CHAPTER 1

1.1 Introduction

Energy plays a vital role in economic growth and sustainable development of a nation. According to International Energy Agency (IEA), world total primary energy supply in the year 2014 was 13, 699 MTOE (million tonnes oil equivalent) which included natural gas (21.2 %), oil (31.3 %), coal (28.6 %), biofuels and waste to energy (10.3 %), hydro (2.4 %), nuclear (4.8 %) and others (1.4 %). British petroleum statistical review of world energy [June 2016] indicated that the oil persisted the world's foremost fuel and the share of global energy consumption by oil is 32.9 %. Overall, carbon based fossil fuels (oil, natural gas and coal) account for 86% of global energy consumption while renewables (solar, wind, geothermal, biofuels) account for just 2.8 %, up from 0.8% a decade ago. World energy outlook 2016 showed that the world petroleum and other liquid fuels consumption raised from 90 million barrels per day (mb/pd) in 2012 to 100 million barrels per day (mb/pd) in 2020 and to 121 million barrels per day (mb/pd) in 2040. The current rate of population growth seems to be double by 2040 and energy demand raises about 80%. The major energy consumption sectors are transport, electricity, communication and construction. Transportation sector displayed a growth at an annual rate of 1.4 %, from 104 quadrillion British thermal units (Btu) in 2012 to 155 quadrillion Btu in 2040 and industries are the major segments of world fuel energy consumption. World total crude oil production in the year 2012 was 74.7 million barrels per day (mb/pd) at 1.1 (mb/pd) an average annual percent change, which includes OPEC 33.4 (mb/pd), Non-OPEC 42.8 (mb/pd), OECD 15.7 (mb/pd), Non-OECD 27.1 (mb/pd), OECD Americas 12.2 (mb/pd), Non-OECD

Americas 3.8 (mb/pd) and others. Biofuel production (biodiesel and ethanol fuel) is 0.57 %. Overall, most of our present energy needs rely on resources which have a limited availability. As the world energy consumption continues to grow at an average over 1.9 % annually fuelled by strong growth in emerging economies, it becomes relevant for researchers to investigate alternative sources of energy for the future. Moreover, present energy sources are the major contributors of air pollution as well.

According to International Energy Agency (Key World Energy Statistics 2015), emissions like CO_2 have doubled between 1973 and 2013, from 15,515 Mt to 32190 Mt. Poor air quality results in 6.5 million deaths in a year, making it the 4^{th} largest threat to human health. The major source of air pollution is in the energy sector: 85% of particulate matter, hydrocarbons, sulphur oxides and nitrogen oxides. World Energy Outlook Special Report 2016: Energy and Air Pollution, International Energy Agency clearly specified that the use of fuels in the transport sector, especially diesel, generate more than half of the nitrogen oxides emitted globally which cause respiratory problems, as well as other hazardous pollutants. In such a scenario, it is necessary to focus on green energy sources to make clean environment for generations to come. A green fuel should be renewable, non-toxic and shown lower emission and affordable cost to the consumers.

Humans mostly depend on the non-renewable sources of energy like natural gas, coal and a little bit on the renewable sources of energy like solar energy, biofuels, wind power, hydropower, etc. The rate at which the non-renewable sources of energy are consumed, they would be soon eliminated. Petrochemical fuels have a tremendous impact on the country's economy as they are directly used in various applications like agriculture, transportation and the industrial activities. It has been a general thinking that the growth of the country is directly proportional to the usage of these petrochemical fuels. As the world is going for the accelerated growth, the demand for these petrochemical fuels would increase manifold.

World's population is increasing along with an increase in the purchasing power of the middle class and rapid industrialization, the usage of the petro-fuels has increased manifold. Most of the countries fulfil their energy demands from importing the fuels, so there is need be self-development in energy production. The contribution of renewable sources of energy in energy security of countries is less presently, from the past mostly one decade, scientist have been working to develop energy from renewable sources like biofuels such as biodiesel and bioethanol.

1.2 Biodiesel as a renewable and alternative energy source

Vegetable oil has been considered for usage as fuel since early twentieth century. Rudolph Diesel proposed that vegetable oil could power diesel engines in remote areas of the world where petroleum was not available. In every restaurant/shop/eatery uses vegetable oil and generates 100-300 litres of waste cooking oil each month [MacLeod and Assessment, 2009] which can be potentially utilized as fuel. Vegetable oil has a calorific value comparable to that of diesel but its use in direct ignition diesel engines is difficult due to its unfavourable viscosity, which is many times higher than that of diesel fuels and as a consequence, leads to poor fuel atomization, incomplete combustion and engine fouling due to carbon deposits. Different approaches have been considered for reducing the viscosity of vegetable oil and one of these is transesterification with methanol. It results in a product which has physical characteristic very similar to petroleum diesel, commonly known as biodiesel.

