1

INTRODUCTION AND BACKGROUND

1.1 Introduction

Now day's energy, economy, and environment are a very significant issue and challenges for the growth of a Nation. Since the industrial revolution (18 to19th century), energy has become an essential element for humankind to continue the economic and industrial growth and also to maintain a high standard of living. According to Shahid and Jamal [1] and IEA report [2], in 2030 the world will require 50% more energy than the present day, in which 45% will be responsible for China and India. During the last thirty years, there was a steady growth in energy consumption in the transportation sector. Worldwide, from 2007 to 2035, the consumption of energy in the transportation sector is increased by 1.8 % per year [3, 4]. Universally, 30% accounts for the transport sector of the total supplied energy. Currently, the transport sector accounts for sixty percent of the whole world oil demands [3-5]. According to International Energy Outlook 2016 [6], after China and the United States India being the World's 3rd biggest energy consumer since 2013. Worldwide, after the US, China, and Japan, India was the 4rth highest consumer of crude oil and petroleum products in 2015 [6]. In 2009, it evaluated that India holds only 0.4% of the world's total crude oil. The 70% requirement of petroleum in country's has met through the imports and this may be increased in the coming years [7]. During the last 30 years, production of crude oil in the country has been raised from 68.2 lakh tonnes in 1970-71 to 341.2 lakh tonnes in 2007-08 [7, 8]. The import of crude oil was increased by nine-time from 116.6 lakh tons in 1970-71 to 1210 lakh tons in 2007-08. The projected increased in diesel demand with a 5.8% annual rate to 650 lakh tons in 2030. Indian transportation needs 95% energy of total provided, and diesel demands are five times more than the petroleum [7, 8]. The crude oil production of India is around 1% of the world total, while the consumption is approximately 3.1% of the world total [8, 9]. The World Energy Outlook has forecasted that 94% of India's crude oil demand would be met by imports in 2030 [8, 9]. It means India will be needed import of high amount of crude petroleum oil in the future to meets the requirement of energy for the country. For the next 20 years, the demand for energy in the country is expected to grow with a 4.8% annual rate [8, 9].

On the other hand, change in climate is the most critical global environmental issue. About ten lakhs species could become dead, and a thousand lakhs of people could lose their life if the world's average environment temperature rises by higher than 2 ^{o}C [10]. It is expected that the World energy-related CO_2 emissions rise from 32.2 billion metric tons in 2012 to 35.6 billion metric tons in 2020 and to 43.2 billion metric tons in 2040 [6]. It was expected the increase of global energy-related CO_2 emissions from 32.2 thousand million tonnes in 2012 to 35.6 thousand million tonnes in 2020 and 43.2 thousand million tonnes in 2040 [6]. In India, the total increase in energy-related CO_2 emissions from 1.778 million tonnes in 2012 to 2.143 million tonnes in 2020 and 3.732 million tonnes in 2040 [6]. According to the United Nations' IPCC, around 23% of energy-related, the carbon dioxide emission has come from the transport sector. Around 45% of this total was accounted for passenger vehicles [11]. In Europe, more than the fifth of carbon dioxide emission accounted for from the transportation sector. The increase in the release of greenhouse gases (GHGs) from the transportation sector was 20% from 1990 to 2001 [12]. Currently, transport sectors of India consume more than 3rd of total crude oil product, which emitted around 142 million tonnes of CO_2 equivalent. Road transport sector shares about 87 % of total GHG emission [6]. The CO_2 emission is the primary greenhouse gas (95%) from the transportation sector. Additionally, 1% of GHG emissions are composed of methane and oxides of nitrous. The remaining 3% GHG emissions of the transportation sector has come from air vehicle conditioning with the leakage of hydrofluorocarbons. The transportation sector sources are also emitting ozone, CO, and aerosols. These substances have not considered as GHG gases, but assumed that there is an indirect impact on global warming; however, its effect has not been certified with certainty [13].

With the socio-economic development of society, the pattern of consumption depends on the energy resources availability in a particular country because the need for energy has increased in multiple ways globally. The industries, transport, agriculture, and domestic are the different sectors required the energy from the limited sources such as timber, coal, petroleum products, nuclear power, the solar, wind, etc. [14]. Among these, the transportation sector mainly depends on petroleum fuels. Due to the overwhelming depends on fossil fuel; disappointing situations have created with economic and environmental problems [15]. At a global level, awareness about energy problems and GHG issue associated with the fossil fuels burning has motivated various researchers for investigating the feasibility of alternative fuel as energy sources rather than oil and its derivatives. Alternative fuels have gained enormous attentiveness due to lower environmental pollution, feedstocks availability, and fossil fuel depletion. There are several available alternative energy sources such as biodiesel, ethanol, hydrogen, biogas, and syngas. Among these, biodiesel shows similar properties to conventional diesel fuel.

1.2 Biodiesel

According to the ASTM, biodiesel is known as mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats [16]. Triacylglycerol (TAGs); fatty acid esters and glycerol are the main ingredients of vegetable oil and animal fat. The TAGs are also known as the triglycerides; it includes the composition of different fatty acid, which affects the physical and chemical properties of vegetable oil and animal fats. The different sources of oil have different fatty acids compositions with a chemical point of view. The fatty acid contains a long chain of carbon and several unsaturated bonds. The common fatty acids present in biodiesel feedstocks are myristic acid, palmitoleic acid, palmitic acid, stearic acid, oleic acid, linoleic acid, linolenic acid, arachidic acid, and erucic acid [17, 18]. The biodiesel can be obtained from many resources.

