CHAPTER 1

Introduction

CHAPTER 1

1.1 Energy

Energy is designated as the potential to do work. It exists in several forms such as chemical energy, electrical energy, radiant energy, thermal energy, mechanical energy and nuclear energy. Energy can be divided into potential and kinetic energies. Energy can neither be generated nor be destroyed but can be converted from one form to another [Lim and Lim, 2012]. There are mainly two sources of energy, namely non-renewable energy (conventional) and renewable (non-conventional) energy. Non-renewable energy resources cannot be reproduced, regenerated, regrown or reused to accomplish the demand as well as consumption. Hence, availability of non-renewable energy resources are declining continuously and it's very challenging to substitute once it is utilized [Chiras, 2006]. Among various non-renewable energy resources, fossil fuels are widely utilized for transportation, agriculture as well as industrial applications and consume more than 80% of entire energy consumption [EIA, 2008]. Fossil fuels would probably endure world energy upto the end of 21^{th} century but ultimately novel energy resources would be obligatory to overcome on global warming challenges and to fulfil increased population demand. However, renewable energy can be reproduced and regenerated continuously. Usage of renewable energy is advantageous since this form of energy does not produce any greenhouse gases (GHG) which are responsible for global warming. Hence renewable energy is environment friendly and lesser maintenance is needed in comparison to conventional energy resources. On the other hand, major drawbacks of using renewable energy are that some resources are not accessible in some countries which create difficulty in power generation at certain areas and in addition to this, only small quantity of energy can be generated at a time [Abbasi, 2010].

1.2 Global energy crises

In recent years, due to increasing population there is drastic expansion in urbanization and industrialization, which are responsible for energy crises. As a result, the need arises for the use of alternative source of energy which can meet the energy necessities. In such a situation, renewable energy which is also known as non-conventional energy will prove to be only option available. Fossil fuels which are non-renewable sources of energy are diminishing in quality and quantity day by day. Their usage at large scale results in health hazards because of emission of hydrocarbons, sulphur, carbon monoxide, nitrogen oxides, poly aromatic hydrocarbons, GHG, etc. [Ghadge and Raheman, 2005].

The appliance of energy, primarily supplied by fossil fuels has been inexorably expanded over the past few decades and consequently the corresponding rate of emission of greenhouse gases has also increased drastically. Reason of this growth mainly comes from developing countries which are extending in their population as well as economic activity. Energy growth varies between developed and developing nations. The IEO 2011 has projected that the developing countries, India and China consumed about 21% of the world's total energy in year 2008. In 2035, this energy use is expected to be more than their double constituting 31% of global energy usage during that period [International Energy Outlook, 2011]. Morally, all up to 95% of projected growth for energy consumption is in non-OECD nations, with escalating at the rate of 2.3% p.a. in year 2012-2035. As compared to non-OECD nations, OECD consumption increment at 0.2% p.a. over the period and will start decreasing from 2030. The major contributor in the growth of energy consumption is China and contribution from India has almost correlated with that of China. In case of China, demand of global liquid fuel consumption has

increased from 8 Mb/d up to 18 Mb/d during 2035. Whereas India and other Middle East nations are the ensuing major contributors and increases by 4.6 Mb/d and the other non-OECD Asia seems to be about 3.1 Mb/d growths. Though China shows largest rise in demand for liquid energy but during the year 2030-2035, its demand shows a rise up to 0.9 Mb/d which makes India as the largest contributor up to the rising demand of 1.3 Mb/d during 2030-2035 [BP Energy Outlook, 2035].

Greenhouse gases (GHG) concentration has increased due to industrialization up to 25% and approximately three quarters of carbon dioxide has increased due to excess use of fossil fuels [Demirbas, 2009]. Energy sectors and transportation are one of the major sources which are responsible for 60% and 20% emission of GHG respectively in European Union [European Environmental Agency (EEA), 2004]. One of the considerable problems in decreasing crude oil reservoir with extraction and processing difficulties causes increment in their cost [Laherrere, 2005]. Currently, there are many alternative sources being studied and executed in practice. Examples are Hydropower, Geothermal, Solar, Wave (Tidal), Wind and Biofuels [Dewulf and Van Langenhove, 2006] and each of these sources has its own merits and demerits.