Biodiesel can be produced by transesterification of triglycerides of long-chain fatty acids. A variety of feedstock such as vegetable oils (soybean oil, rapeseed/canola oil, cottonseed oil, sunflower oil, palm oil, coconut oil, etc.), animal fats and waste cooking oils and greases can also be used. Different oil sources have different ranges of fatty acids and hence, biodiesel quality and cost are highly dependent on the raw oil. Synthesis of high-purity biodiesel is a major challenge for researchers and manufacturers.

Biodiesel is an eco-friendly and sustainable fuel for compression ignition (C.I.) engines. It can be used in a diesel engine with little or no modifications [Agarwal and Rajamanoharan, 2009] and has the ability to be blended in any proportion with conventional diesel since biodiesel exhibits similar properties with conventional diesel.

Furthermore, the by-products of the production process result in glycerol, which itself has commercial value. The use of biodiesel as a replacement for diesel leads to the substantial reduction in particulate matter (PM), hydrocarbons (HC) and carbon monoxide (CO) emissions [Dorado et al., 2003a; Shahir et al., 2015] with ever tightening emission standards for motor vehicles, biodiesel is being considered as a capable alternative fuel for IC engines.

Biodiesel is mainly produced by transesterification reaction catalysed by (i) Acids (ii) Bases (iii) Enzymes or produced by (iv) Supercritical method. Acid and alkaline catalysts are of further two types: homogeneous and heterogeneous. Enzymatic catalysis, in which an immobilized enzyme is used as catalyst for transesterification reaction, though environmentally friendly, suffers from a high cost of bio-catalyst, which adds to the biodiesel production cost [Madhu et al., 2016]. Biodiesel can also be produced without catalyst above critical temperature and pressure of alcohol. The main advantage of this method is bypassing of saponification side-reaction of Free Fatty Acids (FFAs). Another advantage is that it takes less time to produce biodiesel compared to conventional alkaline-solid catalysis. However, high temperature (350°C), high pressure (43 MPa) and a very high oil to alcohol ratio of 1:42 make the use of this process industrially unsuitable [Kusdiana and Saka, 2001]. Out of these methods, use of alkaline (homogeneous) catalysts is more prevalent as they tend to be faster than acidic catalysts [Lotero et al., 2005].

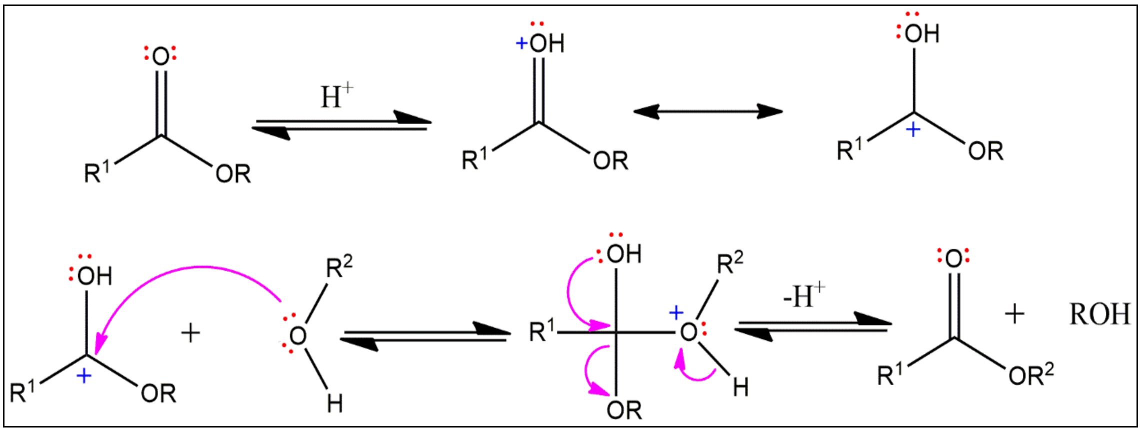
Biodiesel replaces fossil fuel and serves as energy security, stimulates development in rural areas, encourages to generate income from rural areas and reduce carbon emission as well as greenhouse gas emissions.