1.3 Source of biodiesel

The natural and renewable sources like vegetable oils and animal fats are the sources of alternative diesel fuels. The vegetable oil obtained from different sources having different compositions of fatty acid. Fats and oils are mainly water-insoluble, hydrophobic substances in plants and animal kingdoms, produced from a mole of glycerol and three fatty acids, and generally known as triglycerides. Soybean, castor, neem, sunflower, palm, rapeseed, canola, and jatropha, etc. are the commonly used oil to make the biodiesel. There are many sources of biodiesel, categorized as edible oil, non-edible oil, and waste or recycled oil and animal fats.

1.3.1 Edible plant oils

The vegetable plants oil such as soybean, coconut, palm, sunflower, mustard, linseed, rapeseed, etc. is a source of the edible oil. These oils are pondered as the first generation of biofuel feedstock as they were the first crop used for the production of biodiesel. Food industries and biodiesel feedstock are the two main reasons for a sudden increase in the requirement of edible oil plants in the last few decades. The edible oil plant including; soybean, coconut, sunflower, rapeseed, and palm are extensively used as a feedstock of biodiesel in the USA, Argentina, Brazil, European countries, Malaysia, and Indonesia. The 95% of total world biodiesel produced from edible oil plants, including 84% from rapeseed, 13% from sunflower, and 3% from palm [19, 20]. Although there is some big problem such as raising the food prices, hunger, deforestation, and usage of arable land only for oil-bearing agriculture plants are arises due to the continuous extensive use of edible oils plant for the production of biodiesel. Moreover, edible oil plants highly depend on the conditions of environment. Besides, its transportation to the biodiesel production industry will probably adversely affect the capital cost of biodiesel. Since the edible vegetable oils having a higher price in comparison to diesel; therefore waste cooking oil, and non-edible oils preferred as possible sources of lower-cost biodiesel. In India, there is a massive gap in demand and supply of such oils; therefore, it is not possible to make the biodiesel from edible vegetable oil.

1.3.2 Non-edible plant oils

The vegetable plants including; jatropha, mahua, neem, karanja, jojoba, tung, rice bran, cottonseed, etc. are the source of non-edible oil to produce the biodiesel [21]. All the above edible and non-edible oil plants have not a similar composition of fatty acid due to which biodiesel possess different chemical as well as physical properties. As a biodiesel feedstock non-edible oil have gained great attention due to their high of content oil , easy availability and also it can grow in wasteland not suitable for agriculture. Additionally, these plants do not affected by regional weather conditions and need less attention and ultimately reduced the cultivation cost.

1.3.3 Waste oils and animal fats

The waste oil obtained after the cooking is not further used for cooking purpose and usually discarded, this residual oil used as biodiesel feedstock. Recently, because of the lower cost of waste cooking oil, it considered as a potential feedstock for biodiesel production [22]. Although the residual oil obtained after cooking is highly contaminated and containing a higher amount of free fatty acid (FFA). Therefore, waste cooking oil can be classified into two groups, based on contents of FFA: the yellow oil (FFA < 15%), and brown grease (FFA > 15%). After the filtration and purification, these oils can be used for the production of biodiesel. There are different animal fats including; beef tallow [23], duck tallow [24], chicken fats [25], fish fats, etc. are also used as feedstock to produce the biodiesel. The biodiesel production from these sources has a higher cetane number, which leads to reducing knock in an engine. Although, the biodiesel of such resources has high cold filter plugging point due to the presence of higher level of saturated fatty acids. Also, because of the absence of natural antioxidants, they offered a few resistant during the process of oxidation.

1.4 Processes/methods to produce the biodiesel

The investigators have consistently tried to make vegetable oil derivatives that possess comparable properties as to the petroleum diesel fuel. The main issues with the use of triglycerides as a substitute for conventional diesel fuel are higher viscosity, lower oxidation stability, and lower volatility [26]. These characteristics can be improved through mainly four methods, namely direct use and blending, micro-emulsification pyrolysis/cracking and transesterification.ossess comparable properties as to the petroleum diesel fuel.

1.4.1 Blending/Dilution

The first method is straightforward. In this biodiesel and diesel fuel is mixed in a specified proportion and it can be used directly in CI engine. Several experiments have been done successfully regarding the blending of vegetable oil with conventional diesel fuel. In 1980 Caterpiller Brazil Company mixed 10% vegetable oil with 80% diesel oil and tested it for pre-combustion chamber engines. It was found that this blended fuel retained its total power without modification in the engine [27]. Subsequently, 95% cooking oil and 5% diesel was tested in 1982. Later on, it has been proved that 100% of vegetable oil can also be used in an engine with little modifications. The viscosity and volatility of vegetable oils may improve with heating and blending. However, the molecular structure of oil remains unchanged; consequently, the polyunsaturated character does not change [28]. The use of vegetable oil needs the significant modifications in diesel engines such as changing of piping and injector construction materials unless decreased the engine operating time, increased in cost of maintenance because of high wear, and this leads to a higher chance of engine failure.

