Literature Review

2.1 Background

In today's world, petroleum is clearly the most important energy source, providing more than half the world's power, as well as being a basic material used in the manufacture of fertilizers, synthetic fibers, plastics, and synthetic rubber. Demand is ever-increasing worldwide, yet petroleum resources are finite and non-renewable. According to the reports of international agencies there will be 53% increase in the demand of energy by the year 2030. It is anticipated that the petroleum demand will increase from 84.40 million barrels to 116.00 million barrels per day by 2030 in USA alone. Ejaz M. Shahid et al [1]. The consumption ever increasing over production, this can be clear in the figure (2.1) which represents the trends of oil production and consumption between 1965 and 2009.

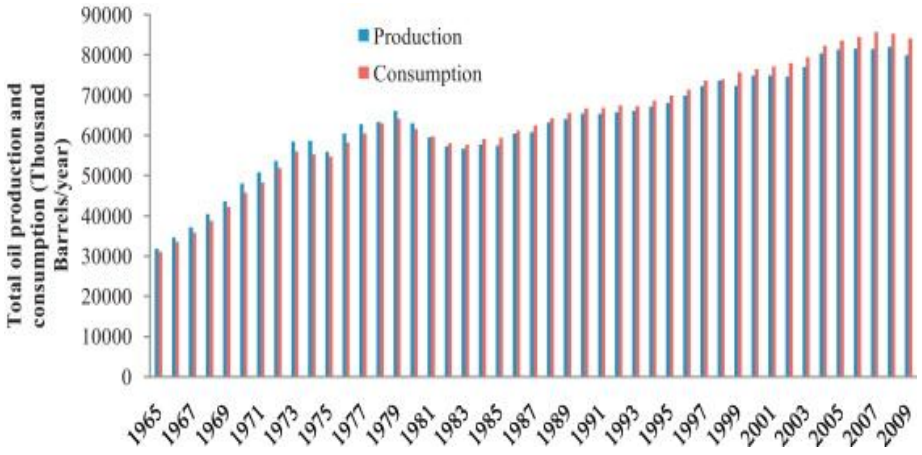

Figure (2-1) Total oil proved reserves between 1980 and 2009
(Thousand million barrels)

According to the current prediction of World Energy Forum, worldwide reserves of fossil-based oil, coal and natural gas will be exhausted in less than 10 decades D.N. Tewari et al [2] with world

consumption level of 85.4 million barrels of oil and 261 billion cubic feet of natural gas per day P.T. Vasudevan et al [3].

Oil is expected to remain the largest source of energy; therefore the oil share of world marketed energy consumption is expected to decline from 35% in 2007 to 30% in 2035 as can be seen in Fig (2-2) A.E. Atabani et al [4].

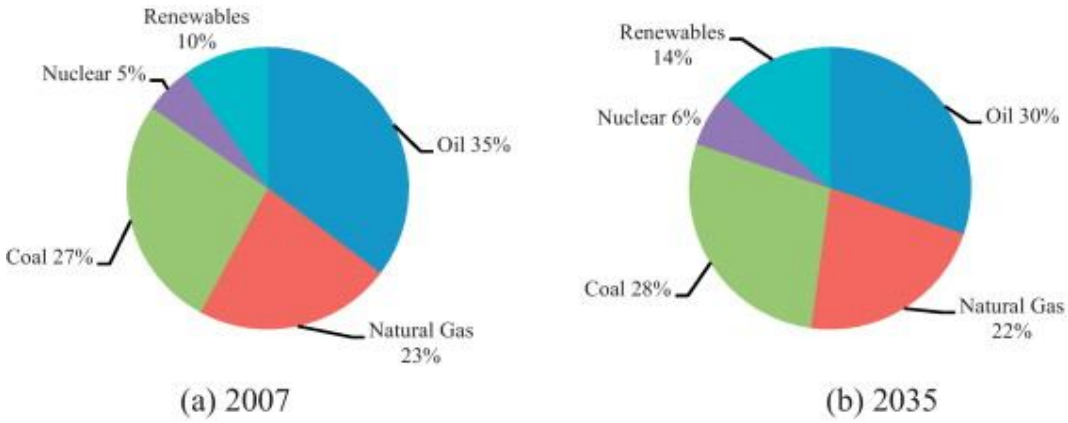

Figure (2-2) Breakdown of world marketed energy consumption by fuel in 2007 and 2035

The depletion pace of energy resources is synchronized with global population and industrialization growth rate. Search for a renewable and environment friendly alternative fuel source has become an urge globally to overcome the increasing demand of fuel using techno-economically competitive technology and more attractive sources for energy production Balat M [5].

Among these alternative sources, biodiesel has gained considerable attention since its derived from renewable resources, can be domestically produced, and is not as harmful as petroleum to the environment. Using of vegetable oils as a fuel for diesel engines is not new; Rudolp diesel used 100% peanut oil to fuel one of his engines early in 1893 and demonstrated this engine at the World Exhibition conducted in Paris 1900 M. Canakci et al [6]. Later in 1937, G. Chavane introduced a new

concept coming out from his patent “Procedure for the transformation of vegetable oils for their uses as fuels which known as “biodiesel” today. First patent of industrial process for biodiesel was applied by ExpeditoParente from Brazil in 1977; then in 1979 researcher in South Africa worked in transesterifing of sunflower oil and refining it to diesel fuel standards Lin L [7]. For evaluating the performance of this alternative fuel in the engine, Blumberg and Ford 1982 made short and long term engine performance and emission tests using eight different fuel samples, and they reported that short term results have been more desirable than long terms results, because of carbon deposits, ash and wear in the combustion chamber and sticky gum content in fuel line elements.