Currently high cost of biodiesel is a major problem to its commercialization. It is reported that approximately 70%-85% of the total biodiesel production cost arises from the cost of the raw materials. Estimated cost of biodiesel is approximately by1.5 times higher than diesel fuel due to use of food grade oil for biodiesel production. More focus on low cost feedstock and better implementation of technology will make cost of biodiesel competitive to petroleum fuels. These low cost feed stocks could include enormous amount of waste lipids generated from restaurants, food processing industries and fast food shops every day and non-edible crops with a very high biodiesel yield.

1.3 Process for biodiesel production

Importing fossil fuel from other countries viz. oil producing countries is need of the countries like India because of limited oil reserves and consumption of limited fossil fuel reserves increasing, if a country has resource to produce biodiesel, it can substantially reduce the dependency on other countries as well as it increases the self-economy. Biodiesel can also reduce environmental problems such air pollution, global warming and conserves non-renewable oil reserves. Vegetable oils, animal fats, waste oils or microalgae (triglycerides and free fatty acids) with alcohol are converted into fatty acid methyl esters (FAME) (biodiesel) through different process such as transesterification, blending, microemulsions, and pyrolysis (Ghadge and Raheman, 2006). Transesterification method is the best method to synthesize biodiesel from vegetable oils and fats. Transesterification can be carried out by using acid or base catalyzed reactions. In acid catalyzed transesterification mechanism, formation of carbocation occurs due the protonation at the carbonyl group, thereafter nucleophilic attack of the alcohol takes place which leads to the formation of tetrahedral intermediate. This tetrahedral intermediate gets transformed to new ester by eliminating alcohol (Figure 1.1.) [Ejikeme et al., 2010].

In base catalyzed transesterification, the complete conversion of triglycerides into corresponding alkyl esters (biodiesel) via diglycerides and monoglycerides proceeds through step wise process. One mole of triglyceride will produce three mole of alkyl esters in the base catalyzed transesterification reaction. In presence of base, alcohol will form alkoxide ion which will attack at the carbonyl group of the triglycerides leading to formation of tetrahedral intermediate.



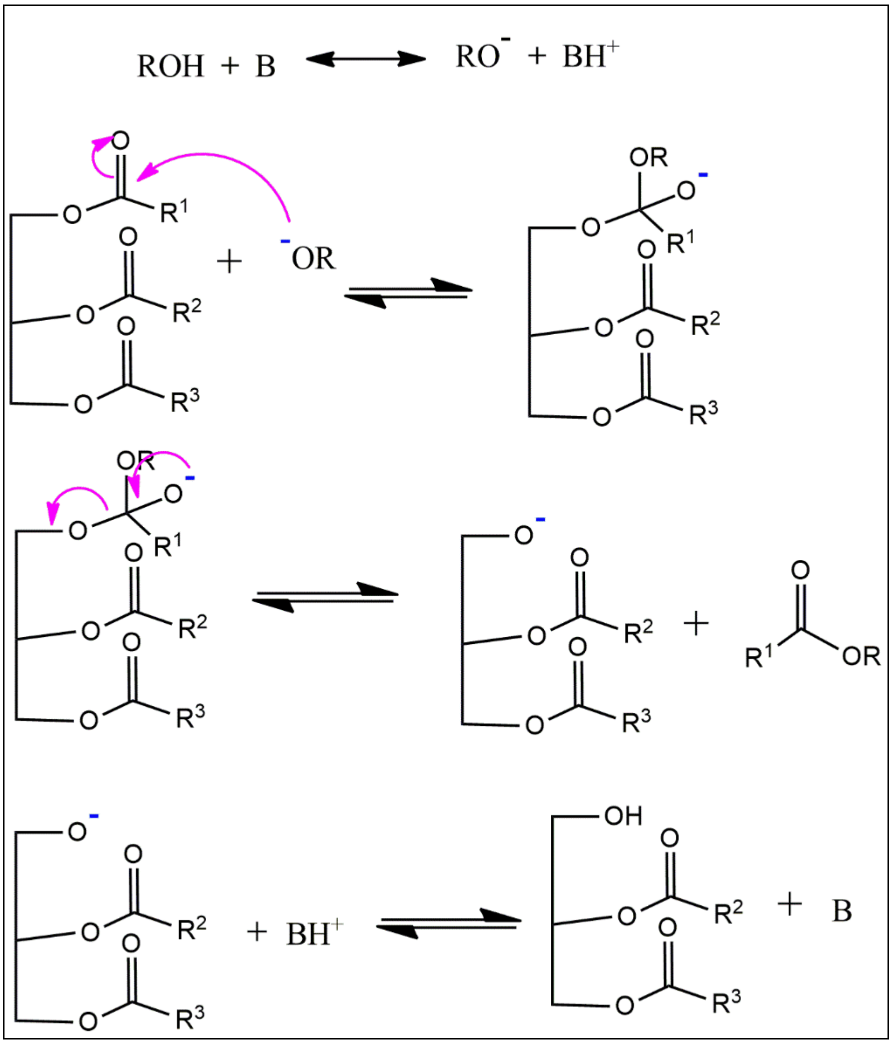
R^1 = carbon chain of fatty acid, R^2 = alkyl group of alcohol.