1.4.2 Micro-emulsification

In the micro-emulsion process**,** methanol, ethanol, and butanol are used as a solvent to reduce the high viscosity problem of vegetable oil fuel. A microemulsion is a colloidal equilibrium dispersion of optically isotropic fluid. According to Ramadhas et al. [29], microstructures in liquids have the dimensions ranges from 1 to150 nm. Both liquids are immiscible, and at least one of them must be ionic or non-ionic amphiphiles. It helps in improving the spray characteristics through explosive vaporization of a constituent in micelles. The microemulsions show maximum viscosity limitation when butanol, hexanol, and octanol are used as a solvent for the CI engine. Czerwinski [30] produced emulsions, which consist 13.3% ethanol, 33.4% butonal, and of 53% sunflower oil. It had cetane number of 25 and viscosity 6.3 centistokes at 40 ^{o}C. It was also observed that increasing the butanol percentage leads to better spray patterns and lower viscosities. The micro-emulsion process decreased the viscosity of vegetable oils but appeared in uneven injector needle sticking, massive deposition of carbon particles, and incomplete combustion throughout the 200-hour laboratory screening endurance test [31].

1.4.3 Pyrolysis/Thermal cracking

Thermal cracking can be defined as the conversion of one substance into another by application of heat in the presence of a catalyst. In this process, heating is done in the absence of air, which leads to smaller molecules. The methyl esters of fatty acids, vegetable oils, natural fatty acids, and animal fats can be used as pyrolyzed substances. For more than 100 years ago, pyrolysis of fats was done where there was a scarcity of petroleum [32]. After World War I various researchers have been trying to study the pyrolysis process to obtain the engine fuel from vegetable oil. The thermal cracking and pyrolysis equipment are very costly for moderate throughout. Furthermore, the products are chemically comparable to petroleum-derived gasoline and diesel fuel, the removal of oxygen during the thermal processing also removes any environmental benefits of using an oxygenated fuel. It produces few low-value materials and, sometimes, more gasoline than diesel fuel [33].

1.4.4 Trans-esterification (Alcoholysis)

The transesterification or alcoholysis is the conventional processes for the production of biodiesel by the assist of alcohol having 1-8 carbon atoms in the presence of catalyst [34]. Generally, methanol used as alcohol because of its easy availability and lower cost [35]. Transesterifications have been taking place to produce the fatty acid alkyl ester (FAAE).

In which a mole of triglyceride reacts with the 3 moles of alcohol that produces 3-moles FAAE and 1-mole glycerine. There are three consecutive reversible reactions have been taken place for conversion from a triglyceride to FAAE. Initially, a mole triglyceride produces one mole of diglyceride and one mole of FAAE and this one-mole diglyceride to delivered one mole of monoglyceride and one mole of FAAE in secondary reaction, and finally, a mole of monoglyceride is also formed one FAAE and one glycerol. Therefore, a mole of biodiesel (FAAE) is producing in each reaction. The catalyst used to increase the rate of reaction and yield [29]. The transesterification reaction can be categorized into homogeneous and heterogeneous based on the use of catalyst; acid, base, acid-base, etc [figure 1.1]. Recently, various investigators have concentrated on finding bio-catalytic pathways in the production of biodiesel. The catalytic super-critical and non-catalytic transesterification process is also getting the idea as one of the developing techniques in the production of biodiesel.

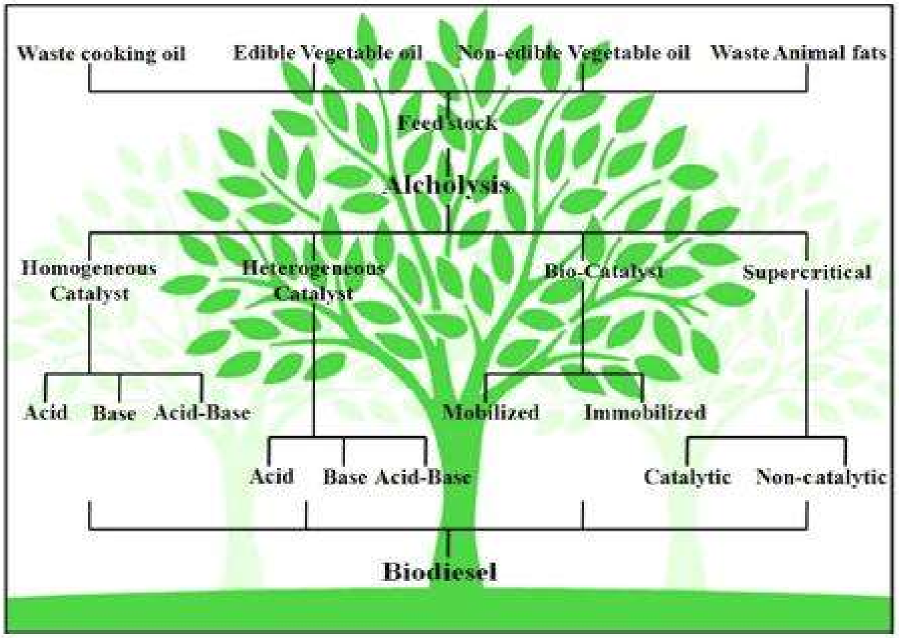

Figure 1.1: Schematic diagram for transesterification/alcoholysis reaction [36]

1.5 Homogeneous catalysis for trans-esterification process

The acids and base both catalysts have come under homogeneous catalysis transesterification process. They are the most preferred biodiesel production process. The homogeneous catalytic process is very simple, less time consuming, and the reaction takes place the mild working conditions. For the production of large amount biodiesel, several washing and purification steps required. The major drawback of this process is that it creates enormous amounts of wastewater [37]. There are several investigations have been conducted and developed new technologies to overcome these issues. Table 1.1 shows some common homogeneous and heterogeneous catalyst for transesterification reaction.

