Chapter 1

Introduction and Literature Review

1.1 Introduction

Energy has the most significant impact on nation's economic and social development. Energy describes the ability of an object to do work. Energy cannot be created or destroyed; it can only be changed one form to another form. Energy is categorized into two major classes: kinetic energy and potential energy. A moving object has kinetic energy in form of sound, thermal, radiation, electricity etc. Potential energy is stored in a stationary species in form of nuclear, chemical, gravitational energy, etc. When the species moves, the potential energy transformed in kinetic energy. Potential energy and kinetic energy cumulatively describe the mechanical energy of the system (Asif and Muneer, 2007). The energy resources are categorized into two types: conventional and non-conventional. All non-renewable resources such as coal, petroleum, and natural gases come under conventional energy resources which are also exhaustible; whereas, non-exhaustible renewable resources like solar, geothermal, wind, hydropower, biofuel etc. are included in non-conventional resources (Demirbas and Demirbas, 2010). Till the twenty first century, we are completely dependent on conventional energy resource for fulfilling our energy demand. Growing population and modernization across the globe are intensifying the global energy demand. Fossil fuel reservoirs are going to demolish at the end of this century. Thus, concern about the upcoming future energy crisis and its negative impact on human life and global development has motivated the scientific community to establish the non-conventional sources as the major energy producer for continuous energy supply in future. Though, the renewable sources are the only option for resolving the future energy crisis, but complete substitution of fossil fuels by these alternative fuels is not possible till the date. The challenges of diversifying the renewable energy are low efficiency, complications in large quantity power generation from the sources and high installation cost of power plants (Dincer, 2020).

1.2 Current energy scenario across the globe

International energy agency (IEA-2018) reported that around 83% of world's energy consumption is appeased by non renewable energy sources (Figure 1.1A); which seems that at present, the world energy supply system is highly dependent on fossil derived fuels. Thermal energy need in industrial sector is satisfied by coal which has share of 21% in world's total energy consumption. However, the transportation sector is completely dependent upon petroleum (37%) and natural gas (25%). Globally, nuclear sources are used to generate electrical power, which contributes around 9% of world's total energy consumption. Rest 8% energy is consumed from renewable resources such as solar, geothermal, biomass waste, wind, biofuel, wood, and hydropower. In 2017, total world energy consumption is around 13.5 Gtoe of which only1.4 Gtoe energy is consumed from the renewable resources (BP Statistical Review, 2018). The major contributed renewable resources are hydropower (35%), wood (24%) and biofuel (20%). IEA- 2018 has reported that the dependence on non-renewable resources for energy requisition has increased sharply from 2005 to 2018 (Figure 1.1B). It is also claimed by this agency that at 2040, the dependence on fossil fuel will be intensified around double of 2015 (World energy outlook, 2018). The causes of such devastating incrimination in energy demand are worldwide growing population, industrialization, transportation, economic and social development. The world will be facing severe energy crisis very soon. According to an estimate, the fossil fuel resources will be completely worn out in coming 20-30 years (Rincon et al., 2014).

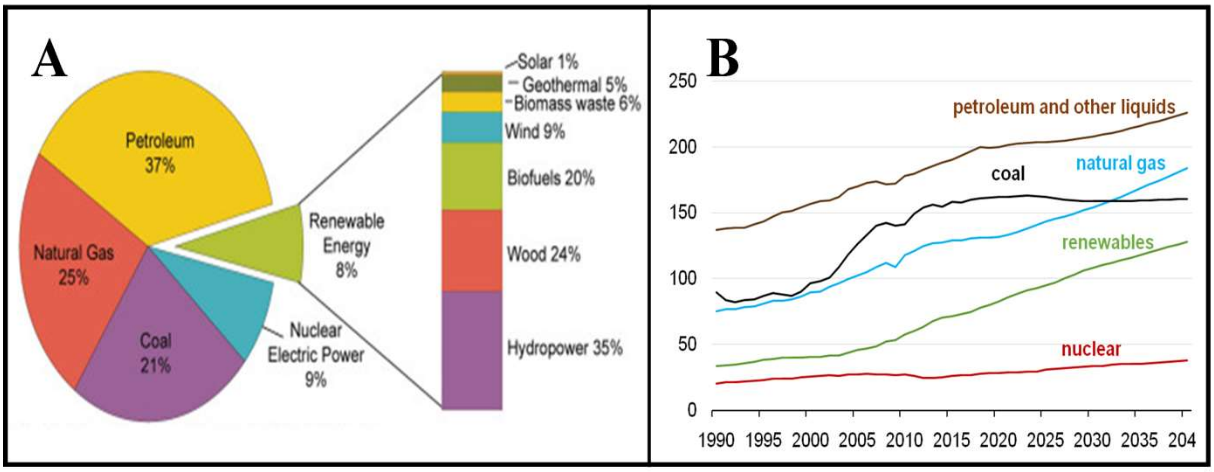

Figure 1.1 A) Global energy consumption in fraction of year 2018, B) Energy consumption from different sources by the years 1990 to 2040 (reference)

1.2.1 Energy crisis

Industrialization, economic growth and growing population have led to raise the global energy demand in every passing year. According to IEA-2019 report, the total world's energy consumption in 2050 will be 911 quadrillion British thermal units (Btu) of which 287 quadrillion Btu will be consumed in countries comes under Organization for Economic Co-operation and Development (OECD), and 624 quadrillion Btu will be consumed in non-OECD countries (World energy outlook, 2019). Since 1990, non-OECD countries have led the world economic growth, accompanied by strong growth in energy demand in those countries. Most increases in energy consumption come from non-OECD countries; where, strong economic growth, increased access to marketed energy and rapid population growth lead to rising energy consumption. Energy consumption in non-OECD countries increases nearly 70% between 2018 and 2050 in contrast to a 15% increase in OECD countries. More than half of the projected increase in global energy consumption occurs in non-OECD Asian countries, a group that includes China and India. These two have been among the world's fastest-growing economies during much of the past decade, and they remain primary contributors to future growth in world energy demand. Energy demand in non-OECD Asia is larger than in any other region in 2018, and it is projected to almost double between 2018 and 2050, making it both the largest and fastest-growing region in the world for energy consumption.

The industrial sector, which includes refining, mining, manufacturing, agriculture, and construction, accounts for the largest share of energy consumption of any end-use sector—more than 50% of end-use energy consumption during the entire projection period. World industrial sector energy use increases by more than 30% from 2018 to 2050, reaching about 315 quadrillion British thermal units (Btu) by 2050. Most of the increase in industrial sector energy use occurs in non-OECD nations. Industrial sector energy use in non-OECD countries grows by more than 1.0% per year in the reference case compared with an increase of 0.5% per year in OECD countries. In 2018, China consumed 29% of the world's industrial energy, and although its energy consumption continues to increase modestly throughout the projection period, its share decreases to 24% by 2050. India's industrial energy consumption nearly triples, growing from 16 quadrillion British thermal units (Btu) in 2018 to 47 quadrillion Btu by 2050 at an average annual rate of 3.4%. India's 31 quadrillion Btu growth in energy consumption from 2018 to 2050 represents 40% of the total world increase of 78 quadrillion Btu (World energy outlook, 2019).

Transportation is the second most energy consuming sector after industrial sector, has shared of 30% in total energy consumption. In non-OECD countries transportation energy demand will be increased around 77% from 2018 to 2050 in the reference case. A few countries, including China and India, have particularly large populations, and their energy consumption for both personal travel and freight movement grows much more rapidly than in many OECD countries. The liquid fuel consumption by the transportation sector in China and India will be enhanced upto 36% and 142%

respectively in between 2015 to 2040. Increases in economic activity, population, and disposable income lead to greater freight movement and passenger travel in non-OECD countries (International energy Outlook, 2019). Transportation energy consumption in non-OECD countries has exceeded that in OECD countries since 2017, and by 2050, non-OECD countries will account for almost 65% of the world's transportation-related energy use. Till the date, the energy supply in transportation sector is running by petroleum and natural gas which have cumulative contribution of 97.6% in the year 2017. The energy consumption rate is projected to increase at a rate of 1.8% per annum in the year 2005 to 2035; however, the liquid fossil fuel is expected to be intensified from 95 million barrels per day (bpd) in 2015 to 113 million bpd by 2040. The World Energy Forum has anticipated that the oil reservoirs will be finished within next 10 decades (International Energy Outlook, 2017). There is no shortcut; only profound changes guided by good policies, can deliver a better energy future. This is a choice for citizens, investors, companies, but most of all for governments (World Energy Outlook, 2020).