Gas and oil play important role to reach energy necessity of various countries in the world and assessed that gas and oil sectors provide up to 45% of the overall energy requirement [Report (MoPNG), 2006]. The International Energy Agency (IEA) has reported that primary energy need of the world projected to rear between 2005 and 2030 by 55% and having 1.8% of annual rate per year [World Energy Outlook, 2007]. 27% of this primary energy is consumed by transportation sector. The International Energy Agency (IEA) released world energy outlook 2013. According to International Energy Agency, World Energy Outlook 2013 [IEA, 2013], energy demand has increased towards

south Asia. Primary energy demand of China will be highest as compared with other countries and that will be 4060 Mtoe in 2035. It also specifies that energy demand grows towards South Asia with prepotence of China and India becoming more attractive in global energy trade. According to EIA, projected energy consumption by United States will remain near to 100 quads through 2040. As compared with United States; China will consume much more energy and will reach up to 200 quads by 2030. In that case, India's consumption will be one fourth of US in 2020 and will likely get doubled by 2040 [EIA, 2013].

In developing countries like India, there is regular increment in fuel import which compels to search for alternative liquid fuels to diesel which has largest application in agriculture and transportation sector [Meher et al., 2006]. As compared to other countries where gasoline is dominant over diesel, inverse is the case in India that diesel consumption is nearly five times more than gasoline. Roughly diesel fuel burns by 64 million tonnes or 450 million barrels per year which is far greater than gasoline consumption up to 84 million barrels [Annual Report (MoPNG), 2007]. Diesel consumption is high and was applied 73.6% for transportation while 26.4% for non-transport sector in India [Nielsen, 2013]. As compared to last year, oil demand has been increased 300,000 b/d in 2015 and will become third largest oil consumer all over the world [Nielsen, 2013]. It was estimated that India will consume 166.87 million tonnes of refined fuel in the year 2015-16.

1.3 GHG emission statistics

According to World Resources Institute (WRI) data, top 10 countries of GHG emitters are China, United States, European Union, India, Russian Federation, Indonesia, Brazil, Japan, Canada and Mexico. These ten countries were responsible for around 70%

emission of GHG [Paris Summit, 2015]. As per Biennial Update Report (BUR), India released 2,136.84 million tonnes of CO_2 equivalent greenhouse gases in year 2010 and per capita GHG emission in 2010 was 1.56 tonne CO_2 equivalent that is less than one third of overall world's per capita emission. With this, in 2030 GHG emission in India will climb around 90% as compared with the current levels [Paris Summit, 2015]. It displays that India's GHG emissions grew up to 40% in the year 2000 to 2010 and CO_2 emission rose by 60%.

The objective of the biofuel policy is to decrease the reliance on imported crude oil to promote energy security in the country. One more reason behind the promotion of biofuels comprises climate change mitigation due to reduction in GHG emission. Planning commission report was released in 2003 for biodiesel endorsed initiation of a National Mission on biodiesel production from non-edible oils. Since edible oil requirement is higher than its production and hence it's not a feasible option for country. Planning commission report anticipated the target of 5% blending of biodiesel in beginning of 2006-07, gradually rising up to 20% in 2011-12 by the end of 11^{th} five year plan [TERI Policy Brief, 2015]. The Confederation of Indian Industry (CII) report assessed the reduction in GHG emission up to 30% for biodiesel in association to petroleum diesel [CII, 2010].

1.4 Introducing biofuel resources

Energy demand is highest for industry followed by transportation which consumed up to 16.9% of total supply of energy in 2005-06 [TERI, 2006]. In transportation sector, utilization of motor spirit that is of gasoline reached to 6.64% in 2008-09 and increment in diesel were observed to be 4.1% [GOI. National Policy on

Biofuels, 2009]. India's energy consumption is expanding up to 132% while production is up to 112% [BP Energy Outlook, 2035] creating a huge difference in production and supply.