1.5.1 Homogeneous base-catalyzed trans-esterification reaction

It is the base-catalyzed transesterification reaction for making the biodiesel in relatively short reaction time (1-1.5 hours). In which, most widely sodium hydroxide (NaOH) and potassium hydroxide (KOH) catalysts are used for transesterification reaction [36]. These catalysts are used because of their higher activity, lower cost, and easily available. Generally, it founded that the sodium-based catalysts are superior to the potassium-based catalysts because it has lower molecular weight. The homogeneous base catalyst transesterification is observed to be 4000 times more active than the homogeneous acid-catalyst process. It has investigated the transesterification reaction occurs at 65 °C by the using of 1:6 oil to alcohol ratio with 1% base catalyst [38]. The transesterification process is susceptible to those oils which have a higher level of free fatty acid (FFA). If the oils contained more than 2% FFA, the saponification would occur and hence decreased the biodiesel yield. Therefore, the biodiesel feedstock should contain low FFA (< 2%) to avoid these problems.

1.5.2 Homogeneous acid-catalyzed trans-esterification reaction

The acids catalyst such as sulphuric and sulfonic acids is used for the transesterification reaction of homogeneous acid-catalyzed. In which needed large quantities of alcohol to get a higher yield of biodiesel. The benefit of this process is that it generally conducted comparatively at lower temperature and pressure. The methyl/ethyl esters procured with the displacement of alcohol on the protonation of ion. The complete biodiesel conversion of high FFA (>2%) content oil has obtained in a single step with acid catalyst transesterification reaction [39]. The major disadvantage of the acid catalyst reaction is that the catalyst deactivated with the presence of water content. This problem appears due to the presence of the polar carboxylic group in the feedstock [40]. Another notable problem with the acid catalyst is that it leads towards corrosion and also reduced the biodiesel yield. The homogeneous acid catalysts including H_2SO_4, HCl, $AlCl_3$ and CH_3Na, are frequently used for the production of biodiesel. The detailed about the reaction time and temperature, oil to catalyst and alcohol ratios, and biodiesel yield have been shown in table 1.1.

1.5.3 Homogeneous acid and base catalysts for the two-steps trans-esterification reaction

The two-step transesterification process is carried by simultaneously conducting the esterification with acid catalyst followed by transesterification process with the base catalyst. This method is worked to that feedstock having higher than 2% free fatty acids [41]. The problems such as separation of the biodiesel from glycerol, slower reaction rate, and saponification are eliminated with two-step transesterification.

1.6 Heterogeneous catalysts for trans-esterification process

These catalysts are also known as a solid catalyst, and at the industrial scale, it shows the effective and suitable catalyst to produce the biodiesel at the commercial level. They are sensitive and tolerate with high free fatty acids and content of water in the feedstock. The heterogeneous catalysts are separated after esterification and transesterification process used, and it used further for in the production of biodiesel. However, the homogeneous catalysts could not reuse, and also they are consumed during biodiesel conversion processes. These catalysts work comparative at higher temperature and pressure and even tolerate the extreme reaction conditions (given in table 1.1). A heterogeneous catalyst is categorized into acid and base catalysts [42]. The benefit of acid catalyst is that they can use for both processes esterification and trans-esterification simultaneously. On the other hand, for the base catalyst lower amount of catalyst are needed for preceding the transesterification reaction. The heterogeneous catalysts, including mollusc shells, eggshell, ashes, and rocks are obtained from waste and renewable biomass or natural resources [43, 44].

1.6.1 Heterogeneous base-catalyzed trans-esterification reaction

Several metal oxides, including MgO, CaO, SrO, alkali, and alkaline earth metal oxide, mixed metal oxides, etc. are the solid base heterogeneous catalyst used for the production of biodiesel [45]. The fixed-bed reactor system has used while producing the biodiesel with these catalyst, that helps in easy separation of catalyst from the products. These catalysts are active at the boiling point of methanol during the transesterification reaction [46]. Among these, CaO is most widely used because of its high basicity, little solubility, longer life, easily handled, and lowers cost. Table 1.1 shows the detail about the reaction time and temperature, requirement of alcohol and catalyst, and percentage biodiesel yield.

1.6.2 Heterogeneous acid-catalyzed trans-esterification reaction

The major advantage of these over the heterogeneous base catalyst, they are tolerant to contents of high free fatty acid and water in feedstocks. Although, the ideal heterogeneous acid catalyst must have several properties such as hydrophobicity, moderate acid strength, a large number of accessible active sites, and porosity to reduce the diffusional problems. Also, with the use of acids catalyst, the severe reaction conditions are required while transforming the oil into the biodiesel; therefore, it is essential that the acid catalyst is thermally stable. However, the acid catalysts have gained less attention compared to the base catalyst because of its slower reaction rate. In the present day, the use of heterogeneous catalysts in the production of biodiesel based on modified inorganic mixed oxides including silica, sulfated and tungstated zirconia, or zeolites, heteropoly acids, super acid, sulfated carbon materials, and resins of cation-exchange . The heterogeneous acid catalyst, sulfated zirconia, and tungstated zirconia are producing a better yield than a homogeneous catalyst [47]. Table 1.1 shows some different heterogeneous-acid catalyst, condition for reaction, and the percentage yield.

1.6.3 Heterogeneous bi-functional catalysts or two-steps trans-esterification process

The biodiesel production by the two-steps homogeneous catalysts process may not be favorable due to the requirement of a significant quantity of catalyst and also used throughout the neutralization step. Apart from this, the homogeneous catalysts also used for treatment related to the separation, purification, and wastewater disposal. The reused of heterogeneous catalysts for two-step biodiesel production may achieve future relevance as a catalyst while replacing with homogeneous catalysts.