Figure 1.1 Represents mechanism of acid catalyzed transesterification.

This tetrahedral intermediate leads to formation of alkoxide ion when reacts with alcohol and finally rearrangement takes place to form diglyceride along with alkyl ester and this mechanism continues up to the formation of monoglyceride. In the final step, alcohol reacts with mono glycerides to form corresponding alkyl esters (biodiesel) as well as glycerol as by product as shown in (Figure 1.2) [Meher et al., 2006].

1.4 Catalysts for biodiesel synthesis

Homogeneous basic catalysts such as NaOH, KOH, CH_3ONa, CH_3CH_2ONa and CH_3OK are used due to their higher kinetic reaction rates. They lead to high-conversions and insignificant side-reactions, despite these benefits, there are a host of downsides including (i) Catalyst recovery is not possible and the catalyst, generally NaOH must be neutralised



R = alkyl group of alcohol, R^1, R^2, R^3 = mixture of various fatty acid chains, B = base

Figure 1.2 Represents the mechanism of the base catalyzed transesterification.

at end of the reaction, generating large amount of undesired waste salt. (ii) These catalysts require high quality feedstock which are anhydrous and have free fatty acid (FFA) content <3% to prevent hydrolysis and saponification side reactions. Thus, they require additional steps to eliminate undesirable FFAs and moisture. (iii) Continuous processing techniques are not widespread [Lotero et al., 2005]. Due to these difficulties, development and application of various heterogeneous catalysts is increasing. A number of heterogeneous catalysts have been investigated by researchers which include zeolites, clays, heterogenized guanidines, aluminium orthophosphate, ion-exchange resins and pure or mixed oxides [Sabudak and Yildiz, 2010]. Heterogeneous catalysts offer advantages as simple catalyst recovery, reusability, less energy and water consumption, and simple glycerol recovery. Since the cost of catalyst is a significant component in the total cost of biodiesel, the development of cheap and effective catalysts for transesterification of a wide range of feedstock is necessary for making biodiesel economically feasible [Raman, 2013]. Employing reusable solid catalysts in a fixed-bed continuous reactor could potentially lead to cheaper cost of biodiesel production.

1.5 Comparison between standard diesel and biodiesel

Scientists have focussed their research towards energy production from renewable resources such as synthesis of biodiesel from vegetable oils since energy demand is increasing day by day but the non-renewable resources are limited to meet the energy demand. Biodiesel has potential to replace the conventional petro diesel. Biofuels derived from the annually harvested crops or monthly grown algae. Pose danger as threat of the food resource chain interruption due to the usage of the field for the biofuels, but if we use non-edible or waste as raw material, it would be economically viable for synthesis of biodiesel. Petrodiesel is a mixture of compounds which consists of 8 to 21 carbon atoms per molecule [Collins, 2007] and this petrodiesel has high percentage of saturated carbons. The kinematic viscosity of biodiesel is slightly higher than that of petrodiesel since kinematic viscosity plays vital role at the atomization of fuel in the combustion chamber of diesel engines but after much research, kinematic viscosity of biodiesel has been reduced to equal to that of petrodiesel [Knothe and Steidley, 2005a]. Petrodiesel has considerable toxicity but biodiesel is essentially non-toxic. Biodiesel, comparatively gave better results over petrodiesel when we drew a graph between Compression ratio vs. heat efficiency and fluid work [Fallahipanah et al., 2011]. Biodiesel synthesized from vegetable oil like sunflower oil can decrease environmental pollutants such as CO (carbon monoxide) and particulate matter [Ilkılıç et al., 2011]. According to [Goodrum and Geller, 2005], failures in engine parts such as fuel injectors and pumps are due to low or poor lubricity of petrodiesel i.e., failures of such parts can be reduced by using biodiesel since biodiesel has high lubricity than the petrodiesel [Knothe and Steidley, 2005b]. Biodiesel not only reduces the hazardous pollutants emissions into the environment except nitrogen oxides (NOx) [Knothe et al., 2006] but also reduces the greenhouse emissions into the environment [Ali, 2011]. Biodiesel can be transported as non-hazardous and non-flammable material which is a major advantage for the manufacturer. Because of this fact they are cheaper to transport from one place to other. This is an important factor because if the fuel is easily prepared but has difficulties in transportation they are most cost effective. With a slight modification, they can be well suited in the available infrastructure since general properties of biofuels are favourable to easy transport. Use of fuels from hydrogen or electricity are completely opposite since they require a complete modification of the engine's design. Biodiesel is the future fuel for generations to come and will serve as the alternative to the traditional fossil fuels. Availability and advantages are major factors which make the biodiesel a favourable fuel.

