

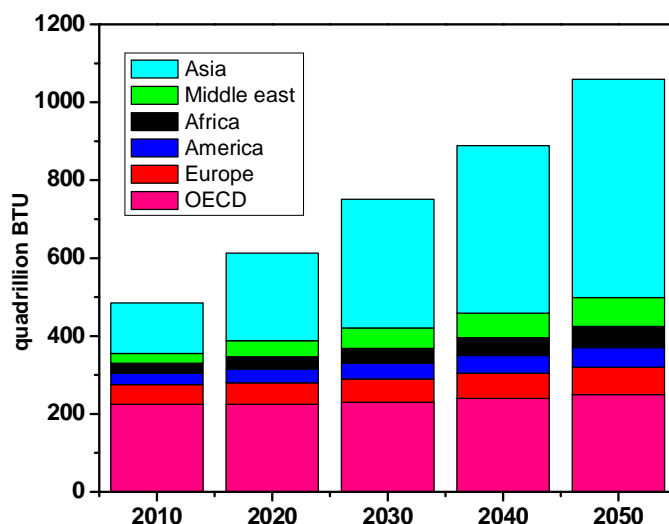
# CHAPTER-1

## 1.1.Introduction

As per energy demand across globe is concerned, fossil fuels are being exhausted expeditiously. According to an estimate, these exhaustible energy sources will last up in some upcoming years say 20-30 yrs (Rincon et al., 2014).

### 1.1.1. Energy crises and uneven distribution

Energy resources always manifest a vital role in growth and sustainable development of a nation. According to IEA (2014), world total primary energy supply in the year 2014 was 13, 699 Mtoe (million tonnes oil equivalent) including 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 %).



**Figure 1.1** Prediction of International Energy Outlook till 2050.

According to projection executed by EIA's International Energy Outlook (2013), world energy demand would be enhanced by 56% right from 2010 till 2040

(Figure 1.1). Overall, carbon based fossil fuels (oil, natural gas and coal) account for 86% of global energy consumption while renewables (solar, wind, geothermal, and biofuels) account for just 2.8 %, up from 0.8% a decade ago. World energy outlook (2016) presented that the world petroleum and other liquid fuels consumption rose 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 doubled by 2040 and energy demand would be rising to 80%. The major energy consumption sectors are transport, electricity, communication and construction. Transportation sector would be displaying a growth at an annual rate of 1.4 % (from 104 quadrillion 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), and Non-OECD (Americas 3.8 (mb/pd) and others). Nonetheless, biofuel production (biodiesel and ethanol fuel) was only 0.57 %. Overall, most of our present energy needs rely on resources which have a limited availability. The world energy consumption continues to grow at an average over 1.9% annually fuelled by strong growth in emerging economies. It becomes quite important for researchers to investigate alternative renewable energy resources for the future. Fortunately, biofuel production is coming up gradually in comparison to that of in 2012 (Figure 1.2). But still, it is not adequate to meet up the current energy requirement.

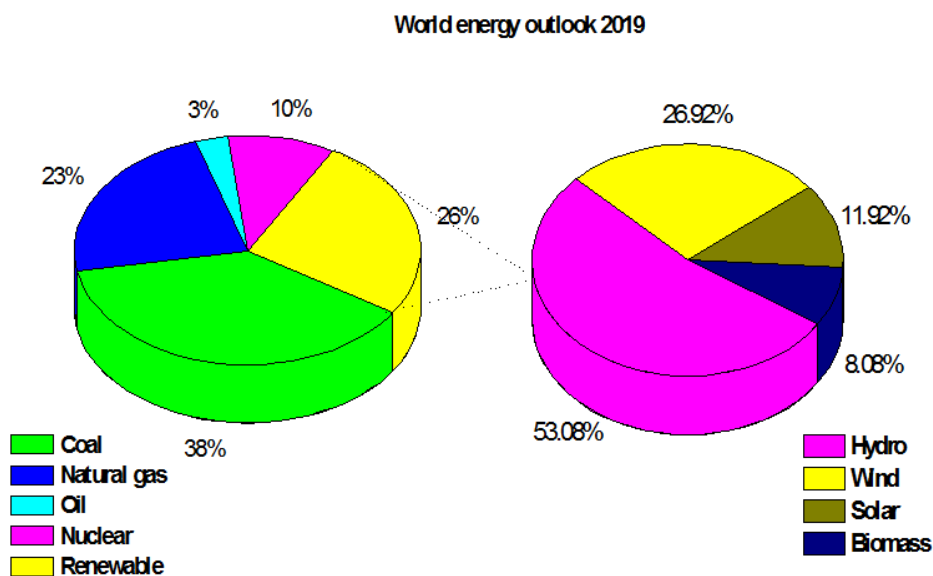
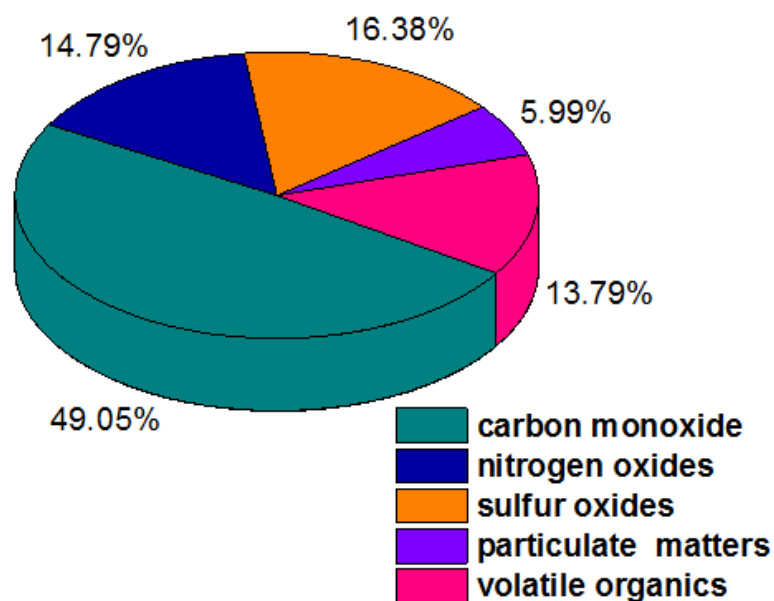