1.7 Biocatalysts for trans-esterification reaction

The bio-catalytic transesterification process can also produce biodiesel in the presence of an enzyme. The researchers have reported the lipase is the best option of the enzyme [65]. The lipase can also be used in intracellular or extracellular nature for enzymatic transesterification [31]. There are several benefits such as easy separation of products, the formation of zero by-products, recycling of catalysts, and moderate process conditions (temperature 35 to 45 ^{o}C) of this process over the chemical catalyst transesterification process. This process can also be used for the low-grade source, tolerant to high free fatty, and water content in feedstocks. On the other hand, the enzyme becomes unattractive due to its higher operating conditions for deactivation and cost [66, 67]. In the present day, there are four different lipases including; Mucor meihi, Candida antarctica, Geotrichum candidum, and Pseudomonas ceracia are being used as catalyst to produce the biodiesel from olive oil, soybean oil and, tallow in the in presence of alcohol.

1.8 Supercritical method

The biodiesel production with this process does not need the catalyst for the reaction. This process has a significant advantage over the conventional method. The product purification is not needed in the supercritical process because of it not involve the use of catalyst. The water content in the feedstock is not affecting the reactions at supercritical condition; therefore, this process could be used effectively for that feedstock, which contains the water. In this process, the reaction is completed in 2-4 min [68]. It was reported that the palm oil biodiesel produced by this process with monitoring of various variables. The main disadvantage of this method is higher operating temperature and pressure with higher methanol to oil ratio for conventional biodiesel production [69].

Table 1.1: Some homogeneous/heterogeneous base and acid catalysts for alcoholysis reaction [48-51, 52-54, 55-60, and 61-64]

Type of catalyst	Catalyst / Catalyst to oil ratio (%)	Alcohol/ molar ratio of oil to alcohol	Temperature (^oC) / Time (min)	Yield (%)	Ref.
Homogeneous base catalyst	NaOH / 1	CH_3OH / 1:6	60/60	90.00	[48]
	NaOH / 0.8	CH_3OH / 1:6	60/60	97.00	[49]
	NaOH / 0.6	CH_3OH / 1:6	60/60	97.00	[49]
	$NaOCH_3$/ 0.6	CH_3OH / 1:6	60/60	97.00	[49]
	$NaOCH_3$/ 0.8	CH_3OH / 1:6	60/60	92.00	[49]
	KOH/ 1.0	CH_3OH / 1:6	60/60	96.00	[49]
	NaOH / 0.5	CH_3OH / 1:6	50/30	96.00	[50]
	KOH/0.5	CH_3OH / 1:7.5	60/60	96.00	[51]
Homogeneous acid catalyst	H_2SO_4/2.5	CH_3OH / 1:6	60/60	96.60	[52]
	HCl/2.5	CH_3OH / 1:6	60/120	87.90	[52]
	$AlCl_3$/2.5	CH_3OH / 1:6	60/120	87.98	[52]
	H_3PO_4/0.1	CH_3OH / 1:3	130/60	50.00	[53]
	H_2SO_4/0.1	C_2H_5OH / 1:3	130/60	82.00	[53]
	H_2SO_4/2.261	C_2H_5OH / 1:6.126	55/240	96.60	[54]
	CaO (Capiz shell)/3	CH_3OH / 1:8	60/360	92.83	[55]

Heterogeneous base catalyst	CaO (mussel shell)/12	CH_3OH / 1:24	60/480	94.10	[56]
	CaO (Egg shell)/3	CH_3OH / 1:9	60/180	94.73	[57]
	CaO (Crab shell)/3	CH_3OH / 1:6	60/240	82.87	[57]
	MgO/3	CH_3OH / 3:20	190/120	82.80	[58]
	Templated-MgO/3	CH_3OH / 3:20	150/180	98.20	[58]
	SrO/5	CH_3OH / 1:6	65/15	82.00	[59]
	K_3PO_4/5	CH_3OH / 1:6	65/180	78.00	[60]
Heterogeneous acid catalyst	propyl-SO_3H-SBA-15/6	CH_3OH / 1:20	140/120	72.00	[61]
	arene-SO_3H-SBA-15/6	CH_3OH / 1:20	140/120	78.00	[61]
	Amberlyst-36/6	CH_3OH / 1:20	140/120	32.00	[61]
	SiO_2-Tosic acid/6	CH_3OH / 1:20	140/120	65.00	[61]
	Nb-MCM 41/7.5	CH_3OH / 1:12	200/240	95.00	[62]
	30%WO_3/$AlPO_4$/5	CH_3OH / 1:30	180/300	72.50	[63]
	$Fe(HSO_4)_3$/1.0	CH_3OH / 1:15	205/240	94.50	[64]

1.9 Availability of biodiesel feedstock

Generally, the feedstock selection for the production of biodiesel is country-specific depends on the availability. The variation in the social aspect, condition of the environment, cost-effectiveness and agroecological parameters play a role in the choice of vegetable oil feedstock to produce the biodiesel. The United States, Europe, Japan, and Malaysia are using soybean, rapeseed, sunflower, animal fat, and palm oil, respectively, for the production of biodiesel. Worldwide, the primary edible oils feedstock is soybean, sunflower, rapeseed, and palm for the production of biodiesel. Earlier, rapeseed oil has been a great choice and still dominant with a share of 80% as a biodiesel feedstock, and oil from sunflower holds the second position with a share of 10 %, followed by oil from soybean [70].