1.2.2 Uneven distribution of energy resources

The conventional energy resources such as coal, petroleum, natural gas, etc. are scattered unevenly over the globe. Some countries are enriched by natural resources, and some countries have nothing. Deposits of fossil fuels depend on the climate and organisms that lived in that region millions of years ago, and the geological processes that have since taken place. For instance, while coal reserves are found in every country, the largest reserves are found in the United States, Russia, China, Australia, and India. Millions of years ago, these areas were lush, swamp forests with many trees that provided the organic material to make coal. Oil and natural gas are also found worldwide, but most of the oil and natural gas reserves are in Saudi Arabia, Russia, the United States, and Iran. The uneven distribution of oil and natural gas reservoirs are shown in Figure 1.2. More than

50% oil reservoirs are present in Middle-East Asia and North Africa; however, near about 40% of natural gas reservoirs are existed in Russia and the former Soviet Union states (Asif and Muneer, 2007). 73% of fossil fuel reserves are found in OPEC countries and roughly 25% natural resources are found in North America. The total proved oil reserves are estimated to be 1696.6 thousand million barrels, of which 47.6% is existed in Saudi Arabia, UAE, Kuwait, Iran, and Iraq. The natural gas distribution is quite even compared to oil distribution. This uneven distribution of fossil fuels creates socio-economic disturbance, dominance and price instability internationally (BP Statistic review. 2018; Shafiee and Topal, 2009).

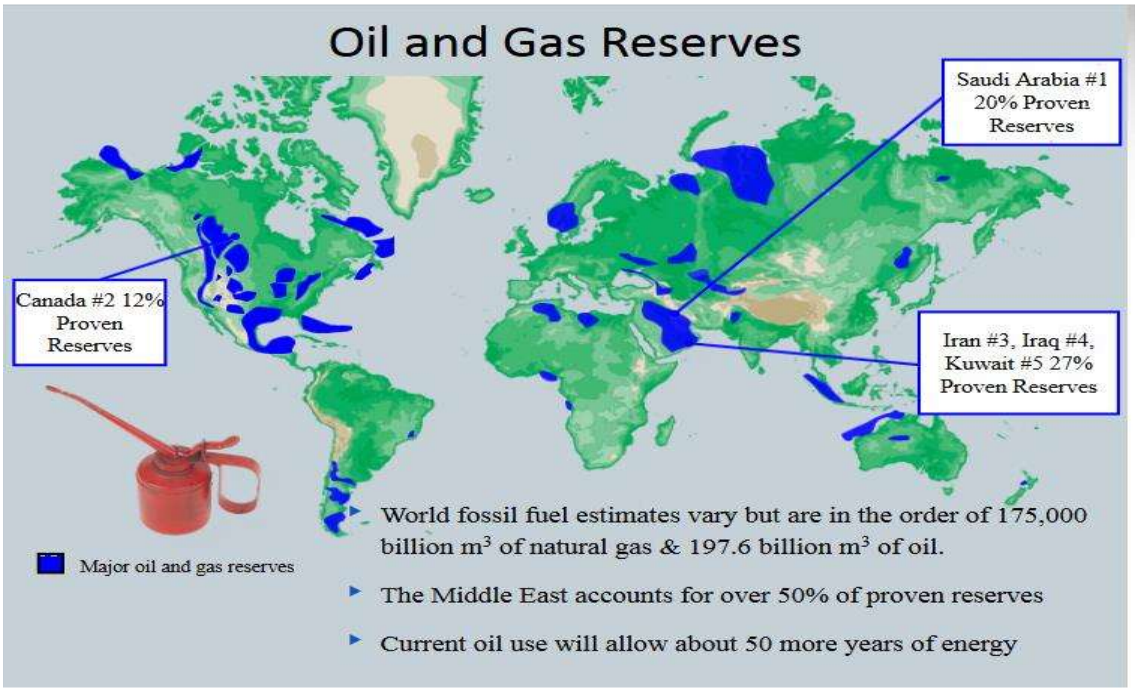

Figure 1.2 Distribution of oil and gas reserves over the world

Growing energy demand, fast depletion of fossil reserves, and hike in prices of petroleum are associated additionally with the concern of future energy crisis and global climate change, are knocking the world to look for its permanent solution. Renewable energy is the only option to sustain with the continuous energy supply; moreover, the renewable resources are diversified and more evenly distributed throughout the world, so, it will definitely help in unanimous energy supply in all countries (Bilen et al., 2008).

1.3 Current energy scenario of India

India's economy, world's third largest, is growing rapidly after China. Most importantly, India's development ambitions stand on energy. For Socio-economic development, different forms of energy are required in different sectors like industrial, transportation, rural infrastructure, household, etc. Very soon, India will be the most populous country around the world and left behind China. In consequence, energy demand is increasing with increasing population. India's energy requirement has almost doubled since 2000 and there has enormous potential for further rapid growth. IEA (2017) has predicted that India's energy demand will be increased upto 51% by the year 2040 (Figure 1.3A). 80% of total energy demand is satisfied by the non renewable resources. Surging consumption of coal in power generation and industry makes India, by a distance, the largest source of growth in global coal use. Oil demand will be increased from 4.1 million barrel per day (mb/d) to 10 mb/d by 2040. India produced 0.9% crude oil but consumed 4.5% of world's total oil demand in year 2014 (Figure 1.3B). The transportation sector in India is completely dependent on imported oil which is mostly comes from Saudi Arabia, UAE and Iran. India stands at the third position in world as largest importer of crude oil as well as consumer behind US and China. India is also deploying a range of more modern bio-energy applications, relying mainly on residues from its large agricultural sector. There was around 7 GW of power generation capacity fuelled by biomass in 2014, the largest share is based on biogases (a by-product of sugarcane processing) and a smaller share is cogeneration based on other agricultural residues. Although modern bio-energy constitutes only a small share of energy use at present, Indian policy has recognized with the launch of a National Bio-energy Mission, the potential for modern bio-energy to become a much larger part of the energy picture especially in rural areas, where it can provide a valuable additional source of income to farmers, as well as power and process heat for consumers. Biofuels are another area of bio-energy development in India, supported by an ambitious blending mandate, dating back to 2009, that anticipates a progressive increase to a 20% share for bio-ethanol and biodiesel by 2017. Implementation has thus far been slower than planned: the present share of bio-ethanol – mostly derived from sugarcane – remains well under 5% and progress with biodiesel has been even more constrained. The main concern over biofuel and some other forms of bio-energy is the adequacy of supply: land for biofuels cultivation can compete with other uses, as well as requiring water and fertilizers that may be limited and is required in other sectors (India Energy outlook, 2015).