The process for producing fuel-quality, engine-tested biodiesel was completed and published internationally in 1983; and researches continued; 1988, Schinstock et al used 25/75 blends soybean and sunflower oil fuel with diesel and the performance test has been done in 200h engine. They concluded that the engine torque values with mixtures have been greater than with pure diesel operation. Later Schumacherb1991; reported on Soybean methyl ester as a fuel in a Dodge truck and concluded that it can be used in diesel with minimum rate of difficulty, and also found that increasing the soybean methyl ester ratio in diesel fuel mixtures will decrease the power smoke intensity, CO and HC emissions and increase fuel consumptions. The same results reported also by Shay EG 1993; Sinha S, Misra 1997 and Altin R.1998.

A lot of experiments has been done for testing the feasibility of using biodiesel as alternative fuel, Christopher et al. 1997 conducted two tests in Chicago using biodiesel as an alternative fuel for in-service motor coaches, in order to determine the effect of fuel on the engine performance characteristics and infrastructure needed to use this fuel; the testing proved that the biodiesel could be used as a feasible alternative fuel.In 2002,

Ghormade et al. used soybean oil as fuel to run a compression ignition engine. He found that there was an only slight variation in part loads efficiency. And there was no improvement in brake specific fuel consumption by blending. Later in 2005 Hengwen Han, Weiliang Cao, Jingchang Zhang worked on the Transesterfication process where they prepared biodiesel from soybean oil using supercritical methanol and CO_2 as co solvent, and they concluded that with an optimal reaction temperatures of 280°C, methanol to oil ratio of 24 and CO_2 to methanol ratio of 0.1, 98% yield of biodiesel was observed in 10 minutes at reaction pressure of 14.3 MPa.

In order to enhance the performance of vegetable oils in diesel engine and solve the problem of its high viscosity, scientists from various parts of the world US, Europe, India, Malaysia and Germany; using different types of oil are used such as rapeseed, sunflower, palm oil, coconut oil and jatropha oil. The first biodiesel pilot plant is established by Gaskoks from an Austrian company in 1987 followed by the first industrial-scale plant in 1989.

The Key milestones in the application of biodiesel standards as follows: A.S. Silitonga et al [8]

- 1991: Austrian's first biodiesel standard, was issued.
- 1997: A German standard, DIN 51606 was formalized.
- 2002: American Standard Specification {ASTM D6751} was first published.
- 2003: A new Europe-wide biodiesel standard, DIN EN 14214 was published.
- 2005: Minnestosa became the first US state to mandate that all diesel fuelled sold in the state contain part biodiesel, requiring a content of at least 2% biodiesel.
- 2008: ASTM published new Biodiesel Blend Specification

Standards.

- 2008: The current version of the European Standard EN 14214 was published and supersedes EN 14214:2003.

2.2 Definition of biodiesel

The National biodiesel board defined biodiesel as the fatty acid alkyl monoesters derived from renewable feed stocks, such as vegetable oils and animal fats A.S. Silitonga et al [8]. It's a fuel resulting from mixing of vegetable oils with alcohol in the presence of catalyst fig (2-3). Biodiesel is a biodegradable, non-toxic, almost sulfur less and non-aromatic environmentally friendly alternative diesel fuel.

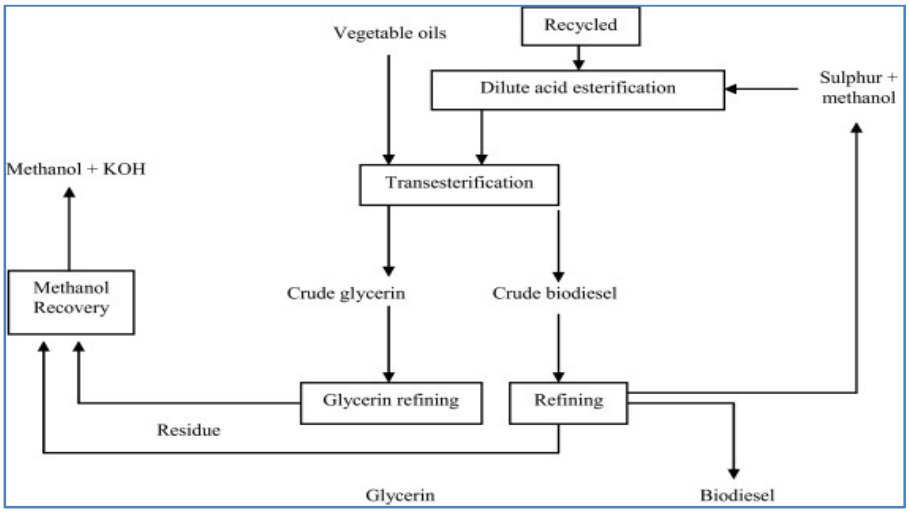

Figure (2-3) basic schemes for biodiesel production

The source for biodiesel production is usually chosen according to the availability in each region or country. European communities are self-dependent in production of edible oil and even have surplus amount to export. Hence, edible oil such as rapeseed is used in European Nations; soybeans are primary source for biodiesel in the United States. Other countries like Malaysia, Indonesia and Thailand used palm oil and coconut oil which considered the main oil in this region because of the nature of the climate. However, some Asian countries are not self-sufficient in edible oil

and exploring non-edible seed oil, like Jatropha and Karanja as biodiesel raw materials basically in India and Southeast Asia. In Brazil, the most used oil source for the biodiesel productions are soybean, castor bean and palm kernel H.C. Ong. 2011 [9].