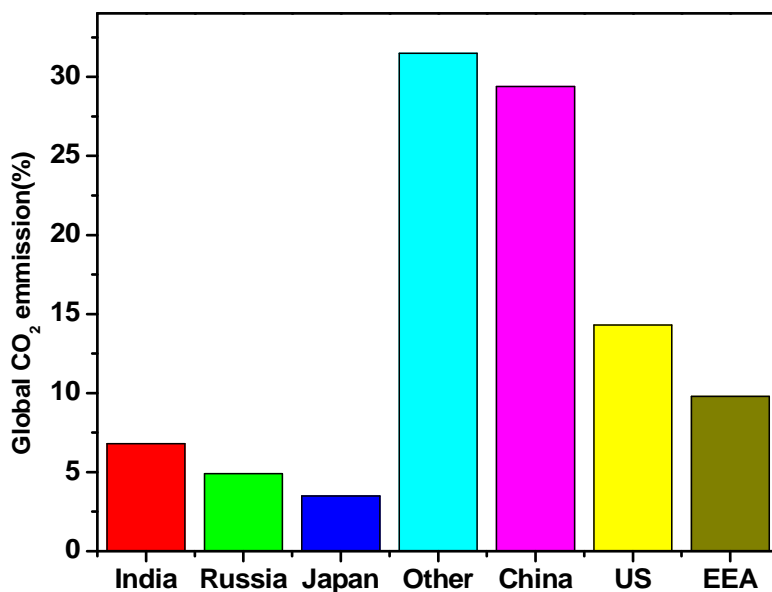
Figure 1.2 Estimated world energy consumption (World energy Outlook, 2019).

### 1.1.2. Environmental issues

Humans mostly depend on exhaustible conventional energy resources such as natural gas, coal and petro-based fossil fuels and they insignificantly rely on the renewable energy resources such as solar energy, wind power, biofuel, and hydropower. Moreover, a higher rate of consumption of non-renewable energy sources would lead to their disappearance very soon. Petro based fossil fuels impart a great influence on the country's economic status because they are leveraged for much of applications such as agriculture, transportation, domestic and the industrial activities. It is apparently understood that the development of any nation is reflection of the rate of consumption of petro derived fossil fuels as supplement of energy requirement for various commercial and domestic purposes. Increasing world population has accelerated the exploitation of petrochemical fuels abruptly.



**Figure 1.3** Emission profile of fossil fuel combustion.



**Figure 1.4** Global CO<sub>2</sub> emission per region/country report (updated in 2019).

Most of the countries fulfill their energy demands from importing the petro-fuels. Hence, the combustion of these fossil fuels produces the primary air pollutants and ultimately secondary air pollutants. Especially, carbon dioxide is predominantly

emitted which is a prominent green house gas as manifested in Figure 1.3. Now, the carbon dioxide emission is getting beyond the permissible limit as it is increasing at an alarming rate. According to IEA report on 'Global Energy & CO<sub>2</sub> Status (2019)' China, US and India are three top emitters of carbon dioxide as reflected in Figure 1.4.

According to IEA report (Key World Energy Statistics, 2015), emissions of CO<sub>2</sub> have been doubled between 1973 and 2013, from 15515 Mt to 32190 Mt. Poor air quality results in 6.5 million deaths in a year, making it the 4<sup>th</sup> largest threat to human health. The major source of air pollution is in the energy sector: 85% of particulate matter, hydrocarbons, sulfur oxides and nitrogen oxides. World Energy Outlook Special Report (2016) by IEA over Energy and Air Pollution, clearly specified that the use of fuels in the transport sector, especially diesel, produces more than half of NO<sub>x</sub>s as well as other hazardous pollutants emitted across the globe creating severe respiratory issues to human beings and other organisms (Perera, 2016). In such a scenario, it is necessary to focus on green energy sources to make clean environment for the generations to come. A green fuel should be renewable, non-toxic with lower emission and affordable in terms of cost to the consumers. Since the contribution of renewable sources to overall energy supply is very less presently as shown in Figure 1.2, so scientists have been working to develop techniques to draw energy from renewable sources. Overall, the report of IEA, World energy outlook (2019) suggested the share of energy generation from renewable resources net capacity could nearly double, from 26% today to 44% in 2040, surpassing coal as early as 2026. Infact, many alternatives have already been brought in implementations which are quite renewable in nature.

## **1.2. Renewable energy resources**

Till date many renewable energy sources are being exploited to draw the huge amount of required energy in many developed and developing countries. Even there are some countries which are being independent of use of traditional non renewable energy sources (IEA, World energy outlook, 2019). They are using renewable energy sources for their 100 % energy demand of their indigenous people belonging to their boundary like Iceland, Norway, Sweden, and many more. Now other countries are also exerting their full efforts to satisfy their energy needs from renewable sources. In our country, 60% of overall energy demand is gratified by coal and other petro based fuels. Remaining part is supplied by hydel energy, wind energy, solar energy, nuclear energy, geothermal energy and some other energy sources based on biomass. There are many sources providing an enormous amount of biomass derived energy including from plant or animal resources including waste materials from domestic and commercial units (Quah et al., 2019). Furthermore, biodiesel is found as potential and renewable alternative of fossil fuel among all existing biofuels derived from biomass which could be commercially produced by using economically viable feedstock from biomass. Biodiesel production is rather a better way to utilize the abundant biomass generated throughout the nation.

### **1.2.1. Biofuel policies across globe**

Nearly, 26 % of total energy demand is fulfilled by renewable energy resources across globe as depicted in Figure 1.2. Among all existing sources of energy, biofuel has come up as promising sources of energy supply with 8% contribution, which further can be scaled up high in near future. In this direction, India is continuously feeding its efforts to enhance the biofuel production. Now a day, many countries are

investing their time and money to devise policies to escalate the contribution of renewable resources to total energy demand. Onward January 1, 2020, Indonesia has decided to enhance blending of diesel and crude palm oil by 30% for B30 (Chain Reaction Research, 2019). This would certainly raise the consumption of crude palm oil for blending to 7.8 MMT. France will discontinue biofuel tax breaks for palm oil starting January 1, 2020. France also has shown a move regarding wider EU action upon palm oil derived biofuels. In 2018, approximately two-thirds of the 7.7 million tonnes of palm oil was imported into the EU which was employed for generation of biodiesel. It is also anticipated that the decarbonization in shipping industry may be comfortably dependent upon biomass derived biofuels for longer period. In this direction, The International Maritime Organization has laid down some curbs on sulfur content of fuel oil to be used in ships onward January 1, 2020. This would definitely stimulate unexpected craving for alternative low-sulfur emissive fuels like biofuel. Especially, the aviation industry has declared to pursue the carbon neutral growth right from 2020 and ahead. However, civil societies and other related organizations have shown their apprehension that biofuel production from vegetable oils such as soy and palm have caused 3.2 million hectares of additional deforestation. Moreover, China is continuously enlarging the consumption of palm oil derived biofuels as a reasonable substitute of conventional fuel. In August 2019, China has decided to circumvent the import levies on crude palm oil so that imports may bounce to 7 million tonnes in market in year 2019-2020.