In India, the two most sensitive and vital raw materials are oil-seeds and edible oils. Despite the production of huge quantities of oils by a different type of plants, India does not become independent of edible oils. From the last 20 years, the average growth rate of edible oil consumption has increased by 4.25% from 49.59 lakhs tons in 1986-1987 to 121.91 lakhs tons in 2007-2008 [71]. It has predicted that the edible oil requirement in India will be 200 lack tonnes per year in 2015 [72]. According to the situation of India, non-edible oil is the only alternative sources that can be used as biodiesel feedstocks. In-country, the non-edible oil sources produced in a considerable amount and it will grow in vital range on non-cropped marginal lands and wastelands. India has about 630 lack of hectare wasteland. This land categorized into namely three parts; degraded pastures and grazing land; underutilized degraded notified forest land, and degraded land under plantation crop categories [73]. Consequently, the government of India has determined to explore the sources of non-edible oil as an alternative feedstock for the production of biodiesel. And it becomes the most suitable raw material for the production of biodiesel as the demand for edible oil exceeds the national supply. In India, there is an enormous untapped capacity of different type non-edible oil plants (about 300 or more) which spread to a different place of the country [74]. It has recognized that almost 75 types of plants generally having more than 30% oil in its seed/kernel. As per Government of India policy, only non-edible oils are used for biodiesel.

The non-edible oil sources like Jatropha, Canola, Tung, Mahua, Karanja, Babassu, Neem, etc. are very cheap in comparison to edible oils and are easily available at the different place of the world comprising India [75]. In India, there are various plants produces seeds that bear non-edible oils such as Azadirachta indica (Neem), Madhuca indica (Mahua), Simarouba indica (Simarouba), Pongamia pinnata (Pungam) and Jatropha curcas (Jatropha), which can be used for the production of biodiesel [76]. It has estimated that the possibilities of such oil are available in the country about to be 10 lakh tonnes per annum [77]. Table 1.2 shows primary sources are Sal oil (1.8 lakh tonnes), Mahua (1.8 lakh tonnes), Neem oil (1.0 lakh tonnes) and Karanja oil (0.55 lakh tonnes). The fruiting and seed yield depends on the gestation period and maturity time of the plants. The gestation period of Jatropha, Mahua, Neem, Karanja and Simarouba are about to 1-2, 8, 5, 4 and the 6 years, and maturity time about to 6, 14, 13, 11 and the 8 years respectively. Density of these plants are about to 2500, 200, 400, 500 and 500 plants/ha, and a mature trees produces 1-1.6, 60-80, 30-100, 8-24 and 15 kg seed/tree [78-82]. In India, there are huge areas of degraded lands and most of the areas are unfavorable to agricultural climatic conditions, where rarely tree born oilseeds can be cultivated easily. Area (ha) under major trees such as jatropha (748782 ha), Mahua (62500 ha), neem (617500 ha), Karanja (36000 ha), and Simaroa (1885 ha) cultivated in the different state of India [83-85].

Table 1.2: Potential of tree born non-edible oils in India [86-88]

S.No.	Tree born oil sources	Botanical name	Potential seed and oil yield (lack tonnes per year)	
			Seed	Oil
1	Karanja	Pongamic pinnata	20000	55000
2	Jatropha	Jathropha Curcas	50000	15000
3	Kusum	Scheleichera oleosa	80000	25000
4	Neem	Azadirechta indica	500000	100000
5	Sal	Shorea robusta	1500000	180000
6	Mahua	Madhuca indica	500000	180000
7	Mango	Mangifera indica	500000	45000
8	Tumba	Citrulluscollocynthis	--	17000
9	Kokum	Garcinia indica	--	500
10	Jojoba	Simmondsia chineaca	--	--
11	Chullu	Prunus armeniaca	--	100
12	Nahar	Mesua ferrea L.	--	10000
13	Pilu	Salvadora oleoides	--	17000
14	Rice bran	Oryza sativa	--	474000
15	Phulware	Cheura	--	3000

In India, a lot of research has been done on Jatropha, Pongamia, Karanja, and Mahua for their suitability in the country situation. Though, Neem considered as an extremely deserving tree for its multipurpose uses and efforts are need to focus on them. 'Azardiratchi' is the primary biochemical ingredient derived from neem oil for medicinal purposes. After deriving this vital element, the remaining part of the oil used for making the biodiesel, which can be viewed as a good way for its integrated use.

1.10 Biodiesel used in CI engine

The various researchers have conducted the experiments, and after evaluation of results, it has been founded that there are differences in engine performance like engine torque, power, and BSFC with comparison to diesel fuel. Apart from these results, there is a reduction in exhaust emissions like sulfur dioxide, unburnt hydrocarbon, carbon monoxide, particulate matter, nitric polycyclic aromatic hydrocarbons, and polycyclic aromatic hydrocarbons but increased in nitrogen oxides from most of the experimental results [89, 90]. C Carraretto et al. [89] have carried the experimental analysis of 6-cylinders DI compression ignition engine. They have revealed that there is little reduction in engine torque and power with enhancing the percentage of biodiesel in the blended fuel for the whole range of engine speed. Hanbey Hazar et al. [91] have evaluated the performance and emission characteristics of DI Rainbow-186 diesel engine fuelled with blended fuel of preheated neat rapeseed oil and diesel. They have reported that the value of smoke density and CO emissions are significantly decreased; on the contrary, slightly increased the formation of nitrogen oxide (NOx). There was a slight decrease in BSFC. Also, with preheating, the viscosity of oil and blended fuel are considerably reduced. H.G. How et al. [92] have evaluated the performance, emission combustion characteristics of a 4-stroke diesel engine fuelled with coconut biodiesel blends (B10, B20, B30, and B50) at varying load. There was a slight increased the BSFC and reduced the BSEC at all load. The value of brake specific carbon monoxide (BSCO) was increased, and reduction in smoke opacity with enhancing the proportion in the blended fuel. Increase in the brake specific nitric oxides (BSNOx) with raising the load. At all loading condition, Lengthen the combustion duration and shorten ignition delay for the biodiesel blends. Slightly lower peak heat release rate and RMS (root mean square) for biodiesel blends than diesel fuel. The experiment conducted on Ricardo E6 diesel engine to study the effects of injection timing, CR, engine speed and load output on the combustion noise, engine output torque, maximum pressure, and maximum heat release rate, fuelled with neat Algae oil and its biodiesel. There was a slight reduction in engine output torque and increment in combustion noise. The above results can be improved with controlling the engine parameters, including; the fuel injection timing and compression ratio [93].