According to Central Intelligence Agency (CIA), India is the country whose land area is 2.4% as compared to the world but its contribution in to the world's population is up to 15% [Bajhaiya et al., 2010]. In case of both developed and developing countries, economic growth is highly dependant on increment in the energy consumption. In India, public policy has discussed the different envirnomental issues based on energy use and economic development. Though majority of India's total population stays in villages, industrilization and urbanization have been continuously increasing since 1971 [Baka, 2014]. Hence, there has been constant increment in consumption of energy which are non renewable and it will cause scarcity of fuels in future. This scarcity of energy can be overcome by using viable alternative sources of energy. Biofuels are the real contributors in decreasing the emission from transportation and in GHG reduction with increment in the energy supply. Most commonly used biofuels are bioethanol and biodiesel which are capable of replacing gasoline and diesel respectively.

Biodiesel is known as clean fuel since it is derived from various renewable resources. Raw materials used for biodiesel synthesis include various kinds of edible and nonedible oils. In developed countries, use of edible oil is surfeit, but in developing countries, there is shortage of edible oil, hence it is imported from other countries. In developing republics like India, it is costly and illogical to apply cooking oil as a feedstock for biodiesel production. So, nonedible oil is one alternative for developing countries. There are many nonedible oils like Karanja, Mahua, Jatropha, Neem, Tobacco, Waste cooking oil, Algal oil, etc. which can be used as feedstock materials for biodiesel production [Sharma and Singh, 2009]. Raw materials play a crucial role in deciding the

cost of biodiesel production. The choice of raw material is based on its various characteristics such as acid number, saponification number, cetane number, flash point, viscosity, etc. [Azam et al., 2005]. Up to 20% blending of biodiesel with diesel poses no problem in engine parts [Canakci et al., 2006]. The transportation sector in India consumes up to five times more diesel as compared with gasoline and probably the highest in comparison to other developing countries [Ramachandra et al., 2011]. Consumption of diesel fuel has been increased up to two fold in the last few decades [Ramachandra et al., 2011] in India. For increment in GDP and to decrease transport cost, Indian government has put subsidies on petroleum diesel fuel, due to which gasoline cost is 2.5 times greater than diesel.

1.5 Biofuel policies and production in various countries

Though biofuels are one of the most suited alternative sources for fossil fuels, they are more expensive as compared to fossil fuels. Production of biofuel in various countries around the world has increased by encouraging biofuel policies and its global production which is evaluated to be above 35 billion litres [COM, 2006] by 2020. Biofuel policies play significant role in progress of energy sector. Brazil is the only country which has succeeded in production and use of biofuels. The reason behind that is Brazilian government has initiated world's first biofuel policy to expand ethanol as a fuel and its blending with gasoline. In case of United States, current production of ethanol is up to 49.2 Bnl and that of biodiesel is up to 3.7 Bnl but target is 36 billion gallons of biofuels by 2022 [Blanco et al., 2010]. Recent production of ethanol is 22.7 Bnl with biodiesel production of about 2.5 Bnl in case of Brazil, mandate for ethanol is blending of 20-25% and mandate for biodiesel sets at 5% from 2010, with a proposal to enhance it up to 10% by 2020 [Sharma and Singh, 2009]. As compared with United States and Brazil,

developing countries like China and India have different mandate depending on biofuel policies and current production. In China, target is set up to 12.7 Bnl ethanol and 2.3 Bnl biodiesel by 2020 which are much higher than current production that is 2.3 Bnl ethanol and 0.6 Bnl biodiesel. India produces 1.08 Bnl ethanol while 0.24 Bnl of biodiesel, mandate will be blending up to 20% for both ethanol and biodiesel by 2017 [Blanco et al., 2010].