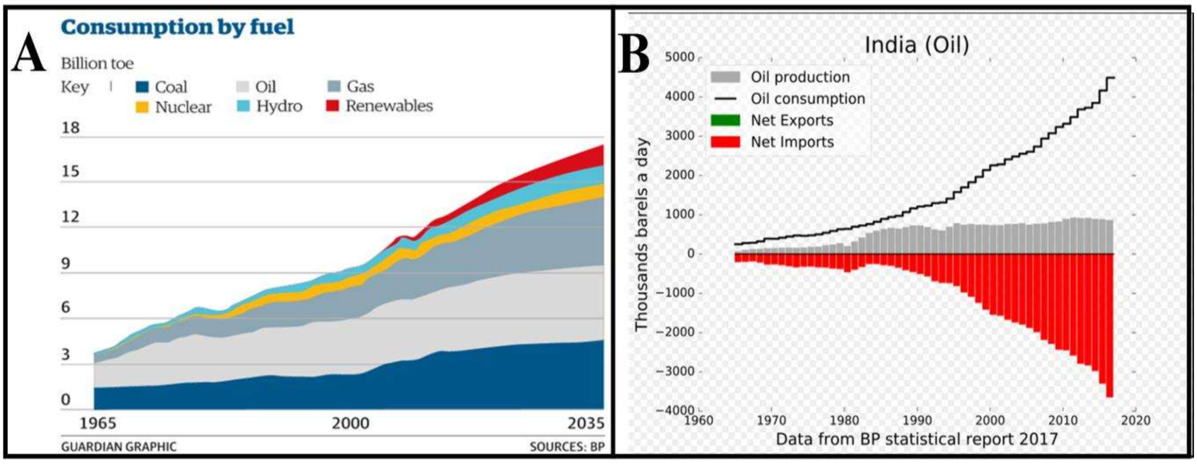

Figure 1.3 A) Energy consumption from different sources in India, B) Report of produced oil, imported oil, and consumed oil per year till 2017 in India

1.4 Environmental pollution

Both OECD and non-OECD countries fulfill their energy requisition from exhaustible non renewable fossil fuels. The combustion of these fossil fuels for heating, electricity production, transportation, etc. causes primary air pollution. Carbon dioxide (CO_2) is the major pollutant emitted due to burning of fossil derived fuels. Alongwith carbon dioxide, carbon monoxide (CO), nitrogen oxide (NO_x), sulfur dioxide (SO_2), particulate matter

(PM10 and PM2.5), and volatile organic compound (VOCs) are emitted during the combustion of fossil fuels. These emissions are responsible for air pollution, global warming, green house effect and acid rain (Demirbas, 2009). The transportation sector, itself emitted 28% share of global green house gas emissions in 2010 due to combustion of liquid fossil fuel. Fossil derived diesel used in transports causes greater NO_x and other hazardous gas emission which creating serious respiratory problem in human lungs (Perera, 2016). Globally, the carbon dioxide emission is increasing at an alarming rate. Global Carbon Budget has reported 9.9 billion metric tons of CO_2 was released in year 2016; moreover, it is projected to be increased 2.7% by the year 2017. It is also estimated that 43% increment in CO_2 emission will be possible in between 2020 and 2035, which accounts 8.6 billion metric tons of CO_2 that can be released to the atmosphere (Friedlingstein et al., 2014). Using fossil fuel, the atmospheric CO_2 concentration is intensified from 383.79 ppm in 2007 to 406.55 ppm in 2017 (Global Carbon Budget, 2018). As per IEA report, China, U.S and India are top three CO_2 emitter countries in the world (Global Energy and CO_2 status, 2019). In the near term, energy-related CO_2 emission growth is slowed by increasing in energy efficiency and a gradual shift from coal toward natural gas and renewable energy sources. China’s liquids-related CO_2 emissions grow at a decreasing rate as growth in the country’s population slows. From 2030 to 2050, China and U.S. liquids-related CO_2 emissions levels will be similar. However, India experiences continuous growth in liquids-related CO_2 emissions as its economy expands, although it starts from a lower level. By 2030, India’s emissions exceed those in OECD Asia and non-OECD Europe and Eurasia (World energy Outlook, 2019).

1.5 Non conventional or Renewable energy

Renewable energy, fastest growing sources for energy requisition in world, is referred as clean energy acquired from natural sources which can be replenished for short duration. It will become the leading source for primary energy consumption by the year 2050. Renewable energies are utilized in electricity generation, heating and cooling process in industry and transpiration. Renewable resources have greater impact on nation's energy security and economic stability; moreover, through developing the renewable energies, new industries can be set up, more jobs can be created, rural development can be boosted, local pollution can be reduced, reliable and affordable energy can be supplied for all citizens. Driven by electricity demand growth and economic and policy drivers, worldwide renewable energy consumption increases by 3% per year between 2018 and 2050 (International Energy Outlook, 2019). Renewable energy is found as various forms namely solar, wind, hydro, geothermal and biomass (Bull, 2001); however, most the renewable energies come either directly or indirectly from sun (Bilgen et al., 2008). Globally, biomass, is one of the important renewable resources for energy production, which countering around 24% of total energy demand (International Energy Agency, 2016). By traditional use of biomass (cooking and heating), 8% energy of total is consumed from wood, dry leaves, and agricultural waste. Modern bio-energy supplies 6% heat demand in industry, 4% heat demand in buildings, 3% liquid fuel demand in transportation and around 2% energy demand in global electricity generation. Biomass can be derived from forest, agricultural field, fishery waste, poultry waste, municipality waste etc. They may be found as solid like wood, charcoal, wood pellets, etc; or they may be liquid like bioethanol, biodiesel, biobutanol etc; or even they can be gas also. The liquid form of biomass is known as 'Biofuel' used to meet the transportation fuel needs; however, the gaseous form biomass is known as 'Biogas' used fuel in heating appliances

(Goldemberg, 2006). Biofuel and biogas can be generated from solid biomass by using different technologies. Worldwide growing liquid fuel demand, fast depletion of oil reserves and high fuel pricing have forced to look the long term alternatives. Biofuels are the only options for being alternative of liquid fossil fuels. Moreover, biofuels has number of advantages mentioned below:

- Biofuels are easily produced from natural abundant biomasses like waste vegetable oils, inedible oils, animal fats, etc.
- They all are carbon neutral.
- Using biofuel as primary energy source has no energy insecurity in future.
- These are non hazardous, bio-degradable and more eco-friendly.
- They can reduce green house gas emissions.
- There have many benefits in industrial development, economic growth and pollution control if the focus shifts from fossil fuel to biofuel.

To being price sensitive and reliable for the customers, biofuels development relies strongly on polices or mandated of government and administrative body of the nation.

1.6 Global biodiesel polices

Future energy crisis is a serious upcoming global issue which can be resolved by boosting interest for acquiring energy from non renewable resources to renewable resources. Among the renewable resources, biofuel is the only substitute of fossil derived liquid fuels in transportation sector, contributes around 2% of global energy demand which can be scale up to satisfactory level by enforcing policies and investing money and time. Nowadays, many countries across the globe have already implemented strict policies regarding energy management and escalation of biofuel production along with other renewable energies.

Recently in 2017, USA has updated the National Biofuel policies under *Energy Independence and Security Act of 2007*. Now the target is set to produce 36 billion gallons of biofuel by 2022. To boost the interest of citizen for acquiring blended biofuels, Government has announced additional subsidies and tax relaxation; moreover, the dependency on oil for transportation fuel is expected to be reduced upto 20% in next 10 years.

In the biofuel policies of EU, one of the targets specifies that 10% of final energy consumption in transportation sector must be met by biofuels by 2020, and it is expected to be fulfilled by the first generation biofuels. In 2018, EU imported 7.7 million tons of palm oil, of which around two third was employed in biodiesel production.

The biofuel development in Indonesia started from 2006 with the presidential mandates on biofuel supply and utilization. Onward 2025, Indonesia has set a target to increase the blending in transportation fuel upto 30% by biofuels. The increase of 10-15% biodiesel blending in transportation and industrial uses, and 25% blending in electricity production are mandatory clauses in their current biofuel policies (Kharina et al. 2016).

Brazil has the most integrated and successful biofuel program in the world. The National Program on Biodiesel Production and Usage (PNPB) was inaugurated in 2005, which has initially required 2% of petrol based diesel to be replaced by biodiesel from 2008 to 2012 and increase to 5% from 2013 onwards (Colares, 2007). Currently, this requirement is enhanced upto 10% in March of 2019 (Sorda et al., 2010).

The Chinese biofuel policies highlight more on ethanol production, which have resulted China becoming world's third largest ethanol producing country. Currently, China produces 3 billion liter of ethanol and 1.14 billion litter of biodiesel from their indigenous resources (Dyk et al., 2019).