When a diesel engine is operated with biodiesel, exhaust emissions decrease approximately 20% in CO, 30% in HC, 40% in particulate matter (PM), and 50% in soot emission, compared to the diesel fuel Domkundwar V [10]. In contrast to these decreases, its NOx emission increases about 10–15. However, the high NOx problem can be overcome by retarding the injection timing. Lubricity property of biodiesel is much better than that of diesel fuel, especially low-sulfur diesel fuel. Little biodiesel additive ,even as little as 1%, is enough to significantly improve the conventional diesel fuel's lubricity However, the use of these oils is restricted to diesel engines, since they contain free fatty acids (FFAs), phospholipids, sterols, water, odorants, and other impurities. In addition, vegetable oil's high viscosity, about 11-17 times higher than diesel fuel, which affects the flow properties of the fuel, such as spray atomization, consequent vaporization, and air-fuel mixing in the combustion chamber, leading to an adverse effect on the combustion process, to overcome these drawbacks, the oil has to be chemically treated.

2.2.1 Biodiesel feedstock

Globally, there are more than 350 –oil-bearing crops identified as potential sources for biodiesel production, the availability of feed stocks for producing biodiesel depends on the geographical locations and agricultural practices of the country, and from the literature the more commonly feed stocks used are soybean, palm, sunflower, safflower, cottonseed, rapeseed and peanut oils A.E. Atabani et al [4].

Mainly, The biodiesel cost is affected by the cost of feedstock, as shown in the figure (2-4), feed stock represent 75% of the overall biodiesel production cost, and the rest 25% goes to the chemicals additive, equipment depreciation, management and overhead cost. These conclude that selecting of the feed stock should meet two significant requirements, low production cost and large production scale.

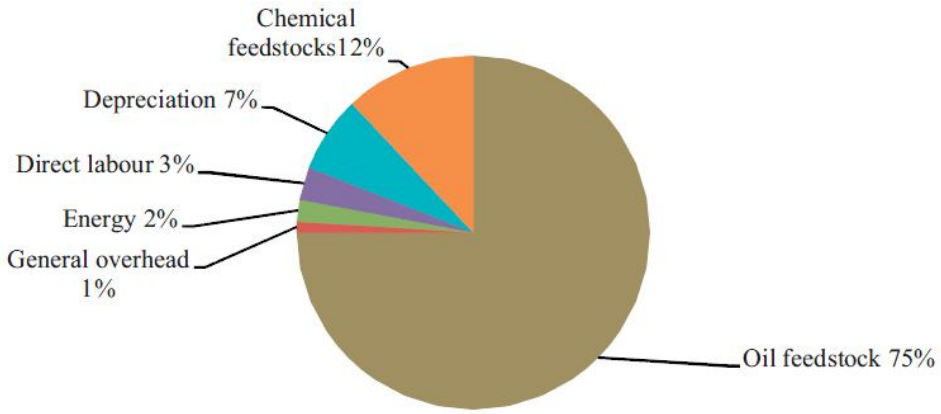

Figure (2-4) general cost breakdown for production of biodiesel A.E. Atabani [4]

In general these biodiesel feed stocks can be divided into four main categories; edible vegetable oils, non-edible vegetable oils, waste or recycled oils and animals fats, and there are other resources available. Some of these are presented in the table 2-1 below B.K.Barnwal [11]; A.E. Atabani [4].

Vegetable oils have the potential to be considered as appropriate alternative, as they possess fuel properties similar to that of diesel. When vegetable oils adopted as fuel in diesel engine; they reduces harmful exhaust emission, particularly HC, smoke, and CO, as compared to diesel. The major problem associated with the direct use of vegetable oils is their high viscosity; this can be overcome by transesterification of potential oils to produce esters of respective oils S. R. Kalbande [12].

Table 2-1 Main biodiesel feedstock

Edible oils	Non-edible oils	Animal fats	Other sources
Barely	Camelina	Beef tallow	Algae (Cyanobacteria)
Canola	Cotton seeds	Chicken fat	Bacteria
Coconut	Cumaru	Fish oil	Fungi
Corn	Jatropha curcas	Pork lard	Microalgae
Groundnut	Jojoba	Poultry fat	Miscanthus
Palm and palm kernel	Karanja		Latexes
Peanut	Moringa		Poplar
Rapeseed	Neem		Switchgrass
Rice bran oil	Passion seed		Tarpenes
Sesame	Pongamia		
Soybeans	Rubber seed		
Sun flower	Salmon oil		

Most of the oils used for the production of biodiesel by various researchers were soybean, sunflower, safflower, cotton, rapeseed and palm oil. Their plantations have been well established in many countries around the world such as Malaysia, USA and Germany. Currently, more than 95% of the world biodiesel is produced from edible oils such as rapeseed (84%), sunflower oil (13%), palm oil (1%), soybean oil and others (2%) A.E. Atabani [4]. However the edible oil are in demand, their use is getting rise and the price increased dramatically during the 10 last year's which will affect the biodiesel production industries Balat M. [5], Deng X [13].