### **1.2.2. Biofuel policies of India**

National policies on biofuel (2019) in India have recommended the application of ethanol derived from unfit food grains and other biomass derived waste. In session 2017-2018, petrol was blended by 150.5 crore litres of ethanol resulting in foreign exchange saving of nearly Rs. 5070 crore. It also reduced the carbon emission nearly

29.94 lakh tonnes. National Policy on Biofuels (2018) mandated by the central government has planned to achieve an anticipated aim of 20% ethanol blending in petrol and 5% biodiesel blending (B5) till 2030 completely. This would be executed by the Oil Marketing Companies under EBP programme across the country avoiding two union territories i.e. Andaman Nicobar and Lakshadweep where OMCs would blend up to 10 % ethanol in petrol under the same scheme. Recently, on the occasion of world biofuel day i.e. 10 August, 2019, FSSAI in coordination with Biodiesel Association of India (BDAI) has proposed an effective and well planned mechanism to collect WCO from its sources for its further conversion into biodiesel. According to recent data published by FSSAI, India uses tentatively 225 lakh tons of cooking oil and around one third of it is sold to small scaled vendors at very low rate which is completely undesirable as it makes the processed food inedible.

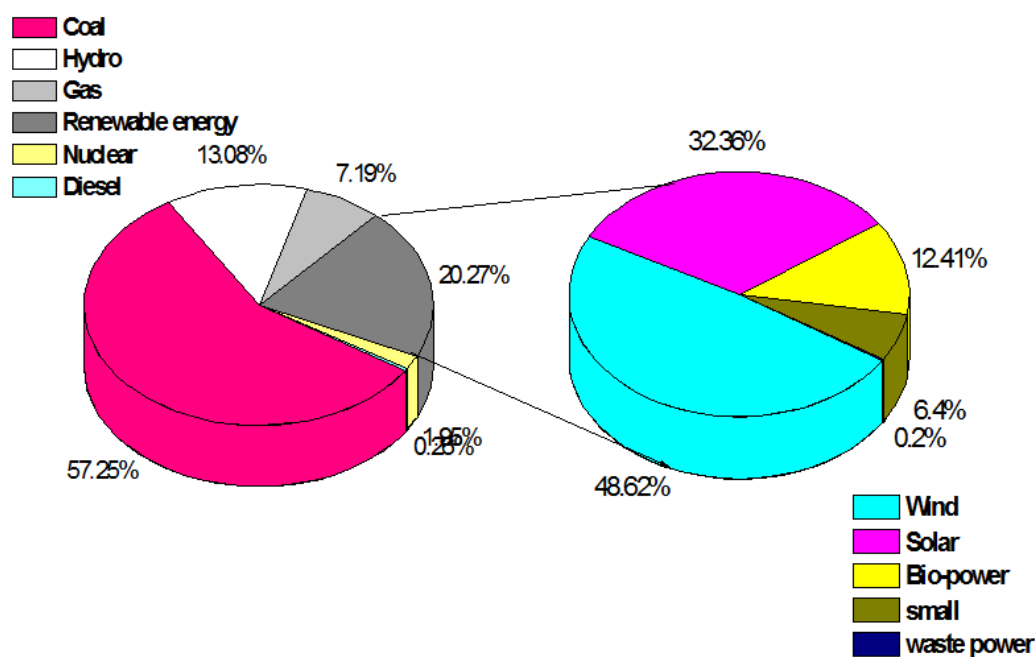


Figure 1.5 Cumulative Installed power capacity Mix (%) in India.



Currently, around 64 companies, 200 aggregators, 350 hubs and some 26 plants at 101 locations spread throughout nation especially southern west portion of country are performing task in combined way for coordinative collection and conversion of waste cooking oil into biodiesel through transesterification. Among all the existing biofuels, biodiesel has come up as a prominent renewable energy resource due to its potential production capacity and similar characteristics to mock the conventional diesel fuel. The idea of biodiesel was enunciated by a veteran German inventor Rudolph diesel long ago (Balasubramanian and Steward, 2019). Having the thought that diesel engine would substantiate agricultural growth of the nation. He worked on diesel engine which was basically designed to run on fuel derived from peanut oil in early years of twentieth century. But at that time, it involved a lot of money in addition to man power. Contemporary fossil fuel overweighed this idea of biofuel usage because of its cheapness and ample presence. But since 1980, the gradual depletion in petro reservoirs has compelled the research community to seek alternatives of same. As the energy demand which is directly linked with social and individual development is fed by petro based fuels so far, need to be satisfied by renewable energy sources. Among all the accessible renewable energy resources biodiesel has sought the significance attention.