The energy strategy of India targets at efficiency and security. The ongoing plans are focusing on development of renewable resources (mainly solar, wind and biofuel) for energy supply, and achievement of an optimum mix of primary resources for energy generation. India brought the first National Policies on Biofuels during 2009 aiming 20% blending of biodiesel with petrodiesel by the year 2017. In 2018, the policies have been improvised with associating with the ongoing initiatives of the Government such as Make in India, Swachh Bharat Abhiyan, and Skill Development. The salient features of the approved 'India's National policy on Biofuel, 2018' are

- The policy classify the biofuels generation wise like bioethanol and biodiesel are included in 1^{st} generation or 'Basic Biofuels', ethanol, municipal fuel derived from Solid Waste are categorized as 2^{nd} generation biofuel or 'Advanced Biofuels', and Bio-CNG is considered as 3^{rd} generation biofuel.
- This policy encourages expanding the variety of raw materials for ethanol production. Sugar containing materials like sweet sorghum, sugar beet, etc., starch containing materials including damaged food grains, rotten potatoes, etc., which are unhealthy for human consumption can be used as raw material for ethanol production
- To reduce the stress of farmers for not getting appropriate price at surplus production phase, the policy allows surplus food grains as raw material for ethanol production.
- Showing thrust on 2^{nd} generation biofuels, the policy proposes to provide the financial support along with tax incentives, higher purchase price that of bioethanol, etc. to the 2G ethanol bio-refineries.
- The policy initiates to scale up biodiesel production from short gestation crops, non edible oilseeds, Used Cooking Oil by developing supply chain mechanism.

- The policy documents the role and responsibilities of concerned authorities to synergies the efforts.

The expected major benefits of this ongoing Biofuel Policies are

- **Reduce Import Dependency**: current rates, 1Cr liters of E10 (10% ethanol blending) can save Rs.28Cr of forex. In 2017-18, 150Cr liters of ethanol was used which approximately saved Rs.4000Cr of forex.
- **Cleaner Environment**: around 20,000 ton of CO_2 emissions can be reduced by using 1Cr liter of E10. During 2017-18, 30 lac tons of lesser CO_2 was emitted because of using ethanol as fuel, reducing crop burning and conversion of agricultural residues or wastes to biofuels.
- **Health benefits**: Prolonged reuse of Cooking Oil is unhealthy for human consumption. In India 220Cr liters of Used Cooking Oil is produced per year, which can be used as potential feedstock for biodiesel; this can prevent diversion of used cooking oil in the food industry.
- **MSW Management**: annually 62 MMT of Municipal Solid Waste is generated in India. This amount of MSW can be dropped to fuel imposing appropriate technologies. One ton of MSW causes around 20% of drop in fuels.

Rural development, urbanization, employment generation, and diversion of agricultural economics into new market are the additional benefits of the current Biofuel Policy of India.

1.7 Biodiesel as a supplementary of petrodiesel

Chemically, biodiesel is a mixture of alkyl esters of long chain fatty acids derived from vegetable oil, non edible oil, algal oil, waste cooking oil and animal fats. Worldwide, biodiesel gets more attention as a substitute of diesel owing to following characteristics (Sharma et al., 2008):

- Biodiesel can be produced from renewable resources, thus, there has no insecurity for continuous energy supply.
- It is oxygenated fuel which means complete combustion increase the energy output.
- It is carbon neutral because the carbon dioxide emitted has been reabsorbed by the plants grown for feedstock production.
- Non hazardous, biodegradable and non toxic nature of biodiesel make it cleaner and greener fuel compare to diesel fuel.
- High flash point and high fire point of biodiesel provide the handling safety.
- Emission of carbon dioxide and other exhausting gases are lower in case of biodiesel compare to diesel; moreover, biodiesel has sulfur free emission.
- Biodiesel has around 90% energy efficiency (or calorific value) of petrodiesel.

Due to limited resources and increasing consumption, most of the non OPEC countries import oil from oil producing countries to fill the gap between production and requirement. If these countries have enough resource to produce biodiesel and have strict governmental policies for biodiesel, then the dependency on oil rich countries will be lessen as well as it can better the country's economy. Biodiesel can reduce the dependency on petrodiesel alongwith reducing environmental issues like air pollution, fast deduction of non renewable oil resources and global warming. Globally, biodiesel is accepted as the best substitute of petrodiesel owing to its numerous benefits and importance. Day by day, biodiesel production is escalated from 1 billion liter in 2001 to 34.08 billion liters in 2016, and 39.30 billion liters is projected in 2027. Worldwide, major biodiesel producing countries are European Union (37.01%), USA (18.22%), Brazil (9.68%), Indonesia (9.24%) and Argentina (7.8%) in 2016. These all countries have invested a significant amount of their economy to establish the biofuel production hubs; thus, in near future, these will be key players for global biodiesel market (Global Biofuels Market Outlook Report, 2018).

1.8 Technologies for biodiesel production

The unsaturated fatty acid content is found in higher level in vegetable oils and animal fats and this unsaturation causes high density and viscosity. The problems like injector needle sticking, carbon deposition, chocking, contamination, smoke formation etc. are come out when these highly viscous oils or fats directly used in engine. So, some chemical and thermal procedures are used to reduce the viscosity of the feedstocks, and turned to be compatible for existing engines. In literature, four methods for biodiesel production have been mentioned (Figure 1.4) as direct blending, thermal cracking or pyrolysis, microemulsion and transesterification (Abbaszaadeh et al., 2012).

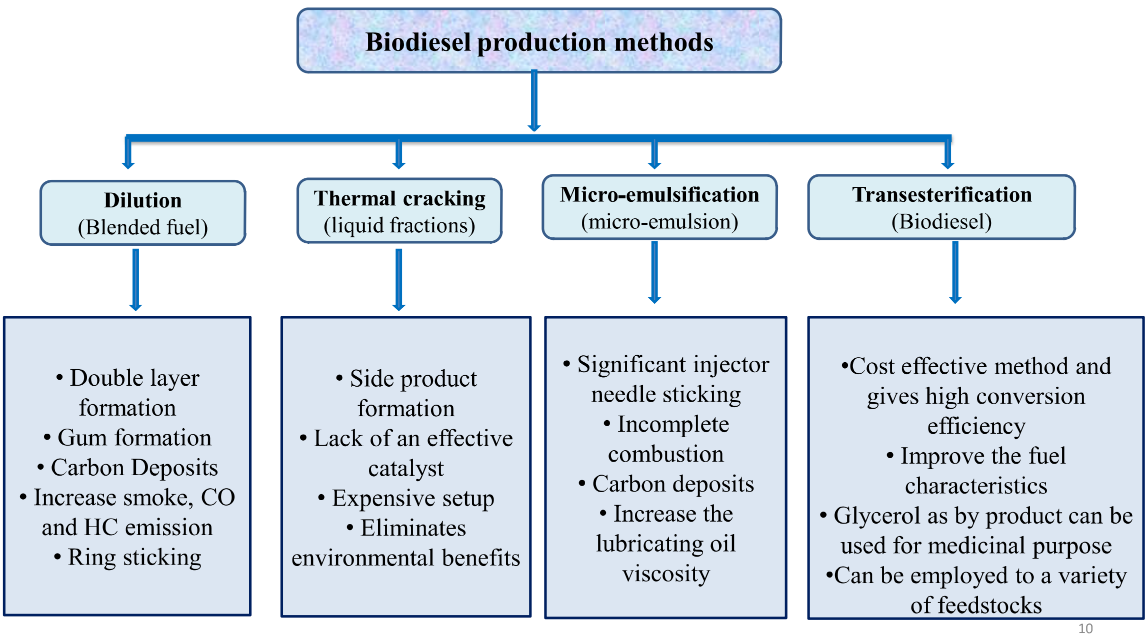

Figure 1.4 An illustration of biodiesel production methods

1.8.1 Direct blending

It is an outdated method in which viscosity of vegetable oil is reduced by blending with petrodiesel for using in CI engine. In 1890, Rudolf Diesel first tested pure peanut oil as biofuel for CI engine, but unfortunately, he failed due to unaware of the facts regarding role of physicochemical properties of vegetable oil. Low volatility, high viscosity, corrosion by the acidic components, etc. associated with vegetable oils were the key reasons for failing the experiment (Lin et al., 2011). The viscosity of vegetable oils is 10 to 20 times more than diesel. So, to reduce the viscosity, vegetable oil was diluted with diesel, solvent or ethanol. Blending was effective for short-term experiments but for long-term experiment it was not accepted as a practical method because of several issues like carbon deposition, double layer formation, oxidation and polymerization during combustion and storage (Ma and Hanna, 1999).