US Energy Information Administration (EIA) displays that in the year 2013, leading nations in biofuel production were U.S followed by Brazil, Germany, Argentina, France and China. Rest individual nations had produced less than 3% of biofuels [BP Statistical Review of World Energy, 2013]. Biodiesel production continuously increases every year and in future it may become main biofuel resource produced worldwide [Biofuels Knight, 2010]. There is gradual increment observed in biodiesel production from 1991 onwards. In the year 2005, global biodiesel production was 995 million gallons which rose up to 5,670 million gallons in 2012 [Licht, 2012]. According to 2014 world market outlook, USA is the highest biodiesel producing country with its production of 14.3% while Brazil produces up to 11.3%, Germany 9.4%, Indonesia and France produce 8.6% and 7.8% respectively [Merchant research and consulting ltd., 2014]. India does not figure in this list. Global biofuel production has been drastically expanding over the last few decades but extending industries based on biofuel have recently made important concerns.

1.6 India's biodiesel policy and its features

The Government of India approved India's National Biofuel Policy in July, 2009 and the announcement of this policy has been made in December 2009. The policy countenances appliance of renewable fuel as a substitute to fossil fuels and reach up to

20% biofuel mandate by the end of 12th Five Year Plan (2017). Features of India's Biofuel Policy are mentioned as follows [GOI, National Policy on Biofuels, 2009]:

i. Use of nonedible feedstock to derive biofuel that can utilize wastelands which are unsuitable for agriculture purpose.
ii. To accomplish the energy demands of India's rural population by enhancing rural development and generating employment opportunities with considering global concern.
iii. To strengthen the energy security of India by promoting use of renewable source of energy as a fuel and
iv. Bring the biofuels under the circumference of Declared Goods by the Government of India (GOI) to ensure about their restriction, etc.

Intervene target by 2007-2008 of blending up to the 5% and 10% of bioethanol and biodiesel respectively have not been accomplished. The reason assigned is non availability of adequate raw materials.

In India, diesel requirement is five times more than that of the gasoline. India's recent technology developed for biodiesel production is based on transesterification of oils and fats. As there are crises of edible oil, it is very difficult to use edible oils as feedstock for biodiesel production and hence government of India decided to utilize non edible oil obtained from various sources. Recent biofuel policies are based on expanding renewable energy usage in transportation sector as well as diminishing fossil fuel dependency with decreasing greenhouse gases [GOI, National Policy on Biofuels, 2009].

The new Indian administration considers an increment in Government of India's (GOI) mandate for ethanol blending from the current status of 5% to 10% in 2015. Currently, in India, oil and coal contributes up to 66% consumption of total primary energy [GOI, National Policy on Biofuels, 2009]. According to Ministry of Road

Transport and Highways, the transportation section considers for 6.4% of India's Gross Domestic Product (GDP), and with that road transportation estimation up to 4.5 percent [Annual Report (MoPNG), 2007]. The Ministry of Environment and Forest describes the growth in transportation with increment in consumption of fossil fuels and holds it responsibility for India's poor air quality. For introduction of biodiesel crops up to the area 1 million square kilometres, Indian Oil Corporation Limited (IOCL) has understanding with Indian Railways. Madhya Pradesh and Jharkhand have tied up with the IOCL to encourage the cultivation of Jatropha in a large area.

1.7 Biodiesel production in India

After United States, China and Japan, India is the fourth greatest consumer of petroleum importing up to 80% of its total requirement. Hence, Government of India has formulated National Biodiesel Mission (NBM) for development as well as for commercialization of biodiesel. After extensive research based on agriculture, it was concluded that for India's biodiesel policy, *Jatropha curcas* oil seed can be used as considerable feedstock. Previously, in India *J. curcas* has been used on small scale as a substitute to diesel in remote areas for many years. But in the policy, it was proposed that to use up to 3 million hectares of wastelands for cultivation of *J. curcas* because *J. curcas* have abeyant to utilize wasteland [Chankya et al., 2012]. The central government and some state governments dispense monetary incentives for promoting plantation of these nonedible oil plants. In India, the commission had marked to cultivate this feedstock plant in the area of 11.2-13.4 million hectares in the year 2011/2012 [Avinash et al., 2014]. But there are numerous problems regarding use of *J. curcas* as its production never achieved level of commercial scale due to unavailability of its seeds, lack of cultivators and improper marketing channels and low productivity. Due to high cost requirement for