### **1.2.3. Biodiesel as a renewable and alternative energy source**

Importing fossil fuel from other countries viz. oil producing countries is need of the countries like India because of their limited oil reserves and increasing consumption but if a country has resource to produce biodiesel, it can significantly lessen the dependency on other energy resourceful countries as well as it can increase the self-economy. Biodiesel can also reduce environmental problems such air pollution, global

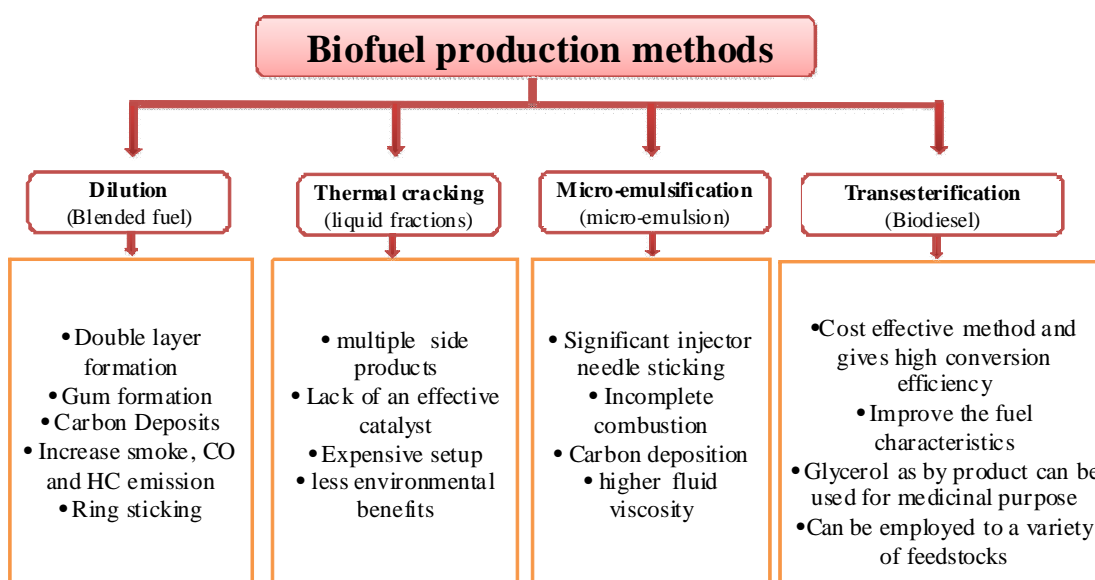
warming and conserves non-renewable oil reserves. Now a day's, biodiesel is being escalated to industry level to fulfill the energy demand of growing population and commercial units across the globe. Additionally, biodiesel is found as environmentally benign renewable fuel as a substitute of diesel owing to following characteristics (Sharma et al., 2008).

- (i) Oxygenated fuel (Complete combustion increase the energy output).
- (ii) Better lubricant (Increase the usable life of fuel injection equipments of engine)
- (iii) Carbon neutral (forming closed carbon loop).
- (iv) Biodegradable and non-toxic in nature.
- (v) High flash point and high fire point (provides handling safety at high temperature), High cetane number (Lowers ignition delay).
- (vi) Comparable calorific value (~90% of diesel fuel).
- (vii) Nitrogen and sulfur free emission.

Furthermore, biodiesel is more oxygenated than conventional diesel and hence its combustion results in less emission of hydrocarbons, carbon dioxide, and particulate matter. Accordingly biodiesel is chemically defined as mono alkyl esters of long chain fatty acids derived from vegetable or animal oil (Kim et al., 2017). According to recent estimate, one hundred grams of fat or oil would yield approximately 95 grams of different kinds of fatty acids. Both the physical and chemical properties of oil are governed by its composition having different free fatty acids (FFA) and those fatty acids attached to glycerol molecule (triglyceride esters of fatty acid) (Mladenovict al., 2018). Predominantly, saturated and unsaturated fatty acids with an even number of carbon atoms with carboxylic group are enriched in different available feedstocks.

### 1.3. Process for biodiesel production

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 processes such as transesterification, blending, microemulsion, and pyrolysis (Sharma et al., 2011). Figure 1.6 manifests the possible ways of biofuel production showing the pros and cons of the methods.



**Figure 1.6** An illustration of biofuel production methods.

#### 1.3.1. Direct blending

Direct blending or dilution was very first time enunciated during late 1980s where vegetable oil was adulterated with petrodiesel. Initially, industry started inculcating raw vegetable oil in petrodiesel having no idea about the physicochemical properties of crude bio-oil. Onwards, it took the shape of biodiesel instead pure triglycerides. Owing to high fluid viscosity, free fatty acid composition, gum generation, carbon deposition and lubricating oil thickening as a result of oxidation and polymerization over prolonged duration of storage and combustion (Qi et al., 2010), the

direct blending of vegetable oil lost its utility and biodiesel came into picture having better physicochemical properties which mock that of conventional diesel fuel. Ma and Hanna (1999) reported three widely applicable techniques for biodiesel production i.e. micro-emulsion, pyrolysis and transesterification. Amongst, transesterification is most applicable method for biodiesel production applied at laboratory as well as industrial scale due to its cost effectiveness and easy handling procedures.

### **1.3.2. Pyrolysis**

Pyrolysis is a thermal treatment which causes chemical decomposition of matter in inert atmosphere. During pyrolysis, organic materials are converted into gaseous combustible fraction, a liquid fraction and a solid residue consisting carbon content and ash (French and Czernik, 2010). It produces biodiesel with better fuel properties quite compatible with diesel fuel from edible and non-edible oil feedstocks. Now various reports on the production of paraffins and olefins through this thermal treatment in inert atmosphere are available (Cheng et al., 2012). Still many aspects of pyrolytic behavior of feedstocks have not been explored much so issues regarding yield, conversion and selectivity remain doubted. In fact many researches are being carried out for catalytic pyrolysis reactions (Wang et al., 2016; Hansen et al., 2020). Czernik and French (2014) observed an auto-thermal reforming process for producing hydrogen from biomass through pyrolysis using 0.5% Pt/Al<sub>2</sub>O<sub>3</sub> from BASF at 800°C to 850°C. During pyrolysis, a suite of chemical reactions including dehydration, decarboxylation, cracking, aromatization, alkylation, condensation, and polymerization occur which convert oxygenated organic compounds into respective hydrocarbons. Basically, the pyrolyzed products are simply hydrocarbon synonymous to that of conventional fuel.