1.6 Advantages of biodiesel

Energy plays vital role in providing a standard life style in the early 19^{th} century and late 18^{th} century when industrial revolution occurred. Transportation and industries are the sectors consuming major part of energy but world oil demand around 60 % goes to transportation sector only. According to United Nations, 23 % emissions were released by transport sector in the year 2014. Biodiesel production has got attention since it is sustainable alternative renewable energy resource and environmentally friendly in nature. In recent times, melting of polar, rice in sea level and global warming is increasing day by day [Barbir et al., 1990]. Biodiesel is not only reducing environmental gas emissions, but also it reduces unemployment [Langeveld et al., 2012] through supporting agriculture sector. According to renewable fuel standard [Wu et al., 2012], production of biodiesel has been commercially viable and meets the commercial fuel standards (ASTM D6751). Biodiesel is being used as fuel in many countries such as United States of America, India, Malaysia, Indonesia, Brazil, Germany, France, Italy, other European countries etc.

1.6.1 Energy independence

Urbanization and industrialization are responsible for consumption of more energy. Major part of this energy comes from fossil fuels and is used in industry and transport sectors. In recently, alternative energy resources such as biodiesel synthesized from renewable resources have been emerging for the replacement of petrodiesel. Many countries are now focussing on use of biodiesel because of growing energy demand. This shift in energy demands could be devastating on economies of the world which depend on revenue generated by exports of oil to balance their economy, like the countries in the Middle East. Biodiesel reduces the energy dependency and also it helps economy and employment of nation. Use of biodiesel can reduce economy damage and push each nation to shift their commercial and industrial focus.

1.6.2 Global warming and the greenhouse gas

Most of the global warming and environmental pollutants such as methane (CH_4), carbon dioxide (CO_2), nitrogen oxides (NO_x) and carbon monoxide (CO) are released by automobiles. According to IEA (World Energy Outlook), carbon dioxide (CO_2) emission in the year 2015 was 32.14 Gigatonnes, but in the year 2013, was 32.07 Gigatonnes, thus increment in two consecutive years was 0.07 Gigatonnes. In recently, Mauna Loa Observatory, Hawaii (Scripps Keeling Curve) released preliminary atmospheric CO_2 data and it was to be found 401.01 ppm for the month of September, 2016. Now, this emission will be governed by emission standards established by the different regulating authorities all over the world. Biodiesel B100 (100 % biodiesel) is one which reduces net emissions of CO_2 by 78.45 % compared with the conventional petrodiesel and in the case of B20 (20 % biodiesel and 80 % conventional petrodiesel) net emissions of CO_2 reduced to 15.66 % [Sheehan et al., 1998].

1.6.3 Sulfur and atmospheric contamination

One of the components of acid rain is caused due to the presence of sulfur containing compounds in the atmosphere. The reason of sulfur in the atmosphere is burning of fossil fuels like coal, gasoline, etc. Use of biodiesel as a fuel in place of fossil fuel can reduce sulfur content in the atmosphere since biodiesel has no sulfur content [Candeia et al., 2009]. Thus, we can reduce the sulfur component of the acid rain if biofuels are used. The downside of the biofuels is that it produces less amount of nitrogen containing compounds which are also an acid rain component but the net effect of the acid rain is negative when compared to fossil fuels. Biofuels have potential to reduce the contaminant as low as possible which is not possible in case of fossil fuels.