1.8.2 Thermal cracking

Thermal cracking or pyrolysis is a thermo-chemical process in which organic substrates are decomposed by application of heat in inert atmosphere. The larger molecules of organic matters are converted into simple molecules including gaseous fraction, liquid fraction and solid residue (French and Czernik, 2010). During pyrolysis, the following reactions are taken place: dehydration, decarboxylation, atomization, cracking, aromatization, alkylation, condensation and polymerization. Triglyceride of long chain fatty acids present in vegetable oil and animal fat is thermally cracked into small hydrocarbons like alkanes, alkenes, alkadienes, carboxylic acids, aromatics, etc. These pyrolyzed products have low viscosity and density which improve the cetane number and flow character of the fuel. Demerits of this process include high set up cost, high utility cost, additional equipment cost for distillation and production separation (Fukuda et al., 2001).

1.8.3 Microemulsion

This process is a potential solution to mitigate the extent of viscosity of feedstock. Microemulsion is defined by IUPAC as '*dispersion made of water, oil, and surfactant(s) that is isotropic and thermodynamically stable system with dispersed domain diameter varying approximately from 1 to 100 nm, usually 10 to 50 nm*' (Arpornpong et al., 2014). For biodiesel production, an emulsion of three components namely oil, solvent, and surfactant are prepared with prominent proportion. Smaller alcohols like methanol, ethanol, propanol and their alkyl esters are used as additives for lowering the viscosity. Higher alcohols like butanol, hexanol, etc. are used as active surfactants (Balat and Balat, 2010). Explosive vaporization of low boiling constitutes during micelle formation improves the spray character; however, cetane number is improved by using alkyl nitrates as additive. Prolonged usage of microemulsion causes problems like injector needle sticking, incomplete combustion, and carbon deposition (Zhang et al., 2003).

1.8.4 Transesterification

In 1937, a Belgian inventor proposed that triglycerides present in vegetable oils could be converted in alkyl esters of fatty acid by using transesterification process. Worldwide, it is accepted as the best method for biodiesel production because of its reliability, efficiency, good product quality and low production cost. In the transesterification reaction, stoichiometrically one mole of triglyceride reacts with three moles of alcohol and produces three moles of fatty acid alkyl ester and one mole of glycerol (Figure 1.5a). When methanol is used as alcohol then fatty acid methyl esters are formed as product called FAME. In literature, it is proposed that transesterification reaction occurs into three consecutive reversible reactions (Figure 1.5b); triglyceride to diglyceride formation, diglyceride to monoglyceride formation and monoglyceride to glycerol formation, producing one molecule of alkyl ester in each step (Mulzar, 1992).

Transesterification is not thermodynamically favored reaction, so, to make it kinetically favorable, catalyst or critical reaction condition is necessarily required which has been externally provided. Thus, on the basis of this requirement, transesterification is classified into two categories: catalytic transesterification and supercritical or no catalyst transesterification. The catalytic transesterification requires an efficient catalyst and moderated reaction condition; however, supercritical reaction needs high temperature and high pressure which increase the utility cost as well as equipment cost. So, in present, researchers as well as industries prefer more the catalytic transesterification for biodiesel production (Lin et al., 2011).

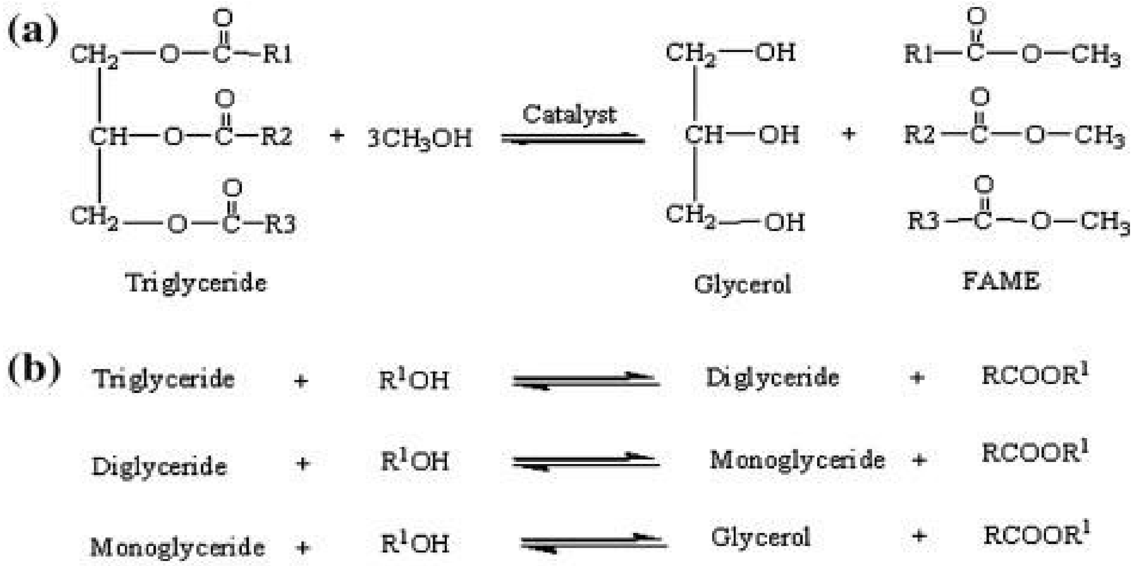

Figure 1.5 a) Transesterification of triglyceride, b) General representation of transesterification reaction of triglyceride

Biodiesel production via transesterification is more beneficial among the other methods in terms of improved physicochemical properties and fuel qualities such as density, viscosity, cetane number, calorific value, fire point, flash point, etc; moreover, production of high quality glycerol as byproduct is more profitable for industry.

1.9 Raw materials used for solid-base transesterification

1.9.1 Alcohol

Alcohol is an important ingredient for biodiesel production via transesterification reaction. It acts as solvent as well as acyl accepter which interacts with the carbonyl carbon of the triglyceride. Generally, small alcohols like methanol, ethanol are used in this process. Other long chain alcohols like propanol, isopropanol, butanol, hexanol, etc. are avoided poor reactivity and high cost. To mitigate the steric problem short chain alcohol, methanol and ethanol are commonly used for biodiesel production (Musa, 2016), but among these two, methanol is extensively used because of its low price, wide abundance and advantageous physicochemical properties like high polarity, smallest size in alcohol family, and low boiling point (Verma et al., 2016). Methanol gets easily dissolve the alkali catalysts and reacts with verity of feedstocks (Sanli and Canakci, 2008)

1.9.2 Lipid feedstock

In literature, the lipid feedstocks used for biodiesel production have been categorized in three generations on the basis of their sources and level of development (Figure 1.6). The first generation feedstocks include vegetable oils like palm oil, sunflower oil, rapeseed oil, soybean oil, peanut oil, corn oil, etc. (Silermarinkovic et al., 1998). Initially, these edible oils were only sources for biodiesel production; in fact these are still utilized for more than 95% global biodiesel production. According to report on Biofuel Outlook

(Alizadeh, 2020), 31% of total biodiesel production is accompanied from palm oil followed by soybean oil (27%) and rapeseed oil (20%). Western world is mostly uses first generation feedstocks because the western countries are enriched by the natural sources and also due to low population, demand of vegetable oils is not so high. However, highly populated countries in middle-east and south-east Asia like China, India can't fulfill their demand without importing oil from other countries. So, biodiesel production from edible oil is not suitable for these countries but utilization of non edible oils which come under second generation feedstock, is preferred as they do not compete with food. Hence, application of non edible oils like jatropha oil, castor oil, mahua oil, etc. and waste cooking oil as feedstock is appreciated throughout the world. Non edible oil plants can grow in short time and harsh condition. They can be even cultivated in wasteland with maintenance cost (Canakci, 2007). So, biodiesel production from non edible oil can cause the agricultural and rural development alongwith additional benefits of green belt on wastelands (Singh and Singh, 2010; Canoira et al., 2006). The lipid extracted from microalgal biomass gets attention as third generation feedstock. Microalgae are non food material, fast growing and reduce wasteland surface but using algal oil as feedstock in biodiesel production has many challenges like bacterial contamination, advanced processing etc.