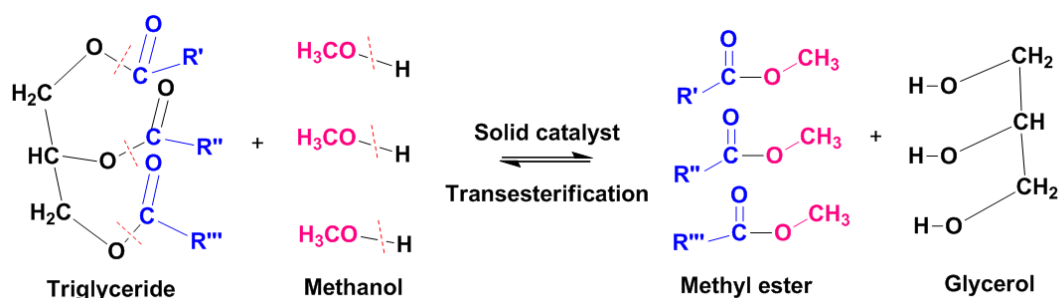
### **1.3.3. Micro-emulsion**

To mitigate the extent of viscosity of feedstock, their micro-emulsions are prepared with variety of solvents. Generally, micro-emulsions are known to be thermodynamically stable and isotropic liquid mixtures of water, oil and surfactants with dispersed domain diameter varying approximately from 1 to 100 nm, and usually 10 to 50 nm (Arpornpong et al., 2014). Their spray characteristics can be improved by explosive vaporization of the low boiling constituents during micelle formation (Amais et al., 2010).

### **1.3.4. Transesterification**

Biodiesel is economically produced by transesterification, an economically viable method also termed as methanolysis where methanol is used as acyl acceptor in process (Sharma et al., 2011). In this reaction, a triglyceride molecule reacts with three molecules of methanol to form three molecules of FAME and one glycerol molecule stoichiometrically (Sahani and Sharma, 2018). Transesterification is widely applicable method to synthesize biodiesel from vegetable oils and fats. Transesterification can be carried out by using acid or base catalyzed reactions (Sharma et al., 2011). 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 (Sharma et al., 2008). This tetrahedral intermediate gets transformed to new ester by eliminating alcohol. 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 as represented in Figure 1.7. In presence of base, alcohol forms alkoxide ion which will attack at the carbonyl group of the triglycerides leading to formation of tetrahedral intermediate (Sahani et al., 2019). 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 (Kawashima et al., 2008). There are three very important components required for transesterification reaction i.e. triglyceride source (feedstock), alcohol, and catalyst.



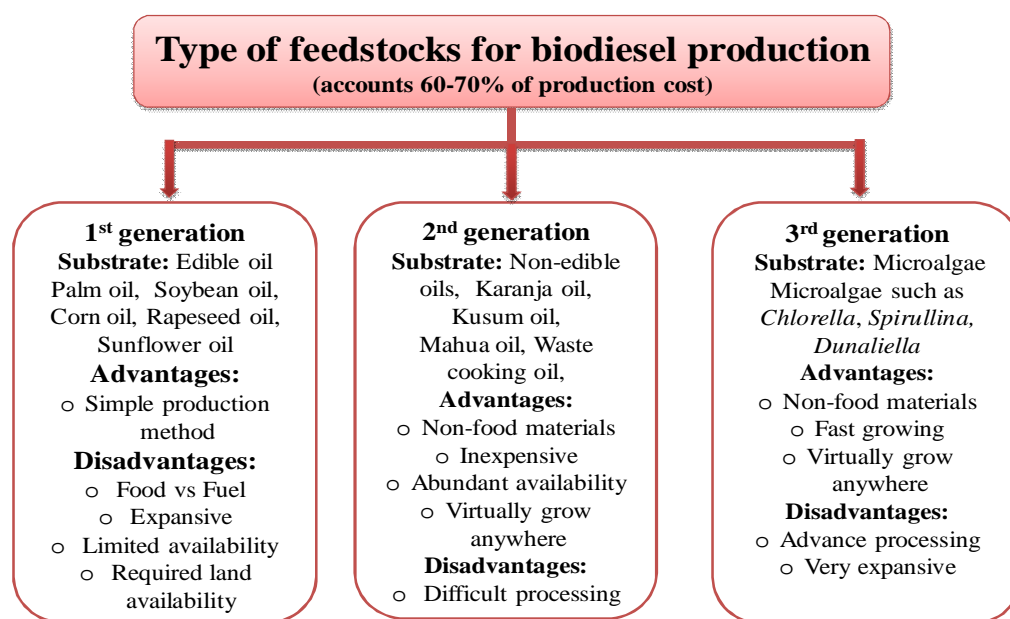
**Figure 1.7** Stoichiometrically balanced transesterification reaction.

Transesterification reaction is not kinetically feasible reaction so catalyst presence is demanded to carry out the reaction.

#### 1.3.4.1. Feedstock

So far three generations of triglyceride sources have been explored for FAME production. Initially, vegetable oils were used predominantly; in fact still they are significantly utilized in western countries at large scale. According to report on Biofuel outlook (EPA, 2020), 31% share is contributed by palm oil followed by soybean oil

(27%), rapeseed oil (20%) and others including non-edible oil feedstocks. But now usage of vegetable oils is no more appreciated throughout the globe because they compete with food especially in Asian countries like heavily populated China and India. So, application of non-edible oil feedstocks is preferable over edible one (Junior et al., 2019; Malani et al., 2019; Arumugam et al., 2019). Hence, non-edible feedstocks such as *Madhuca longifolia* oil, *Schleichera oleosa* oil, *Millettia pinnatta* oil and waste cooking have been employed in transesterification in present study. An overview of feedstocks is depicted alongwith their pros and cons in Figure 1.8 (Borah et al., 2019; Liu et al., 2019; Malani et al., 2019; Yesilyurt and Cesur, 2020).



**Figure 1.8** A depiction of various kinds of feedstocks.

#### 1.3.4.2. Alcohol

The second substrate of transesterification reaction is alcohol. The application of alcohol suggests the alternative name of the transesterification reaction i.e. alcoholysis. Many researchers have explored transesterification reaction with alcohols with larger carbon chains like ethanol and propanol (Musa, 2016). Nonetheless, alcohol

with higher carbon number increases the viscosity and density of resultant fatty acid methyl ester i.e. undesirable as fuel. The lower members of alcohol family are known for their hygroscopic and volatile nature while higher members are very much prone towards water contamination (Verma et al., 2016). Considering above facts and cost of entire process, methanol is widely applied in methanolysis reaction also attributing to its wide abundance. The researchers have verified the application of various kinds of alcohols unless the resultant fatty acid methyl ester fulfills criterion laid by ASTM D6751 standards (Sharma et al., 2008). Nonetheless, usage of higher members of alcohol family is not appreciated due to their stearic hindrance effect and higher cost (Musa, 2016).