1.6.4 Carbon neutrality

Figure 1.3 represents the process of carbon neutrality phenomenon in which carbon dioxide released into the atmosphere through the burning of fossils fuels. This carbon dioxide absorbed by plants and produces seeds containing oil through photosynthesis. Process of synthesis of biodiesel using these vegetable oils extracted from seeds, is considered as carbon neutrality since released carbon dioxide will no longer be present in the atmosphere. Use of biodiesel in place of fossil fuel creates a similar amount of useful energy along with compensating the carbon emissions. The present study focuses on production of biodiesel economically. The candidate has used waste fish parts for extracting feedstock and preparing catalyst. Another feedstock material drew from a non-edible oil plant karanja and catalyst from crab shells. Application of these materials ensures economically viable production of biodiesel.

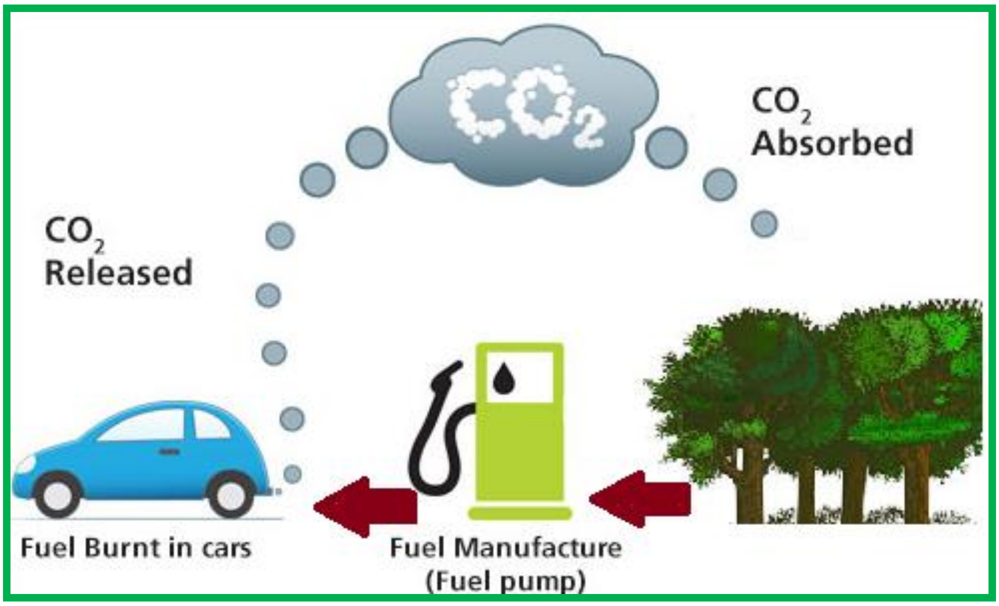


Figure 1.3 The carbon neutrality phenomenon.

1.7 Objectives of the present work

Point wise objectives of the present work can be written as follows:

i. Extraction of raw *Pongamia pinnata* oil from its seeds through solvent extraction using different solvents.

ii. Extraction of waste fish oil from waste parts of fish through mechanical expeller followed by solvent extraction using petroleum ether.

iii. Preparation and characterization of solid base catalysts for the synthesis of biodiesel from waste fish parts and waste crab shells.

iv. Biodiesel synthesis from raw *Pongamia pinnata* oil as well as waste fish oil using prepared solid base catalysts through transesterification reaction.

v. Characterization of biodiesel using different analytical techniques.

vi. Effect of process parameters on biodiesel synthesis with and without co-solvent.

vii. Physical and chemical properties of synthesized biodiesel were studied according to ASTM standards.

1.8 Scope for future work

(1) *Pongamia pinnata* oil from its seeds as well as waste fish oil from waste parts of fish can be extracted using different solvents or solvent mixtures.

(2) Insignificant amount of metals present in the *Pongamia pinnata* oil and waste fish oil can be detected and work on their removal for biodiesel be conducted.

(3) Surface area, pore size and pore volume of prepared catalysts (calcium oxide and β-tricalcium phosphate) can be measured to know more about catalytic activity.

(4) Different co-solvents can be used for synthesis of biodiesel at optimum reaction conditions.

(5) Biodiesel can be synthesized by taking mixture of both oils such as *Pongamia pinnata* oil and waste fish oil in the fixed molar ratio.

(6) Response Surface Methodology (RSM) and Liquid-Liquid Equilibrium (LLE) techniques can be applied for optimization of biodiesel parameters.

(7) Kinetic study can be carried out using both the catalysts (calcium oxide and β-tricalcium phosphate).

(8) Biodiesel can be synthesized using ultra/microwave as a heating source to decrease time of the reaction.

(9) Biodiesel can be synthesized at commercial scale using biodiesel plant.