One of the possible solutions to reduce the utilization of the edible oil for biodiesel production is by exploiting non-edible oils. Non-edible

oils resources are gaining worldwide attention because they are easily available in many parts of the world especially wastelands that are not suitable for food crops, eliminate competition for food, reduce deforestation rate, more efficient, more environmentally friendly, produce useful by-products and they are very economical comparable to edible oils A.E. Atabani [4].The main sources for biodiesel production from non-edible oils are Jatropha, KaranjaNeem, Moringa, Rubber seed, Cotton seeds and Tobacco seed.

Several studies have been done on the production of biodiesel from waste oils or animal fats such as; Beef tallow, Chicken fat, Pork lard and Fish oil; describing the feasibility of making quality biodiesel from this feedstock while identifying the problems with the free fatty acids present in the raw materials. The presence of free fatty acids and water in this feedstock results in the production of soap in the presence of alkali catalyst. Thus, additional steps to remove any water and either the free fatty acids or soap from the reaction mixture are required. Despite the lower reaction rate associated with sulfuric acid-catalyzed transesterification processes, this approach has several advantages over the base-catalyzed method Palligarnai [3]. The advantages of using waste cooking oils to produce biodiesel are the low cost and prevention of environment pollution. Due to the high cost of disposal, many individuals dispose waste cooking oils directly to the environment especially in rural area S. Kent Hoekman [14].

The current feedstock used for biodiesel production all over the world are shown in the table below; Ahmad AL [15], Kumar BP [16].

Table 2-2 Current potential feed stocks for biodiesel worldwide

Country	Feedstock
USA	Soybeans/waste oil/peanut
Canada	Rapeseed/animal fat/soybeans/yellow grease and tallow/mustard/flax
Mexico	Animal fat/waste oil
Germany	Rapeseed
Italy	Rapeseed/sunflower
France	Rapeseed/sunflower
Spain	Linseed oil/sunflower
Greece	Cottonseed
UK	Rapeseed/waste cooking oil
Sweden	Rapeseed
Ireland	Frying oil/animal fats
India	Jatropha/Pongamiapinnata(karanja)/soybean/rapeseed/sunflower/peanut
Malaysia	Palm oil
Indonesia	Palm oil/Jatropha/coconut
Singapore	Palm oil
Philippines	Coconut/Jatropha
Thailand	Palm oil/Jatropha/coconut
china	Jatropha/waste cooking oil/rapeseed
Brazil	Soybeans/palm oil/castor/cotton oil
Argentina	Soybeans
Japan	Waste cooking oil
New Zealand	Waste cooking oil/tallow

2.2.1.1 Main characteristics of vegetable oils

Vegetable oils provide engine performances similar to that obtained with diesel fuels. The following are the important characteristics of good vegetable oil required to substitute diesel fuel Domkundwar V [10]; A.S. Ramadhas [17].

- **Ignition quality**

Satisfactory diesel combustion demands self-ignition of the fuel as it is sprayed near TDC into the hot swirling compressed cylinder gas. Long ignition delay is not acceptable as it leads to knock. Therefore, the cetane number of the substitute fuel should be high enough, which is a measure of knock tendency of the fuel. Satisfactory fuels must have a cetane number between 40 and 60.

- **Viscosity**

Fuel viscosity plays an important role in the combustion of fuel used. The direct injection in the open combustion chamber through the nozzle and pattern of fuel spray decides the ease of combustion and thermal efficiency of the engine. Too low viscosity can lead to excessive internal pump leakage whereas system pressure reaches an unacceptable level and will affect injection during the spray atomization. The effect of viscosity is critical at low speed or light load conditions.

- **Heating value**

Although the diesel combustion chamber system can accept wide variations in heating value, practical systems are only suitable when calorific value of the fuel is high. This helps to reduce the quality of fuel handled and maximizes the equipment operating range. It is always desirable for the vegetable oils to have a calorific value nearer to that of diesel.

- **Important temperatures**

Pour point and cloud point are important for cold weather operations of the I.C. engine. For satisfactory working, the values of both should be well below the freezing point of the oil used. Flash point is an important temperature from a safety point of view values. This temperature should be as high as practically possible. Typical values of commercial vegetable oils fuel range between 50 and 110 C. Vegetable oil–diesel blend should not decrease the flash point temperature.

- **Other properties**

The sulphur content, carbon residue and ash are responsible for corrosion and forming a residue on the engine parts which will affect the engine life. These values should be as small as possible. Practical values are 0.5% sulphur, 0.27% carbon residue and 0.01% ash.

2.2.2 Biodiesel Production Processes

The main reason of not using vegetable oils and fats directly in diesel engines; its high viscosity, this why it should be reduce by breaking down triglyceride bonds, and this can be achieved by four main processes all are suitable to convert vegetable oils and fats into biodiesel Lay L. Myint [18]. They are:

- Blending
- Microemulsion,
- Pyrolysis (thermal cracking) and;
- Transesterification.

Among these four ways, the most commonly preferred process to reduce the high viscosity of reaction is transesterification process FangruiMaa [19]; Dennis Y.C [20].

2.2.2.1 Blending

Blending is the direct mixing of vegetable oil with diesel fuel. Biodiesel can be used as a blend component in petrodiesel in any proportion because it is completely miscible with ULSD. However, ASTM D975 and D7467 only allow up to 5 and 20 vol. % biodiesel, respectively. Biodiesel and petrodiesel are not chemically similar: biodiesel is composed of long-chain FAAE, whereas petrodiesel is a mixture of aliphatic and aromatic hydrocarbons that contain approximately 10 to 15 carbons Bryan R. Moster [21].