### **1.3.4.3. Catalysts for biodiesel production**

Catalyst plays very important role in biodiesel production. Non-catalysed transesterification is not driven swiftly. Catalyst finds a new path of lower activation energy which gives the transesterification reaction a new direction. This enhanced the reaction rate with fair amount of reaction product. Transesterification reaction is usually accelerated by either homogeneous or heterogeneous acid, base, and enzyme catalysts.

#### **1.3.4.3.1. Homogeneous catalyst**

Generally, homogeneous catalysts fasten reaction at high rate owing to the ease of interaction between reaction substrates and catalyst being in same phase (Dash, 2020; Sharma et al., 2008; Sahani et al., 2018). Nonetheless, application of homogeneous catalysts imparts higher cost to reaction procedure as it involves tedious separation procedure making transesterification method costly. Basically, homogeneous



base catalysts like NaOH, KOH, CH<sub>3</sub>ONa and CH<sub>3</sub>OK are used while HCl, H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub> etc. are applied as homogeneous acid catalysts in transesterification reaction as discussed in Table 1.1. Primarily, homogeneous base catalysts are utilized at commercial scale in industries. This might be because of their availability and high conversion rate at comparability low temperature and pressure (Narasimharao et al., 2007).

#### **1.3.4.3.2. Heterogeneous catalyst**

Attributing to their high endurance capacity and reusability, heterogeneous catalysts are preferable over their homogeneous counterparts. Both heterogeneous acid and base catalysts are used in transesterification (Sahani and Sharma, 2018). Though, heterogeneous acid catalysts show comparatively poor performance but they are ideal to be used for low-qualified oil feedstocks with high FFAs (Gomes et al., 2008). Various inorganic and polymeric solid acid catalysts are explored and observed to execute the transesterification reaction at higher reaction temperatures for considerable methyl ester conversion. Hetero-base catalysts are generally more active than their counter acid catalysts in transesterification. So, they are particularly desirable for feedstocks with low FFA content (Singh et al., 2016). Table 1.1 summarizes different homogeneous and heterogeneous catalysts used in transesterification for biodiesel production with their advantages and disadvantages (Meher et al., 2006; Gerpen, 2005; Lee et al., 2014). Nevertheless, heterogeneous basic catalysis overweighs its acidic counterpart as the former is irreversible in nature and also approximately 4000 times faster than latter one (Lee et al., 2014). The metal oxide is composed of positive metal ions (cations) and negative oxygen ions (anions) as Lewis and Brønsted base sites, respectively, where methanolysis begins with sufficient adsorption of methanol on

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active sites followed by the cleavage of O-H bonds into methoxide anions coined as acyl acceptor (Sahani et al., 2018). The methoxide anions then react with the acyl moiety from triglyceride molecules to form the corresponding FAME. Apart from the above catalyzed reaction, transesterification can also be carried out with supercritical method and co-solvent method (Sahani et al., 2018). Both the methods are not found conducive for methyl ester production through transesterification because these methods are quite energy intensive and costly.

Table 1.1

Homogeneous, heterogeneous, and enzyme catalysts used in transesterification.

Catalyst type	Examples	Advantages	disadvantages	References
<b>Homogeneous catalyst</b>				
<b>Acid catalyst</b>	H <sub>2</sub> SO <sub>4</sub> , H <sub>3</sub> PO <sub>4</sub> , HCl	Avoid soap formation applicable for both esterification and transesterification, corrosive	Tedious process involved in neutralization, no recycling capability, high purification cost, energy consuming, low reaction rates	(Sharma et al., 2011; Madhu et al., 2017)
<b>Base catalyst</b>	NaOH, KOH, CH <sub>3</sub> ONa, CH <sub>3</sub> OK	Less corrosive, high reaction rate	Forms soap with feedstock having high FFA, high waste water discharges, high purification cost, not recycle	(Singh et al., 2016; Sahani et al., 2018)
<b>Heterogeneous basic catalyst</b>				
<b>Native metal oxide</b>	Alkali metal oxides, Alkaline earth oxides, Rare earth oxides, p-block metal oxides,	Environmentally benign, easy separation, reusability, less	Leaching issues,	(Gohain et al., 2020; Balajii et al., 2020;

	transition metal oxides	discharge of toxics, high	relatively slow rates	Sai et al., 2020; Balajii et al., 2020)
<b>Zeolites</b>	Alkali metal ion-exchanged zeolite, Alkali metal ion-supported zeolite, rare earth metals ion- supported zeolite	purity glycerol, lower cost of separation, insignificant leaching of active alkali or alkaline earth metal in native oxide		(Pavlovic et al., 2020; Chen et al., 2020)
<b>Doped or supported metal (mostly alkali or alkaline earth metal )</b>	Alkali metal ions on p block or transition metal oxide (alumina, silica) Alkali metal ions metal or alkaline earth metals on alkaline earth oxides, Alkali metals and alkali metal hydroxides on rare earth metal oxides			(Sahani et al., 2019; Roy et al., 2020; Banerjee et al., 2019; Singh et al., 2016; Yadav et al., 2018; Lakshmi et al., 2020)
<b>Clay minerals</b>	Hydrotalcites, Crysotile, Sepiolite			(Zhang et al., 2019; Correa et al., 2020)
<b>Others</b>	Alkaline alkoxide, Alkaline carbonate, Guanidine-containing catalysts (immobilised organic bases)			(Yancheshmeh et al., 2020)

#### Heterogeneous acid catalyst

<b>Zeolites, mixed oxides, sulfonic acid group,</b>	Mesoporous silica, sulphonated Silica, SBA grafted SO <sub>4</sub> /ZrO <sub>2</sub> ,			Gadekar et al., 2020; Vasic et al., 2020)
<b>Sulfonic acid modified mesoporous silica,</b>	phenylsulfonic acid functionalized silica, PrSO <sub>3</sub> -SBA-15			(Pandian et al., 2020)