cultivation of *J. curcas* and other restrictions, researchers have shifted their focus towards biodiesel synthesis from other nonedible oils obtained from various plants such as *Pongamia pinnata* (Karanja), *Azadirachta indica* (Neem), *Schleichera oleosa* (Kusum), *Madhuca longifolia* (Mahua), Waste cooking oil and Microalgae [Biofuels Annual Report, 2014].

1.8 Problem statement

Expeditious rise in population with industrialization has resulted in energy paucity as well as global warming. According to world factbook in 2014 [The world factbook, 2014], United States, China, Japan, India and Korea are the top five countries in oil import. United States imports 9,213,000 bbl/day of crude oil whereas China, Japan, India and Korea imports 5,664,000; 3,472,000; 3,272,000 and 2,590,000 bbl/day respectively. Oil consumption in these countries are 19,150,000 bbl/day for United States, China consumes 9,400,000 bbl/day. Japan, India and Korea consume 4,452,000; 3,182,000 and 2,195,000 bbl/day respectively. These countries heavily depend on other nations for oil imports; hence it's obligatory to search an alternate fuel source which can reduce this oil demand. This rapid increment in fossil fuel depletion has insisted scientists to look upon alternative source of energy. Biodiesel, a renewable resource of energy is eco-friendly, biodegradable, non-toxic and has potential to replace diesel fuel and fulfil the demand of world energy [Chattopadhyay and Sen, 2013]. Biodiesel exhibits comparable characteristics to diesel and it also shows high cetane number, high flash point, high lubricity and low viscosity [Bari, 2014].

Mostly, homogeneous catalysts are used for biodiesel production through transesterification reaction due to its higher catalytic activity [Sharma et al., 2008]. But, separation of this catalysts from synthesized biodiesel requires washing with large

amount of water which causes loss of fatty acid methyl esters (FAME), additional energy accumulation and produces waste water which increases complete production cost of biodiesel [An et al., 2013]. Therefore, heterogeneous catalysts are supposed to be superior as they can be separated by filtration and can be reused. Selection of feedstock for biodiesel production depends on availability and cost of feedstock. Cost of feedstock is the major problem in commercialization of biodiesel production, since it accounts for ~70–95% of total production cost of biodiesel. Appliance of edible oil for biodiesel production raises energy security issues for developing countries and hence non edible oil has gained attention in recent years, because it lowers cost up to 60-70% and has been environmentally acceptable [Farooq et al., 2013].

1.9 Objectives

The objectives of the proposed studies are as follows:

i. To select suitable feedstock for biodiesel production in laboratory.
ii. To synthesize beta-potassium dizirconate (β-$K_2Zr_2O_5$), barium zirconate ($BaZrO_3$), calcium aluminium oxide ($Ca_2Al_2O_5$) and beta-tricalcium phosphate (β-$Ca_3(PO_4)_2$) as a heterogeneous catalyst.
iii. To characterize the synthesized catalyst by thermogravimetric analysis (TGA), X-ray diffractometry (XRD), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), energy dispersive X-ray spectroscopy (EDS), scanning electron microscopy (SEM), BET surface area and BJH analysis, particle size analysis and basicity.
iv. To study the activity of catalyst for biodiesel production in transesterification reaction by using waste vegetable oil (WVO) and *Pongamia Pinnata* (Karanja) oil.

v. To study the influence of molar ratio (oil: methanol), catalyst concentration, reaction temperature, reaction time, stirring speed and reusability of catalyst.

vi. To characterize produced biodiesel by proton-1 nuclear magnetic resonance spectroscopy (^{1}H NMR) and study of physicochemical properties as per American Society for Testing and Materials (ASTM) standards.