reduction in exhaust emissions, blend in all ratios due to miscibility over petroleum diesel. Biodiesel can be synthesized from renewable sources such as vegetables oils (edible oils as well as non-edible oils), algae, animal fat, and oils derived from waste. Biodiesel synthesis from non-edible oils is economically viable since in edible vegetable oils are scares in developing and underdeveloped countries. Oil derived from waste used as feedstock in biodiesel synthesis will reduce the total cost of biodiesel and it also helps in decreasing environmental pollution. Biodiesel can be synthesized through trancesterification in which alkyl group of an ester is exchanged by an alkyl

group of alcohol. Transesterification process can be carried out using different catalysts such as homogeneous acid/base catalysts, heterogeneous acid/ base catalysts and enzyme catalysts. Biodiesel can be prepared without catalyst by the process called supercritical methanolysis. Biodiesel separation from its by-products as well as reusability is difficult in case of homogeneous catalysts and enzyme as catalyst can increase the total cost of biodiesel since enzymes are more expensive. Biodiesel synthesis from supercritical methanolysis consumes more solvent and occurs at high temperatures which will again increase the total cost of biodiesel. Use of heterogeneous catalysts for the synthesis of biodiesel has attracted the biodiesel manufacturers since they can be reused and effortlessly separated from the reaction mixture.

Calcium oxide (CaO) heterogeneous solid base catalyst was prepared through calcination of waste crab shells and beta-tricalcium phosphate ($Ca_3(PO_4)_2$) heterogeneous solid base catalyst was prepared by calcining the solid matter (contains fins, tails.,etc.) which was left after extraction of waste fish oil from waste parts of fish. *Pongamia pinnata* oil was extracted from its seeds using different solvents such as petroleum ether, diethyl ether and hexane through process called solvent extraction. Waste fish oil was extracted from waste parts of fish through mechanical expeller. Physical and chemical properties of both oils were determined according to ASTM standards. Esterification followed by transesterification reactions were carried out for the synthesis of biodiesel from *Pongamia pinnata* oil as well as waste fish oil using Calcium oxide (CaO) and beta-tricalcium phosphate ($Ca_3(PO_4)_2$) catalysts. Effect of reaction variables such as reaction temperature, reaction time, methanol to oil molar ratio and stirrer speed on biodiesel yield were

studied. Effect of each reaction variable was studied with and without addition of co-solvent (Tetrahydrofuran). High biodiesel yield was observed at optimum reaction conditions. Physical and chemical properties of biodiesel were studied according to ASTM standards. Calcium oxide (CaO) and beta-tricalcium phosphate ($Ca_3(PO_4)_2$) were reused up to five times and were found to display high catalytic activity.

This thesis is well structured based on catalyst preparation and characterization. Extraction of feedstock was carried out and physical and chemical properties of feedstocks were studied. Esterification followed by transesterification reactions were carried out for the synthesis of biodiesel. Effect of reaction variables on biodiesel yield were studied with and without co-solvent. Physical and chemical properties of synthesized biodiesel were determined. The summary of each chapter in this thesis was given bellow.

Chapter 1 deals with introduction about world energy production and consumption. It explored the world energy demand raised along with the current rate of population growth. World energy production from different sources such as carbon based fossil fuels (oil, natural gas and coal) and renewable (solar, wind, geothermal, biofuels) resources were discussed. Limited amount of world fossil fuels as well as hazardous environmental problems with the fossil fuels led to search of alternative energy resource. Biodiesel is a renewable energy resource as well as a green fuel and will be available for the generations to come. Synthesis of biodiesel from different feedstock materials using different catalysts through different methods were discussed in this chapter. Esterification and transesterification processes for the synthesis of biodiesel were explained with

mechanism. Biodiesel properties were compared with the properties of standard petroleum diesel (petrodiesel). Advantages of biodiesel, such as energy independence, global warming and the greenhouse gas emissions, sulfur and atmospheric contamination and carbon neutrality were discussed in this chapter.

Chapter 2 is literature review. Discussion on different generations of biofuels starting from first generation to fourth generation has been provided in this chapter. Synthesis of biodiesel using different feedstocks such as edible oil, non-edible oil, waste oil, and algae were discussed from the reported work. Biodiesel synthesis from waste fish oil as well as *Pongamia pinnata* oil were discussed according to previous literature survey. This chapter also described the biodiesel synthesis using different homogenous and heterogeneous catalysts with relevant literature.

Chapter 3 describes materials and methods used to carried out the present work. Methods adopted for the extraction of oils and synthesis of biodiesel were discussed in details. This chapter also mentioned several reagents and different analytical instruments for characterization of synthesized catalysts as well as synthesized biodiesel.