In case of India, industry level biodiesel production from first generation feedstock and third generation feedstock are not a good idea; thus, the only option left that is non edible oils. Initially, India started with jatropha oil biodiesel production but that was not either cost effective or efficient compare to diesel. India's current biofuel policy encourages using waste cooking oil and non edible oils for biodiesel production. Among the non edible oils, castor oil is a potential feedstock in Indian subcontinent. So, in this present study, waste cooking oil and castor have been selected for biodiesel production. Figure 1.7 shows the advantages to choose waste cooking oil and castor oil as feedstock.

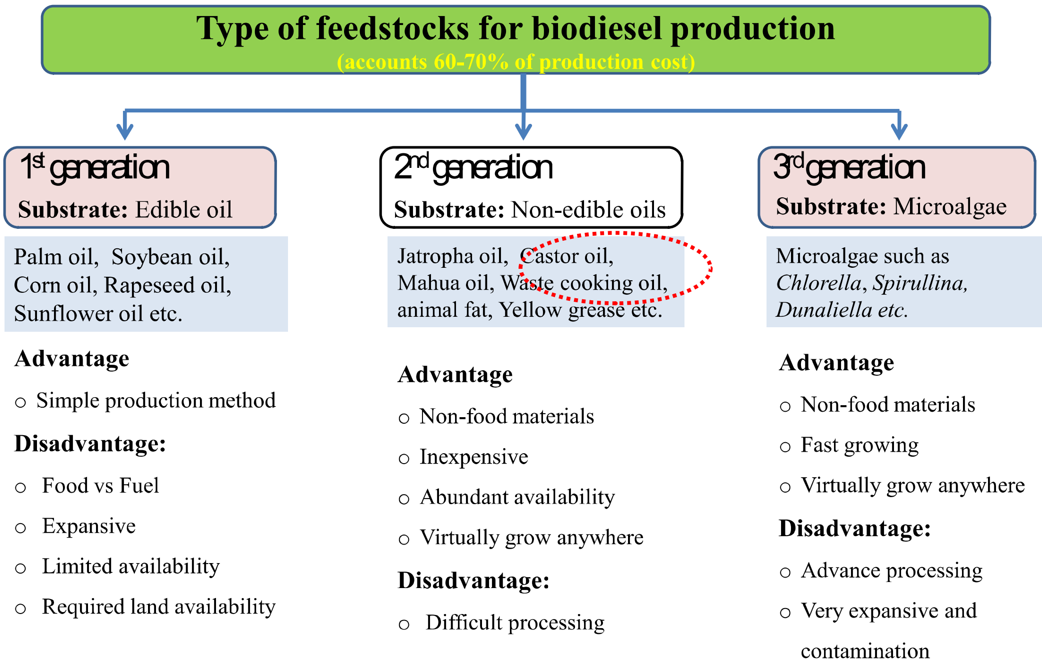

Figure 1.6 Types of feedstocks for biodiesel production

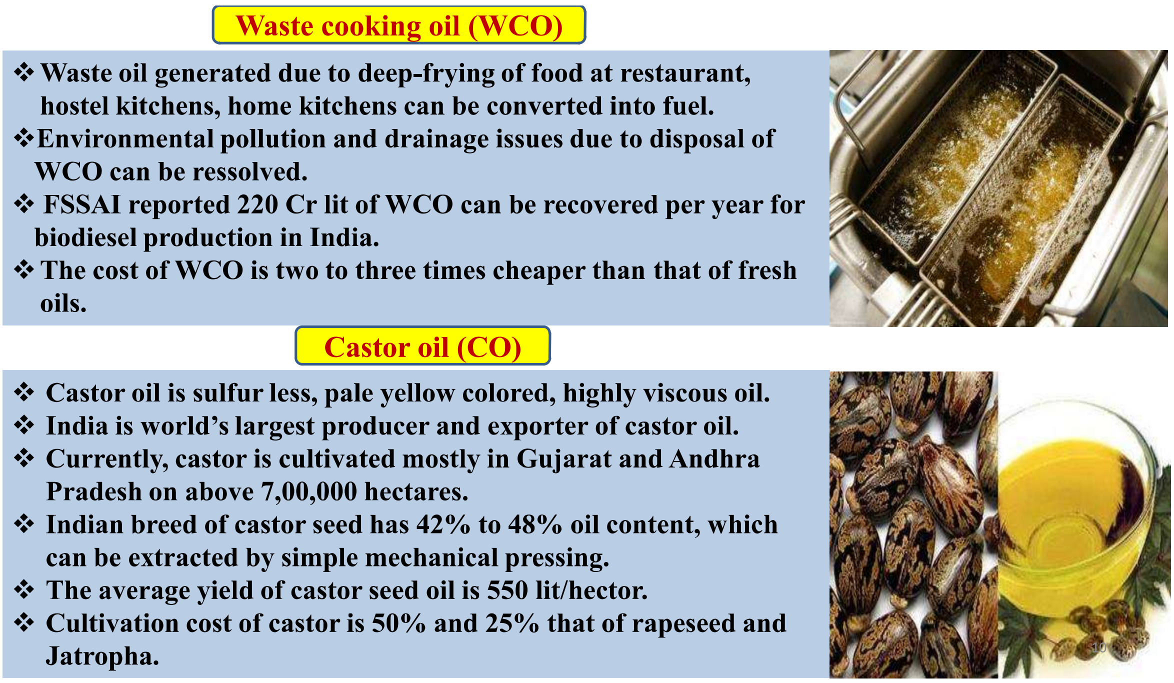

Figure 1.7 Advantages of choosing waste cooking oil and castor oil for biodiesel production in India

1.9.3 Catalyst

Catalyst plays the important role to make the reaction feasible. Transesterification reaction cannot be driven swiftly without catalyst as it is not thermodynamically feasible. Catalyst adopts a new pathway of lower activation energy, so that the reaction can proceed smoothly in forward direction. Catalyst increases rate of the reaction and triggers the process to be completed within a definite time. In literature, homogeneous, heterogeneous and enzymatic catalysts are reported for transesterification of triglyceride. Figure 1.8 shows the advantages and disadvantage of catalytic transesterifications and supercritical transesterification.

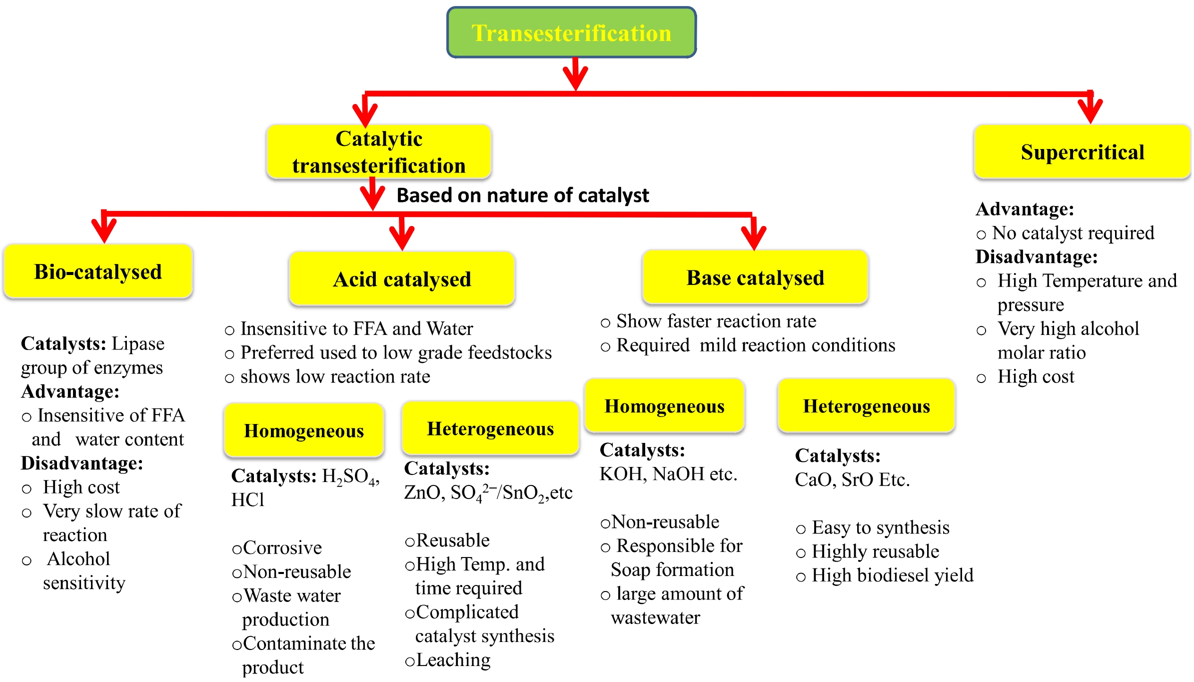

Figure 1.8 Advantages and disadvantages of different types catalytic transesterifications and supercritical transesterification