<b>Heteropolyacids</b>	Cs salts of phosphotungstic acid			
<b>Acidic polymers and resin</b>	<p><math>Cs_xH_{(3-x)}PW_{12}O_{40}</math> and <math>Cs_yH_{(4-y)}SiW_{12}O_{40}</math>, <math>H_3PW_{12}O_{40}</math> supported on magnetic iron oxide particles (MNP-HPA), 12-tungstophosphoric acid (TPA) dispersed over mesoporous MCM-48</p> <p>Sulfonated mesoporous polydivinylbenzene(PDVB)</p>	Applicable for both esterification as well as transesterification	Slow reaction rates, higher catalyst dose, higher reaction temperature	(Gomes et al., 2016; Pan et al., 2017)
<b>Waste carbon-derived solid acids</b>	Sulfonated carbon catalysts prepared from sugar and polyacrylic acid, Bronsted solid acid catalyst derived from peanut shells and other waste products, Sulfonated carbonaceous materials			(Ayoob et al., 2020)
<b>Miscellaneous solid acids catalyst</b>	<p>Ferric hydrogen sulphate <math>[Fe(HSO_4)_3]</math>, supported tungsten oxides (<math>WO_3/SnO_2</math>), supported partially substituted heteropolytungstates, and bifunctional catalysts</p> <p>Candida antarctica B lipase, Rhizomucor meihei lipase, candida rugosa Pseudonas cepacia, M.</p>			

<b>Enzymatic catalysts</b>	meihe (Lypozyme), M. meihe (Lypozyme IM60), Aspergillus niger, immobilized lipase Novozyme 435  P. Fluorescens, R. Oryzae	No saponification products nonpolluting, easily separable, high purity glycerol and biodiesel products, environmentally benign  Simple glycerol recovery	Highly sensitive to water, costly, reusability issues	(Guldhe et al., 2017; Pascacio et al., 2019)
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Table 1.2

Additional methods adopted in transesterification reaction for methyl ester production.

<b>Catalyst type</b>	<b>Examples</b>	<b>Advantages</b>	<b>disadvantages</b>	<b>References</b>
<b>Supercritical method</b>	Methanol, ethanol	No requirement of Catalyst	Higher alcohol to oil molar ratio	(Taher et al., 2020)
<b>Co-solvent method</b>	Tetrahydro furon (THF), diethyl ether, hexane	Higher yield and conversion, faster reaction rate.	Higher cost	(Sahani et al., 2018; Ambat et al., 2020)

#### **1.4. Research gap**

Though, heterogeneous base catalyst is a potential and sustainable catalyst for biodiesel production but still there is problem of saponification in case of feedstocks with high free fatty acids (FFA) content. This issue can be resolved by application of two step biodiesel production i.e. esterification followed by transesterification (Guerra et al., 2014). Inceptively, acid catalysts might convert FFA to methyl ester via esterification process. Anyway, alkali metal based catalysts are highest basic entities but their low endurance capacity makes them ineffective for transesterification reaction. Hence, alkaline earth metals can be most efficient and sustainable base catalysts owing to high basicity after alkali metals. Furthermore, basicity gets enhanced from top to bottom in same group; therefore, the basicity of group (II) metals follows the order of  $Mg < Ca < Sr \leq Ba$  (Lee et al., 2014; Sahani et al., 2018; Singh et al., 2016; Yadav et al., 2018). In spite, strontium is found equally effective as Ba in group (II) when charge density is considered along with basicity for a catalytic reaction (Lee et al., 2014). Attributing to the above fact, Ba and Sr based heterogeneous base catalysts were employed in present study. Nonetheless, the endurance power of active phase was synergistically improved by its doping with relatively stable metal species which can also enhance the catalytic efficiency of solid catalyst (Lee et al., 2014; Roy et al., 2020). Further, rare earth metals and transition metals are known for their catalytic activity owing to thermal stability and excellent oxidation activity ameliorating the catalytic potency of base catalyst due to its variable valences. Regarding aforementioned characteristics of dopants, active Ba and Sr metals were doped with La, Ce, and Ti metals to form highly stable and basic mixed metal oxides as heterogeneous base catalyst for transesterification reaction. In present study, non-edible feedstocks

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have been selected as potential feedstocks as they don't compete with food security. *Madhuca longifolia* oil, *Millettia pinnata* oil, *Schleichera oleosa* oil, and waste cooking oil were used in current work due to abundance. Table 1.3 illustrates the application of various reported homogeneous and heterogeneous base catalysts in transesterification for FAME production from non-edible feedstocks.



Table 1.3

Comparative study of various homogeneous and heterogeneous catalysts employed in FAME production from non-edible feedstocks.

Catalysts	Methods	Catalyst amount	Methanol to oil molar ratio	Reaction temperature (°C)	Reaction time	Conversion (C) or yield(Y)	References
<i>Madhuca longifolia oil</i>							
Mn doped ZnO	Transesterification (Magnetic stirring)	8wt%	9:1	50°C	50 min	Y=97.0%	(Baskara et al.,2017)
KOH	Transesterification preceded by acid esterification (Mechanical stirring)	1.5wt%	0.32(v/v)%	60°C	1.5h	Y=88.0%	(Muthukumaran et al.,2017)
Red mud	Transesterification	15 g/L of oil	20v/v%	60°C	0.5h	Y=80.0%	(Senthil et al.,2016)
Ba-La mixed oxide	Transesterification preceded by acid esterification (Mechanical stirring)	1.5wt%	18:1	65°C	2h	C=97.5%	(Sahani et al.,2018)
KOH	Transesterification preceded by acid esterification	0.7w/v%	0.25v/v%	60°C	1h	-	(Kumar et al.,2017)

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	(Mechanical stirring)						
KOH	Microwave assisted two steps Transesterification preceded by acid esterification	1 wt %	40 wt%	53°C	2min	C=96.0%	(Jothi et al,2013)
ZnO	Transesterification	20 wt%	40:1(supercritical Methanol)	250°C	62min	C=99.0%	(lamba et al.,2019)
<b>Ba-La mixed metals oxide</b>	<b>Transesterification preceded by acid esterification</b> (Mechanical stirring)	<b>1.5</b>	<b>1:18</b>	<b>65°C</b>	<b>120 min</b>	<b>C=97.5%</b>	<b>(Sahani and Sharma., 2018)</b>
<i>Milletia pinnata oil</i>							
$\gamma$ - Alumina	Ultrasound assisted inter-esterification (60 duty cycle)	1 wt%	9:1	50°C	50 min	Y=69.3%	(Kashyap et al, 2019)
Cement waste (Aluminate, Belite, Alite, CaO)	Transesterification preceded by acid esterification (Mechanical stirring)	2.5wt%	30:1	60°C	3h	C=76.0±0.3%	(Kumar et al,2018)
BaZrO <sub>3</sub>	Transesterification preceded by acid esterification (Mechanical stirring)	1.0wt%	27:1	65°C	3h	C=98.0±0.5%	(Singh et al,2016)