Chapter 4 provides the complete procedure about extraction of *Pongamia pinnata* oil from its seeds and waste fish oil from waste parts of fish and also explores the physical and chemical properties of both the feedstock *Pongamia pinnata* oil and waste fish oil according to ASTM standards. This chapter also provides the fatty acid profiles of both the feedstock oils using GC-MS analysis. Preparation of heterogeneous solid base catalysts for the synthesis of biodiesel and characterization of catalysts using different

analytical techniques such as X-ray diffraction patterns (XRD), TG/DTA/DTG analysis, SEM/EDS analysis and FT-IR analysis were discussed in this chapter.

Chapter 5 explores the effect of addition of co-solvent on biodiesel synthesis in all the systems reported. Tetrahydrofuran (THF) was used as co-solvent in all the transesterification reactions, since THF gave high biodiesel yield than the other co-solvent at optimum reaction conditions. The synthesis of biodiesel from *Pongamia pinnata* oil using calcium oxide (CaO) has also been discussed in chapter 5. Effect of reaction parameters such as catalyst concentration, stirrer speed, reaction temperature, reaction time, and methanol to oil molar ratio on biodiesel yield was studied with and without co-solvent. High biodiesel yield (98 %) was obtained in presence of co-solvent at optimum catalyst concentration (2.5 wt %), methanol to oil molar ratio (10:1), stirrer speed (650 rpm), reaction temperature (65 °C) and reaction time (105 min). Synthesized biodiesel was characterized with FT-IR and conversion of *Pongamia pinnata* oil into biodiesel was calculated with proton NMR and a high conversion (99.55 %) was obtained. Catalyst reusability was conducted up to five runs and a high catalytic activity has been reported in this chapter. Physical and chemical properties of synthesized biodiesel were characterized according to ASTM standards.

Chapter 6 explores the synthesis of biodiesel (with and without co-solvent) from waste fish oil using calcium oxide as a solid base catalyst. FT-IR analysis was used to identify the functional groups present in the synthesized biodiesel. Effect of biodiesel parameters (catalyst concentration, stirrer speed, reaction temperature, reaction time, and methanol to oil molar ratio) on biodiesel yield were studied with and without co-solvent. Maximum

biodiesel yield (96 %) was obtained in presence of co-solvent at optimum reaction conditions: methanol to oil molar ratio (10:1), catalyst concentration (2.5 wt %), stirrer speed (650 rpm), reaction temperature (65 °C) and reaction time (120 min). Biodiesel conversion was calculated from proton NMR and found to be 98.52 % in this case. Reusability of catalyst was studied up to five runs the decrease from first to fifth run was insignificant in the case of transesterification with co-solvent. Physical and chemical properties of synthesized biodiesel were determined according to ASTM standards.

Chapter 7 describes the biodiesel synthesis from *Pongamia pinnata* oil using β-tricalcium phosphate as a solid base catalyst. The functional groups in biodiesel were identified with FT-IR analysis. Effect of reaction parameters on biodiesel yield were studied with and without addition of co-solvent. High yield (96 %) and high quality of biodiesel was obtained (in the presence of co-solvent) at methanol to oil molar ratio (10:1), stirrer speed (650 rpm), reaction temperature (65 °C) and reaction runs (114 min) and catalyst concentration (4 wt %). High biodiesel conversion 98.03 % was observed with proton NMR. Reusability of catalyst was conducted up to five times and found high yield in each run from first to fifth in the second case when co-solvent was added to the reaction mixture. ASTM standards were followed to determine the physical and chemical properties of prepared biodiesel.

Chapter 8 demonstrates the preparation of biodiesel from waste fish oil as a feedstock and β-tricalcium phosphate as a solid base catalyst. Biodiesel was characterized with FT-IR analysis and identified the functional groups present in the synthesized biodiesel.

Reaction parameters were studied with without addition of co-solvent. Pure biodiesel and high yield (94 %) was obtained with addition of co-solvent at moderate reaction conditions: catalyst concentration (4.0 wt %), methanol to oil molar ratio (10:1), stirrer speed (650 rpm), reaction temperature (65 °C) and reaction time (129 min). Maximum biodiesel conversion (96.61 %) was observed at optimum reaction conditions as mentioned above. Catalyst reusability was observed up to (with without calcination) five runs and results showed that the high yield was observed in the second method (catalyst was calcined and reused). Physical and chemical properties of synthesized biodiesel were calculated according to ASTM standards.