1.9.3a Homogeneous catalyst

Homogeneous catalysts are highly efficient because of their existing phase is similar to that of substrate. Due to miscible characteristic of catalyst, interaction between substrate and catalyst becomes easy and effective (Dash, 2020; Sahani et al., 2018; Sharma et al., 2008). Nonetheless, using homogeneous catalyst is associated with various demerits like tedious phase separation (product/catalyst), prolonged procedure, high production cost, large amount of waste water generation, etc. Homogeneous base catalysts like KOH, NaOH, CH_3ONa, etc. are used while H_2SO_4, HCl, H_3PO_4 etc. are applied as homogeneous acid catalyst in transesterification of triglyceride as discussed in Table 1.1. Till the date, homogeneous base catalysts are extensively used in commercial scale biodiesel production. This is due to easy availability, low cost, high conversion rate and high yield at moderate reaction conditions (Narasimharao et al., 2007).

1.9.3b Heterogeneous catalyst

Heterogeneous catalysts are preferred over homogeneous catalysts owing to their reusability and high endurance capacity. Like homogeneous catalyst, this also subcategorized as heterogeneous acid and base catalyst (Sahani and Sharma, 2018). Heterogeneous acid catalysts are advantageous over heterogeneous base catalysts for transesterification of low-quality feedstocks having high free fatty acid content (Gomes et al., 2008). In literature, various inorganic and polymeric solid acids are reported as efficient catalysts for biodiesel production from non edible oils and waste cooking oil (Table 1.1). Generally, non edible oils contain high free fatty acids which can be simultaneously converted into methyl esters along with conversion of triglycerides by using heterogeneous acid catalyst. Due to high activation energy of the acid catalysts require high temperature and prolonged time. In addition, cost and meager activity are the major drawbacks of these catalysts. Heterogeneous base catalysts are highly efficient, follows green reaction pathway, non corrosive, reusable, and cheap; moreover, these counter the disadvantages associated with acid catalysts. They are comparatively 4000 times more active than heterogeneous acid catalysts in transesterification reaction (Lee et al., 2014). Considering merits and demerits regarding heterogeneous acid and base catalysed transesterification, the research fraternity has admitted that development of highly active, reusable, stable, environmentally safe and cheaper heterogeneous base catalyst for biodiesel production is essential and it will be the fascinating area for the new comers (Zhang et al., 2016). For transesterification, some reported solid base catalysts such as alkali metal oxides like Na_2O, K_2O, Li_2O, alkali earth metal oxides like MgO, CaO, BaO, SrO, alkali-doped metal oxides CaO/Al_2O_3, Li/CaO etc., alkali based supported mixed metal oxides, transition metal based mixed metal oxides, carbon group based catalysts, boron group based catalysts, waste mineral based catalysts, basic clay materials, magnetic composites, zeolites, etc. have been employed in transesterification exhibiting good to high biodiesel yield as presented in Table 1.1 (Madhuvilakku and Piraman, 2013; Wang et al., 2017) .

1.9.3c Biocatalyst

In literature, lipase group of enzymes like *Candida Antarctica, Novozyme 435, Rhizopus oryzae*, etc. are reported as biocatalyst for transesterification reaction (Watanabe et al., 2001; Halim and Kamaruddin, 2008). These catalysts are not as efficient as homogeneous and heterogeneous catalyst but they perform at ambient temperature to produce considerable yield. Moreover, these are free fatty acid and moisture insensitive, so, these are obvious advantages of biocatalysts for biodiesel synthesis. Nonetheless, biocatalysts are not considered as ideal catalyst because of their high cost, slow reaction rate and poor reusability.

Table 1.1 Literature review on various catalysts used for biodiesel production

Catalysts	Reaction Condition				**Conversion (C) or Yield (Y) %**	**References**
	Oil : Methanol molar ratio	**Catalyst wt %**	**Temperature (°C)**	**Time (h)**		
Homogeneous acid catalysts						
HCl	1:6	2.5	60	2	C= 87.9	(Farag et al., 2011)
H_2SO_4	1:6	2.5	60	1	C= 96.6	(Farag et al., 2011)
H_3PO_4	1:3	0.1	130	1	C= 50	(Aranda et al., 2007)
CH_3SO_3H	1:3	0.1	130	1	C= 91	(Aranda et al., 2007)
$AlCl_3$	1:6	2.5	60	2	C= 87.9	(Farag et al., 2011)
Homogeneous base catalysts						
KOH	1:6	1.0	60	1	C= 95.5	(Dias et al., 2008)
NaOH	1:9	0.5	60	0.75	C= 89.5	(Sharma and Singh, 2008)
$NaOCH_3$	1:6	1.0	65	3	C=83.6	(Chung et al., 2009)
Heterogeneous acid catalysts						
Zeolite Y (Y756)	1:6	-	460	0.37	Y= 26.6	(Brito et al., 2007)
WO_3/ZrO_2	1:19.4	-	75	20	C(FFA)= 85	(Park et al., 2008)

Carbon based catalysts derived from starch	1:30	10	80	8	Y= 92.0	(Lou et al., 2008)
Sulphated TiO_2-SiO_2	1:9	3	200	4	Y= 90	(Peng et al., 2008)
$H_3PW_{12}O_{40}$. $6H_2O$	1:70	3.7	65	14	Y=87	(Cao et al., 2008)
$Zr_{0.7}H_{0.2}PW_{12}O_{40}$	1:20	2.1	65	8	Y= 98.9	(Zhang et al., 2009)
Sulphated SnO_2-SiO_2	1:15	3	150	3	Y= 92.3	(Lam et al., 2009)
Chlorosulphanic Zirconia	1:8	3	100	12	C= 100	(Zhang et al., 2014)
Heterogeneous base catalysts						
CaO	1:26	1	60	3	C= 90	(Kawashima et al., 2009)
Na/Al_2O_3	1:32	1	120	6	C= 97.1	(Tonetto and Marchetti, 2010)
Li/CaO	1:6	5	65	1	C= 99	(Kaur and ali, 2011)
SrO	1:6	5	65	0.25	C= 82	(Chen et al., 2012)
K_3PO_4	1:6	5	65	3	C= 78	(Viola et al., 2012)
Mg Al Fe hydrotelcite	1:21	3	65	4	C= 81	(Wang et al., 2012)
MgO	3:20	3	190	2	C= 82.8	(Jeon et al., 2013)
Cs/SiO_2	1:40	-	135	5	C= 25.35	(Kazemian et al., 2013)
Bio-catalysts						

Pseudomonas cepacia (PS30)	1:6.6	13.7	38.4	2.47	C= 90.4	(Wu et al., 1999)
Candida Antarctica (Novozym 435)	1:3	4	30	50	C= 90.9	(Wantanabe et al., 2001)
Rhizopus oryzae	1:4	30	40	30	C= 88-90	(Chen et al., 2006)
Bacillus subtilis encapsulated in magnetic particles (Magnetic biocatalyst)	1:1	3	40	72	C= 90	(Ying and Chen, 2007)
Novozym 435	1:4	4	40	12	C= 88	(Halim and Kamaruddin, 2008)
Immobilized *Penicillium expansum* resin D4020	1:1	-	35	7	C= 92.8	(Li et al., 2009)