Cs modified BaZrO <sub>3</sub>	Transesterification preceded by acid esterification  (Mechanical stirring)	1.72wt%	22.1:1	65°C	2.3h	C=97.27±0.4%	(Kumar and Singh,2019)
Crab shell derived catalyst (CaO)	Transesterification preceded by acid esterification  (Mechanical stirring)	2.5wt%	8:1	65°C	120min	Y=94%	(Madhu et al,2016)
Mixed metal oxides(ZnO- CaO)	Transesterification preceded by acid esterification  (Mechanical stirring)	5 wt %	18:1	65°C	2h	C=95.8%	(Joshi et al,2015)
<b>BaCeO<sub>3</sub> Perovskite</b>	<b>Transesterification preceded by acid esterification  (Mechanical stirring)</b>	<b>1.2wt%</b>	<b>1:19</b>	<b>65°C</b>	<b>100min</b>	<b>C=98.41%</b>	<b>(Sahani et al., 2019)</b>
<i>Schleichera oleosa oil</i>							
Mg <sub>2</sub> Zr <sub>5</sub> O <sub>12</sub>	Transesterification preceded by acid esterification  (Mechanical stirring)	2.5	18:1	65°C	150min	97.9%	(Singh et al., 2018)
K <sub>2</sub> Al <sub>2</sub> O <sub>4</sub>	Transesterification preceded by acid	1.0	15.:1	65°C	90 min	97.1%	(Yadav and Sharma, 2018)

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	esterification (Mechanical stirring)						
Ba(OH) <sub>2</sub>	Ultrasound assisted Transesterification	3.0	9:1	50 °C	90min	96.0%	(Sarve et al., 2016)
KOH	Transesterification preceded by acid esterification (Mechanical stirring)	1	8:1	55 °C	90min	96.1%	(Silitonga et al., 2015)
<b>Sr-La mixed metal oxide</b>	<b>Transesterification preceded by acid esterification (Mechanical stirring)</b>	<b>1.5</b>	<b>1:14</b>	<b>65 °C</b>	<b>40 min</b>	<b>C=96.6 %</b>	<b>(Sahani et al., 2018)</b>
<b>Waste cooking oil</b>							
Sr-Ce mixed metal oxide	Transesterification (Mechanical stirring)	2wt%	14:1	65 °C	120 min	Y=99.5%	(Banerjee et al.,2019)
KBr/CaO	Transesterification (Mechanical stirring)	3wt %	12:1	65 °C	1.8h	Y=82.5%	(Mahesh et al., 2015)
FeCl <sub>3</sub> - modified resin	Transesterification (Magnetic stirring)	8wt%	10:1	90 °C	120min	Y=92.0%	(Ma et al.,2017)
Encapsulated enzyme	Transesterification (Magnetic stirring)	2g load	12:1	35 °C	60h	Y=93.6%	(Razack and Duraiarasan, 2016)
Supercritical methanol	Transesterification (high pressure of	-	37:1	253.6 °C	14.8min	Y=91.6%	(Aboelazayem et al., 2018)

	198.5 bar)						
Magnetic SO <sub>4</sub> /Fe-Al- TiO <sub>2</sub>	Transesterification	3wt%	10:1	90°C	2.5h	Y=96.8%	(Gardy et al., 2018)
Wastes of peat clay and egg shells CaO/SiO <sub>2</sub>	Transesterification	8 wt %	14:1	60°C	90min	Y=91.6%	(Putra et al.,2018)
Diatomite @CaO/MaO	Transesterification	6wt%	15:1	90°C	120 min	Y=96.5	(Rabie et al.,2019)
<b>Sr-Ti mixed metal oxide</b>	<b>Transesterification (Mechanical stirring)</b>	<b>1wt%</b>	<b>11:1</b>	<b>65°C</b>	<b>80min</b>	<b>C=98.15%</b>	<b>Present study</b>

## 1.5. Objectives of the present work

The following four major objectives were defined in this research work.

- (i) Synthesis and characterization of Ba-La mixed metal oxide as heterogeneous base catalyst for FAME production from *Madhuca longifolia* oil: kinetic and thermodynamic investigation alongwith E-factor and TOF study.
- (ii) Synthesis and characterization of Ba-Ce mixed metal oxide as heterogeneous base catalyst for FAME production from *Millettia pinnata* oil: kinetic and thermodynamic investigation alongwith E-factor and TOF study.
- (iii) Synthesis and characterization of Sr-La based mixed metal oxide as heterogeneous base catalyst for FAME production from *Schleichera oleosa* oil: kinetic and thermodynamic investigation alongwith E-factor and TOF study.
- (iv) Synthesis and characterization of Sr-Ti based mixed metal oxide as heterogeneous base catalyst for FAME production from Waste cooking oil: kinetic and thermodynamic investigation alongwith E-factor and TOF study.

### 1.5.1. Sub-objectives of the each major objective

The point wise sub-objectives of each major objective are as follows where methodologies are common to all.

- (i) Selection of potential feedstock for laboratory scale production of methyl esters.
- (ii) Synthesis of barium and strontium doped mixed metal oxides as heterogeneous base catalysts.
- (iii) Characterization of synthesized solid base catalyst through thermal analysis (TGA/DTA/DTG), PXRD, XPS, SEM-EDX, FT-IR, and BET surface area analysis alongwith basic strength determination.

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- (iv) Study on activity of catalyst for methyl ester production through transesterification reaction using *Madhuca longifolia* oil, *Millettia pinnata* oil and *Schleichera oleosa* oil and waste cooking oil.
- (v) Analysis of the impact of process variables such as catalyst dose, oil to methanol molar ratio, reaction temperature, reaction time, and stirring speed alongwith reusability assessment of catalyst.
- (vi) Kinetic and thermodynamic study of transesterification reaction alongwith E-factor and TOF.
- (vii) Characterization of prepared methyl esters by GC-MS,  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ , and ATR FT-IR spectroscopy.
- (viii) Study of physicochemical properties of prepared methyl ester for its quality check to ensure its compatibility with conventional fuel.