Raheman and Ghadge [94] and Laguitton et al. [95] have been carried out the experiments on a diesel engine to study the variation of compression ratios on performance and emission. As increasing the compression ratio, decreased the BSFC, increased the EGT, and improved the BTE. While reducing the compression ratio, cylinder temperature also drops and hence reduced NOx emission. The CO and HC emission increased when the engine operated at a lower compression ratio. Indeed, there are many researhers have worked on different bio-diesel, but few of them have investigated the performance of different biodiesel available in India, especially tree grown in the north of India. The experimental work has been conducted on the CI engine to analyze the performance and emission for different biodiesel (Castor, Neem, Mahua, and Linseed) at the same configuration of engine and inputs. Additionally, evaluate the performance and emission with respect to long time stored biodiesel. Further, the optimum performance of engine depends on the several parameters; some inputs can easily be handled during the experiments, but others like the design of stroke/bore and size of the valve are difficult to put input for the performance test. At this condition, modeling provides a good predictive result for enhancing the engine performance, and optimization.

1.11 Mathematical and computational modelling

In the present time, the mathematical and computational models have been developed for simulation of engine performance and emissions. Modeling and simulation are extensively utilized in the analyzing of internal combustion engines. The modeling of the internal combustion engine based on the law of thermodynamics, cylinder heat transfer, fluid mechanics, and rate of chemical kinetics and makes use of complete databases of engine parameters like fuel properties, friction coefficients and piping parameters [96]. The IC engine modeling divided into the zero-dimensional, phenomenological, quasi-dimensional, and multi-dimensional model, respectively. In the zero-dimensional model, basic thermodynamics law and fundamental energy conservation law are most frequently used to analyze the engine process. On the other hand, better accuracy obtained by applying the phenomenological and quasi-dimensional models with the use of additional details like the piston geometry and spark plug position. In these models, the most accurate results obtained with the multi-dimensional model by considering the variation of the engine cylinder and geometry of the combustion chamber with the effect of flow [97]. The combustion models of diesel classified into basically two parts (figure 1.2); Thermodynamic and the Multi-Dimensional model. The thermodynamic model further classified into the single-zone and multi-zone. The single-zone model is frequently used if there is a requirement of a quick and preceding evaluation of the engine performance. In this model, considered the uniform composition of charge and temperature and applied the first law of thermodynamics to evaluate the energy of the mixture for enthalpy flux because of the injection of fuel. While injecting the fuel in the cylinder considered that it is instantly mixed with charge already present in the combustion chamber, and which treated as an ideal gas [98]. This model does not consider the air entrainment, fuel vaporization, and spatially changing in the composition and temperature. This model is beneficial due to the simplicity and extensively used with experimental results in the engine industry to create choices for design. The model integrated with an increase of pressure, and it assists in evaluating the heat release rate from the cylinder [99]. The researchers have developed the two-zone combustion model, which gives a more exact prediction of the result in comparison to single-zone [100-103]. Several researchers have developed the multi-zone model to overcome the disadvantages of the single-zone model. In this model, spatial and temporal in temperature and concentration are considered. It also includes a comprehensive evaluation of fuel and air distribution, which allows for estimating the composition of exhaust gases within a reasonable accuracy [104-107].