Biodiesel and petrodiesel have differing chemical compositions; the blended fuel from mixing them, will exhibit properties different from neat fuel of each one. The most important fuel properties influenced by blending of them are lubricity, exhaust emissions, CN, flash point, oxidative stability, low-temperature operability, kinematic viscosity, and energy content.

The literature of the effects of blending in the fuel properties as shown: Bryan R. Moster [21]. Lubricant of petro diesel is positively impacted through blending with biodiesel K. Shaine [22]. Tyson et al. Specifically, B2 and B20 blends of SME in ULSD (contains no lubricity enhancing additives) significantly improve lubricity (60°C according to ASTM D6079) from 551 to 212 and 171 μm, respectively.

- Exhaust emissions of ULSD, with the exception of NOx, are reduced through blending with biodiesel, as previously discussed Mudge SM et al [23].
- The CN of petrodiesel is increased upon blending with biodiesel SrinivasaRao p et al [24]. For example, the CN of petrodiesel, tall oil methyl esters, and the corresponding B50, B60, and B70 blends are 47, 54, 52, 52, and 53, respectively.

- The flash point of petrodiesel is increased upon blending with biodiesel SrinivasaRao p et al [24].The flash points of FAME are much higher than those of petrodiesel and range from around 110 to 200°C versus 50 to 60°C for petrodiesel. When blended with petrodiesel, biodiesel does not impact flash point up to B20, but beyond B20, the flash point increases significantly Canakci [6].
- The oxidative stability of petrodiesel is negatively impacted upon blending with biodiesel. This is because the hydrocarbon constituents of petrodiesel are more stable to oxidation than FAME (especially in the case of unsaturated FAME).
- The amount of gravimetric solids formed (indicators of oxidative degradation) according to ASTM D5304 in the cases of petrodiesel and the corresponding B10 and 20 blends (SME) were 0.6, 4.2, and 9.0 mg/100 mL, respectively C. Muraleedharan et al [25].
- The low-temperature operability of petrodiesel is negatively impacted once blended with biodiesel Canakci [6]. For instance, the CFPP of petrodiesel, tall oil methyl esters, and the corresponding B50, 60, and 70 blends were −8°C, −3°C, −7°C, −6°C, and −6°C, respectively. In another example, the PP of ULSD and B2, 5, 20, and 100 blends (PME) were −21°C, −21°C, −18°C, −12°C, and 18°C, respectively Bryan R. Moster [21].
- The kinematic viscosity of petrodiesel increases upon blending with biodiesel. For example, the kinematic viscosities (40°C) of ULSD and B1, 2, 5, and 20 (SME) blends are 2.32, 2.40, 2.48, 2.57, and 2.71 mm2/s, respectively Bryan R. Moster[21]. In another example, the kinematic viscosities (40°C) of petrodiesel and B50, 60, 70, and 100 (tall oil methyl esters) blends are 2.60, 4.50, 4.82, 5.12, and 7.10 mm2/s, respectively.
- The heat of combustion (energy content) of petrodiesel is reduced

upon blending with biodiesel Dennis Y.C Leung et al [20]. Specifically, the energy contents of petrodiesel and B50, 60, 70, and 100 (tall oil methyl esters) blends are 43,760, 41,901, 41,511, 41,145, and 40,023kJ/kg, respectively. In another example, the energy contents of petro diesel and B2, 5, 10, 20, and 100 (SME) blends are 46.65, 46.01, 45.46, 44.48, 43.75, and 39.09 MJ/kg, respectively Dennis Y.C. Leung et al [20].

2.2.2.2 Micro-emulsification

Micro-emulsification is another approach to reduce the viscosity of vegetable oils. Microemulsions are clear, stable isotropic fluids with three components: an oil phase, an aqueous phase and a surfactant. The aqueous phase may contain salts or other ingredients, and the oil may consist of a complex mixture of different hydrocarbons and olefins. This ternary phase can improve spray characteristics by explosive vaporization of the low boiling constituents in the micelles. All micro-emulsions with butanol, hexanol and octanol can meet the maximum viscosity limitation for diesel engines J-H. Ng. Hoonkiat et al [26]. Microemulsion prepared by blending soybean oil, methanol, 2-octanol and cetane improver in the ratio of 52.7:13.3:33.3:1.0 has passed the 200 h EMA test. May Ying Koh [27].

2.2.2.3 Cracking

Cracking is a process of converting one substance into another by means of heat or with the aid of catalyst. It involves Heating in absence of air or oxygen and cleavage of chemical bonds to yield small molecules. The pyrolyzed material can be vegetable oils, animal fats, natural fatty acids and methyl esters of fatty acids. The pyrolysis of fats has been investigated for more than 100 years, especially in those areas of the world that lack deposits of petroleum SrinivasaRao et al [24]. Since World War I, many investigators have studied the pyrolysis of vegetable oil to obtain

products suitable for engine fuel application. Tung oil was saponified with lime and then thermally cracked to yield crude oil, which was refined to produce diesel fuel and small amounts of gasoline and kerosene Ramadhas et al [25].

2.2.2.4 Transesterification process

Transesterification (alcoholysis) is the chemical reaction that involves triglycerides and alcohol in the presence of a catalyst to form esters and glycerol figure (2-7).It's the most commonly used method for biodiesel production, Palligarnai T et al [3].