1.10 Research motivation

Though, heterogeneous base catalysts are sustainable and potential catalysts for biodiesel synthesis but still there are issues of insufficient reusability, active component leaching, poor stability during storage, long reaction duration, etc. These aforementioned problems are needed to address for large scale and economically feasible biodiesel production. Development of highly efficient, reusable, stable, environmentally benign and cheaper heterogeneous base catalyst for biodiesel production is the major objectives for the researchers (Zhang et al., 2016). In literature, mixed metal oxides such supported catalysts, compound phase catalysts, core shell catalysts, perovskite phase catalysts, spinel phase catalysts are found to have good stability and surface property which are mostly needed criteria for a sustainable heterogeneous catalyst. In supported catalysts, two phases are present; one is active phase, another is support phase. During catalysis, support of a heterogeneous catalyst holds the active component and protects from leaching; whereas the active species interacts with the reactants. For supported base catalyst, the active component should have sufficient basicity for carrying out transesterification of triglyceride. Alkali metals and alkaline earth metals have higher basicity than the other metals in periodic table. The basicity order of alkali metals is Li < Na < K and alkaline earth metals is Mg < Ca < Sr < Ba (Lee et al., 2014, Sahani et al., 2018, Singh et al., 2016, Yadav and Sharma et al., 2018). This means K and Ba have the highest basicity in their corresponding groups. So, in this thesis, K and Ba were selected as active metals for new heterogeneous base catalyst synthesis. Various K and Ba based heterogeneous catalysts are used in transesterification (presented in Table 1.2). They showed good activity but they faced leaching problem, surface passivation, long reaction time etc. Islam et al. (2015) reported that KI loaded alumina was an active for transesterification but it catalysed the process for 8h, and they also found that leaching KI was the sole reason for catalyst deactivation. Later, Yadav et al. (2017) reported that K modified ZnO performed 98% conversion within 50 min but they failed to address leaching problem. Ba/CaO (Balakrishnan et al., 2013) and Ba-Lanthanum oxide (Sahani and Sharma, 2018) catalysts showed sufficient activity but they were associated with poor recyclability and surface passivation issue. After thorough literature survey, the problems associated with potassium and barium based catalysts were clear and defined, which have to resolve. Rare earth metal oxides and group IV metal oxides are addressed as good supporting material in terms of stability and surface area; and these are not still explored enough in the field of biodiesel production (Zhang et al., 2015, Roy et al., 2018). So far, it is expected that a rare earth metal oxide and a group IV metal oxide can be employed as an efficient support for the active metal. Sahani et al. (2019) resolved issues like surface passivation and long reaction time by employing $BaCeO_3$ catalyst in transesterification, which performed 98.41% conversion within 1.6 h. On the other hand, Xie and Zhao (2013) reported that tin oxide can prevent the leaching of CaO upto 4 catalytic cycles. Both ceria oxide and tin oxide are renowned for excellent oxidation stability and large surface area. So, it was anticipated that ceria oxide and tin oxide as support material could provide good stability to the catalyst; moreover it was also expecting that chemistry of active components like K or Ba species with support materials like ceria oxide or tin oxide might form active solid base catalysts having excellent efficiency and good endurance in biodiesel production.

Table 1.2 Literature review on potassium (K) and barium (Ba) based heterogeneous catalysts used in transesterification

Catalyst	Feedstock	Conversion (C) or Yield (Y) %	Comment	Reference
K based heterogeneous catalysts				
K/KOH/ Al_2O_3	Rapeseed oil	C= 84.52	Comparatively lower conversion	(Ma et al., 2008)
KNO_3/ Al_2O_3	Palm kernel oil	C= 94.7	High methanol : oil ratio (65 : 1)	(Benjapornkulaphong et al., 2009)
KF/ Al_2O_3	Canola oil	C= 98	Long reaction time of 8 hr	(Boz et al., 2009)
K_2CO_3/ Al_2O_3	Sunflower oil	C= 99	Large amount of methanol is required	(Hyyan et al., 2010)
KI/ Al_2O_3	Rice bran oil	C= 95.2	8 hr long reaction time	(Evangelista et al., 2012)
20%K/TiHT	Canola oil	C > 95	Large amount of methanol is required (54 :1)	(Salinas et al., 2012)
KF/CaO-MgO	Soybean oil	C= 97.9	Efficient catalyst	(Fan et al., 2012)
Na/K/TNT	Soybean oil	C= 94-96.2	Catalyst preparation is tedious and process is more time consuming	(Hipolito et al., 2015)
KBr-CaO	WCO	C= 80	Blending cause increase in specific fuel consumption, NO_x emission, exhausted gas temperature	(Mahesh et al., 2015)
$\beta K_2Zr_2O_5$	WCO	C= 96.85	Efficient catalyst	(Singh et., 2016)
K/Na/ZIF8	Soybean oil	C= 98	Required materials for catalyst synthesis are costly and catalyst preparation is complicated and lengthy	(Saeedi et al., 2016)
Ba based heterogeneous catalysts				
BaO	Soybean oil	Y= 95	Required very high t temperature	(Singh and Fernando, 2007)

BaO	Refined rapeseed oil	C= 86	Required high catalyst dose of 10 wt% and longer reaction time of 3.5h	(Yan et al., 2007)
BaO	Palm oil	Y= 95.2	Cost ineffective process	(Mootabadi et al., 2010)
KOH/La-Ba-Al_2O_3	Microalgae oil	C≥ 95	Catalyst deactivation occurs when KOH incorporated more than 30%	(Zhang et al., 2012)
Ba/CaO	Waste cooking oil	C= 88	Comparatively poor conversion	(Balakrishnan et al., 2013)
$BaZrO_3$	P. pinnata oil	C= 98±0.5	3h long reaction duration	(Singh et al., 2016)
Barium lanthanum oxide	Madhuca oil	C= 97.5	Catalyst deactivation due to passivation of organic moiety	(Sahani and Sharma, 2018)
Cs modified $BaZrO_3$	Millettia Pinnata oil	C= 97.27	Very long duration of 23h	(Kumar and Singh, 2019)
$BaCeO_3$	Karanja oil	C= 98.41	Efficient and reusable catalyst	(Sahani et al., 2019)

1.11 Objectives

The following four major objectives were defined in this thesis:

i. Synthesis and characterization of potassium modified ceria oxide (K-CeO_2), potassium - tin oxide (K-SnO_2), and barium - tin oxide (Ba-SnO_2) catalyst.
ii. Application of potassium modified ceria oxide (K-CeO_2) catalyst in biodiesel production from waste cooking oil and castor oil.
iii. Application of potassium - tin oxide (K-SnO_2) catalyst in biodiesel production from waste cooking oil and castor oil.
iv. Application of barium - tin oxide (Ba-SnO_2) catalyst in biodiesel production from waste cooking oil and castor oil.

Sub-objectives of the above mentioned major objectives are as follows where methodologies are common to all except the first one.

i. Sub-objectives of major objective 1
    - Synthesis of new heterogeneous base catalysts such as potassium modified ceria oxide (K-CeO_2) by sol-gel auto combustion method, potassium - tin oxide (K-SnO_2) by polymer precursor auto combustion method, and barium - tin oxide (Ba-SnO_2) by wet impregnation method.
    - Characterization of synthesized catalysts via TGA-DTA analysis, XRD analysis, XPS analysis, SEM-EDAX analysis, BET surface area analysis and basicity estimation.
ii. Sub-objectives of major objective 2,3&4
    - Activity check of the synthesized catalyst for transesterification of waste cooking oil and castor oil.

- Study on process optimization of following reaction variables, oil : methanol molar ratio, catalyst weight %, temperature and reaction duration by OVAT methodology.
- Reusability assessment of the catalyst.
- Evaluation of kinetic and thermodynamic parameters.
- Evaluation of yield, TOF, E-factor, PMI of the catalytic process.
- Characterization of product biodiesel by ^{1}H NMR, ^{13}C NMR and GCMS.
- Evaluation of important physicochemical properties of product biodiesel for quality check.