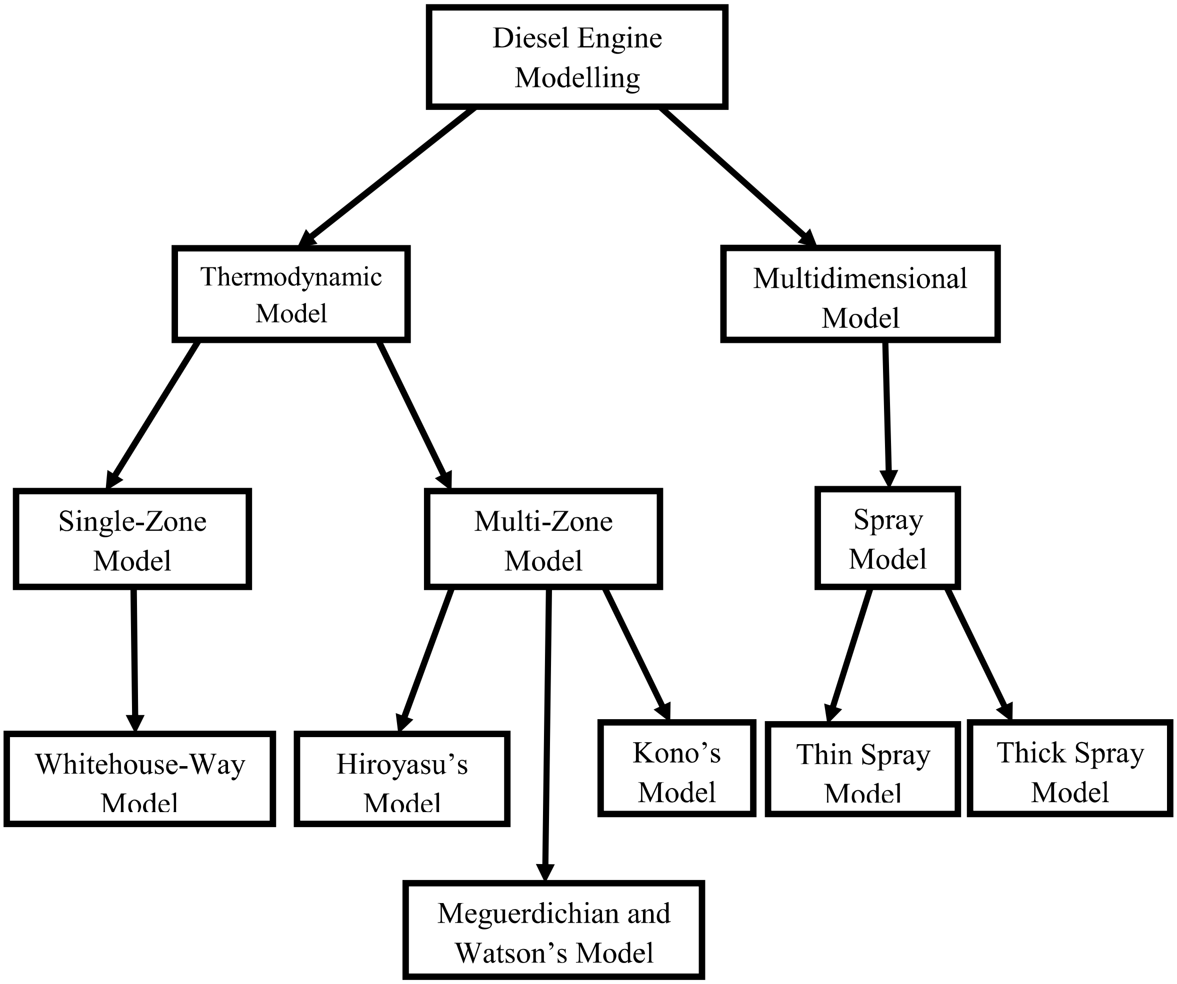

Figure 1.2: Classification of diesel engine model [98]

In the multi-zone models, fuel spray separated into a large and finite number of zones (i.e., small pockets of fuel) that moves through the combustion chamber. Another multi-zone model which is followed the development of equivalent ratio zone around the centerline of liquid fuel core. In this model during the calculation considered the mass, momentum, and energy conservation equations. Later on, stochastic and CFD models are presented to understand the impact of gas-phase turbulence on droplets of the fuel. However, the fuel droplets effect on turbulence in several parts also avoided. The charge in the cylinder divided into several zones, and the behavior of each zone has been studied [96].

1.12 Life cycle assessment of biodiesel

Energy is a necessary element in the process of economic development, as it gives essential services that maintain economic activity and quality of human life. Thus, the lack of energy is a critical obstacle to developing countries [108]. Effective utilization of energy required in agriculture to maintain and the optimal production of yield, because it helps in promoting the economic condition and saving the available fossil resources [109]. Consequently, the objectives of the investigation should be to highlight the energy and economic evaluation of several agricultural practices to plan alternative sources in ecosystems [110]. There are some essential factors which did not consider during the comparison between various feedstocks. Since, to promote alternative fuels, the life cycle assessment has become a vital decision-making tool. Therefore, it has decided that it should systematically conduct the full life-cycle analysis of each feedstock in term of energy efficiency, environmental impacts, and cost benefits. There are several economic and energy indices including; gross production value, gross return, cost-benefit ratios, productivity, energy ratio, energy gain, specific energy, energy intensity, energy productivity have been used extensively to measure the energy efficiency and economic value of biodiesel.

The International Organization for Standardization (ISO) 14044:2006 standards (ISO 2006) defined as the study of life cycle assessment (LCA). It includes the availability of land for the cultivation, input and output energies, emission of GHG, pesticides application, erosion of soil and fertility, participation in losses of biodiversity value, logistic cost (transportation and storage), economic value of the feedstock including its co-products, generation of employment, availability of water and its requirements and feedstock effects on the quality of air [111, 112]. It is essential to estimate the net energy gain in the production of biomass and biofuels. Some authors have evaluated the net energy value (NPV) and net energy ratio (NER) for ethanol produced from corn [113], sugar cane [114], and cassava [115], and biodiesel from soybean [116]. It has obtained from several studies and investigations that feedstock account 70-75% of the total biodiesel production cost. The cost of biodiesel feedstock generally varied from region to region and country to country [117]. De Souza et al. [118] have conducted the life cycle analysis of Palm biodiesel. They have carried out a wide range of investigation on life cycle emissions, and the energy cost. For the LCA analysis, considered the necessary factors including; decrease in GWP, energy balance in the production of biodiesel. Sheehan et al. [116] have studied the life cycle inventory for the consumption of energy in the production of biodiesel from soybean. They have considered all the inputs during the analysis and carried out the studies in the six stages including the soybean agriculture practics, transport of seed and oil, extraction of oil, production of biodiesel, distribution, and uses of biodiesel in CI engines.