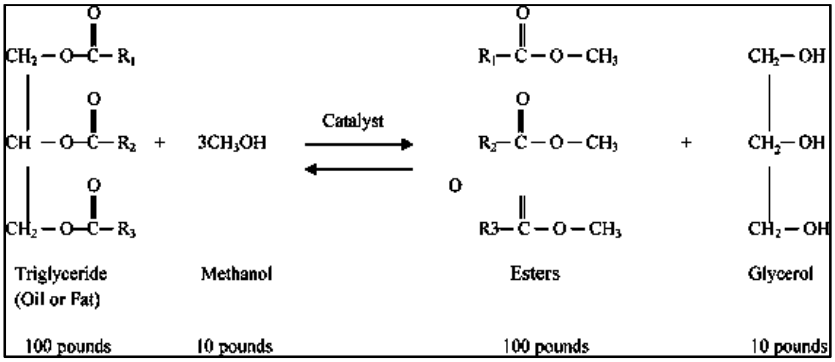

Figure (2-5) Equation of transesterification reaction

In general transesterfication process can be performed in two different methods, catalytic method and non-catalyst method. A catalyst is usually used to improve and enhance the reaction rate so that the reaction can be completed in a shorter reaction time. An alkaline- catalyzed transesterification process is normally adopted for biodiesel production because alkaline metal alkoxides and hydroxides are more effective than acid catalysts. Alkaline catalysts include catalysts such as NaOH, $NaOCH_3$, $KOCH_3$, KOH, NaMeO and K_2CO_3.Most of the researchers reported that both sodium and potassium hydroxide perform equally well. Sodium and potassium methoxides return better yield than all catalysts but they are costly, so they are not very frequently used. However, to use alkaline catalysts, free fatty acid (FFA) level should be below a desired

limit (ranging from less than 0.5% to less than 3%). Beyond this limit the reaction will not take place and the product formed will be soap and water instead of esters and the yield of esters will be too less Shahid EM [28].

Alcohols are any organic compounds which have a hydroxyl functional group bonded to other carbons or hydrogen atoms having. Examples are methanol, ethanol, propanol, butanol and amyl alcohol. Among the alcohols, methanol and ethanol are used commercially because of their low cost and their physical and chemical advantages. They are easily dissolved in and react quickly with tri-glycerides and NaOH. N.N.A.N. Yusuf [29]. However, methanol is the most preferable because of its low cost and its physical and chemical advantages as polar and short chain alcohol. Methanol can also react with triglycerides quickly and easily dissolve the alkali catalyst. However, there is explosion risk associated with methanol vapours due to its low boiling point and there for eversible, excess alcohol is used to shift the equilibrium towards the product.

Transesterification consists of three consecutive reversible reactions; conversion of triglyceride to diglyceride, diglyceride to mono glyceride and monoglyceride to fatty ester and glycerol. The reaction mechanism that takes place is according to this chemical equation:

$$\text{Triglyceride} + \text{ROH} \xrightarrow{\text{NaOH}} \text{Diglyceride} + \text{RCOOR}$$

$$\text{Diglyceride} + \text{ROH} \xrightarrow{\text{NaOH}} \text{Monoglyceride} + \text{RCOOR}$$

$$\text{Monoglyceride} + \text{ROH} \xrightarrow{\text{NaOH}} \text{Glycerol} + \text{RCOOR}$$

Equation of mechanism for transesterification

of triglyceride to FAME and glycerol

The reaction is facilitated with a suitable catalyst. If the catalyst remains in the same (liquid) phase to that of the reactants during transesterification, it

is homogeneous catalytic transesterification. On the other hand, if the catalyst remains in different phase (i.e. solid, immiscible liquid or gaseous) to that of the reactants the process is called heterogeneous catalytic transesterification. In conclusion, the process of transesterification is affected by the mode of reaction condition, molar ratio of alcohol to oil, type of alcohol, type and amount of catalysts, reaction time and temperature and purity of reactants Darnoko D et al [30].

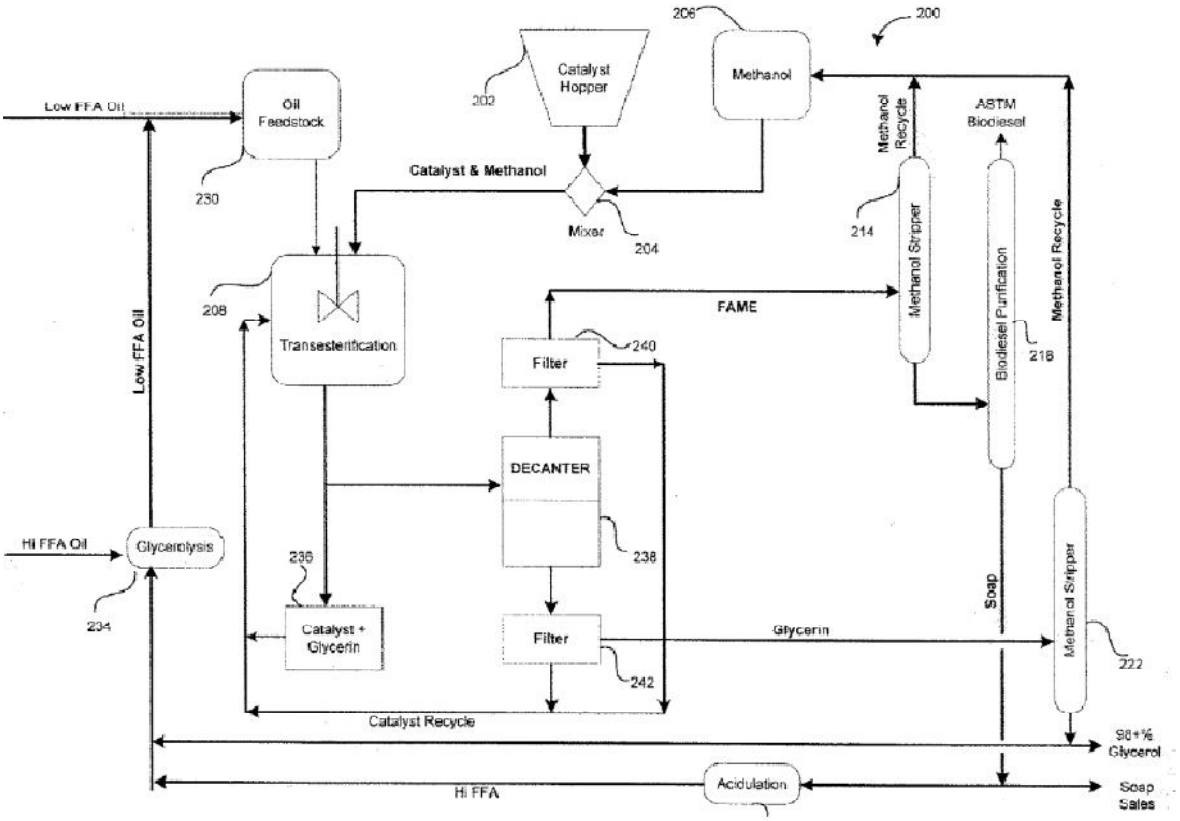

Figure (2-6) the process flow diagram for biodiesel production

Meanwhile, the biodiesel process plant is separated into five sections as follows:

section1: feedstock treatment, section 2: methanol and catalyst feed,

section3: transesterification process, section4: glycerin and catalyst separation, section 5: Methanol separation and section 6: FAME purification and waste by product recycling.

Section 1 involve the feedstock treatment, in this process, the oil is being convert to become low free fatty acid, FFA oil. For the soap that recycles back from biodiesel purification separation, it will under goes acidulation process. Then, it and high free fatty acid oil will be sent to glycerolysis to create low free fatty acid oil. Next, the FFA oil is sent to the oil feedstock.

Section 2 involve methanol and catalyst feed. The catalysts consist of solid metal.

Oxide powder and is inserted into the catalyst hopper. Then, the methanol is placed into the methanol storage tank from the recycle. Both of them will be mixed thoroughly in mixer before entering the reactor.

Section3 involve transesterification process. In transesterification process, the methanol and FFA oil will undergoes transesterification to produce fatty acid methyl ester and glycerin. The reaction is carried out in batch manner at 25°C and 1atm. Meanwhile, the catalyst is in mobilized manner.

Section 4 involves the glycerin and catalyst separation. In this section, the glycerin and catalyst will be separated by using decanter. FAME and methanol will go upward because of their less density (lighter weight) and glycerin and catalyst will go downward because it is heavier.

Section 5: methanol separation. Methanol is separate by using evaporator at its boiling point, 82°C and at 0.09 atm.

Section 6 consist of FAME purification and waste by product recycling. The FAME is purified by using distillation column at 159°C and 30 kPa. FAME will be top product and oil will be the bottom product because it has boiling point of 318°C.

2.2.3 Variables effecting transesterification process

Transesterification reaction is affected by various parameters depending upon the reaction conditions. The reaction is either incomplete

or the yield is reduced to a significant extent if the parameters are not optimized. Each parameter is equally important to achieve a high quality biodiesel which meets the regulatory standards Lay L et al [18]. And the maximum yield of biodiesel should be at the optimum values of these variables.

The most important parameters that affect the transesterification process are mentioned below:

- **Ratio of alcohol to oil**

The transesterification process consists of a sequence of consecutive reversible reactions where the triglycerides is successively transformed into diglyceride, monoglyceride, and finally into glycerine and the methyl esters. One of the most important variables affecting the conversion to methyl esters is the molar ratio of methanol to vegetable oil. The stoichiometric molar ratio of methanol to Jatrophacurcas L. oil for complete transesterification of the fatty acids in the oil to methyl esters is 3:1. However, in practice a higher molar ratio is employed in order to shift the reaction equilibrium towards the products side and produce more methyl esters.

In general, the molar ratio is associated with the type of catalyst used. Previous results have shown that an acid-catalyzed transesterification needs a high molar ratio of methanol to oil (30–150:1), while the molar ratio of methanol to oil 6–15:1 is usually used in alkali-catalyzed system FangruiMaa.et al [19].

- **Concentration of catalyst**

As mentioned before catalyst is used to enhance the transestrfication process and further promote the reaction. As they are less corrosive to

industrial equipment, alkaline catalysts are preferred in industrial processes. A concentration in the range of 0.5–1% (w/w) has been found to yield 94–99% conversion to vegetable oil esters and further increase in catalyst concentration does not affect the conversion but adds to extra cost, as the catalyst needs to be removed from the reaction mixture after completion of the reaction.

- **Reaction temperature and time**

The rate of reaction is strongly affected by the reaction temperature. A higher reaction temperature can decrease the viscosities of oils and result in an increase in reaction rate as more energy is being supplied for the reaction to occur. Thus the yield of the biodiesel product is improved. However, the reaction temperature must be less than the boiling point of alcohol (boiling point of methanol is at 60–70 °C at atmospheric pressure) to ensure the alcohol will not be lost through vaporization. Also, the yield of biodiesel decreases if the reaction temperature goes beyond its optimum level because a higher reaction temperature will accelerate the saponification reaction which results in a lower yield. Depending on the types of oil, the maximum yield is obtained at temperatures ranging from 60 to 80 °C May Ying Koh et al [27].

The methyl ester conversion rate increases with the reaction time. Different researchers have reported different reaction times for the transesterification process. Studied the transesterification reaction,with methanol (6:1), of vegetable oils using NaOH and Na/NaOH/γ-Al_2O_3 as catalysts at 333 K. They reached the maximum biodiesel yield within 1 h both for the case of homogeneous and heterogeneous catalyst system. For the homogeneous catalyst system, the maximum biodiesel production yield was higher by 20% than that of the heterogeneous catalyst system.

Beside these variables there are some other variables affecting the transterfication process, they are:

- Free fatty acids, moisture and water content.
- Rate and mode of stirring.
- Purification of the final product.
- Mixing intensity.
- Effect of using organic co-solvents, and
- Specific gravity.

2.2.4 Biodiesel fuel quality

Same as fossil diesel, the successful commercialisation of biodiesel around the world has led to the development of various national standards which they describe the minimum requirement of important biodiesel properties to ensure its suitability for use in diesel engines J.H. Kent Hoekman [14].

- **Density**

The density of fuel has some effect on the break-up of the fuel injected into the cylinder. In addition, more fuel is injected by mass as the fuel density increases. Higher density of biodiesel allows use of splash blending by adding biodiesel on top of diesel fuel making biodiesel blends else the fuel will not mix.

- **Kinematic viscosity**

The viscosity of an engine fuel is one of the most critical fuel features. It plays a dominant role in the fuel spray, mixture formation and combustion process. The high viscosity interferes with the injection process and leads to insufficient fuel atomization. It was also stated that higher viscosity leads to poorer atomization of the fuel spray and which affects accuracy of the operation of fuel injectors. However the lower the

viscosity of the biodiesel, the easieritis to pump, atomizes and achieves finer droplets.

- **Cetane number**

The cetane number is the prime indicator of fuel ignition quality and the opposite of octane number of a gasoline fuel. It can be defined as the measure of knock tendency of diesel fuel. Higher Cetane number of biodiesel leads to low engine operating noise and good starting characteristics.

- **Calorific value**

The calorific values 10-15% less in comparison to diesel, but because of higher density the volumetric content of heat value is nearly about the same as that of diesel.

- **Flash point**

The flash point is the temperature at which the fuel will start to burn when it comes to contact with fire. It is an important temperature from the safety point of view during storage and transportation. A fuel with high flash point may cause carbon deposits in the combustion chamber.

Flash point of biodiesel is higher than the petroleum based diesel fuel. Thus in storage, biodiesel and its blends are safer than conventional diesel.

- **Cold-flow properties**

Cold-flow quality of a fuel is determined by the cloud point and pour point. The cloud point is the temperature a t which a cloud of wax crystals first appears in a liquid when cooled. These formed crystals can cause operation problems because they can plug the fuel lines and filters. The pour point is the lowest temperature at which the fuel will still flow and can be pumped .All biodiesel regardless of its source have higher

cloud and pour points than that of diesel fuel, and this poor cold flow property is one of the most critical obstacles against the widespread biodiesel usage.

- **Sulfur**

Biodiesel has almost negligible sulfur content which leads to lower Sox emissions as compared to petro-diesel. Oxygen and unburnt hydrocarbon (UBHC) emissions are less with biodiesel and its blends, because biodiesel has oxygen in its molecular structure leading to better combustion**.**

- **Oxidation stability**

This property shows the fuel's resistance to oxidation during extended storage. Oxidation stability is determined by copper strip since it has the strongest catalyzing effect on oxidation. When oxidation occurs at ordinary temperatures, the initial products are hydro peroxides.

2.2.5 Biodiesel fuel standards

European Standard for biodiesel (EN 14214) and the American Standard Specification for biodiesel (ASTM 6751-02) are the two major international biodiesel standards followed all over the world where the characteristics and qualities of biodiesel such as the flash point, kinematic viscosity, specific gravity, free fatty acids and acid value have been introduced Y. Zhang et al [31]. Table 2-3 shows detailed ASTM D 6751 and EN 14214 biodiesel specifications Dennis Y.C et al [20], Mudge SM et al [23]. While table 2-3 shows comparison of fuel properties of Jatropha oil, Jatropha oil methel ester and diesel fuel according to ASTM D6751 and EN 14214 standards.

Table 2-3 Biodiesel Specifications and test methods of ASTM D6751 and EN 14214 standards Dennis Y.C et al [20], Mudge SM et al [23].

Property	Unit	Limits		Test method	
		ASTM D6751	EN 14214	ASTM D6751	EN 14214
Flash point	°C	130.0 min	101.0 min	D93	ISO CD 3679e
Kinematic viscosity at 40 °C	mm^2/s	1.9–6.0	3.5–5.0	D445	EN ISO 3104
Cetane number	-	47 min	51 min	D613	EN ISO 5165
Sulphated ash content	%(m/m)	0.020 max		D874	ISO 3987
Copper strip corrosion	-	No. 3 max	Class 1	D130	EN ISO 2160
Acid value	mg KOH/g	0.80 max	0.5 max	D664	pr EN 14104
Free glycerol	%(m/m)	0.020 max		D6584	pr EN 14105m pr EN 14106
Total glycerol	%(m/m)	0.240 max	0.25 max	D6584	pr EN 14105m
Phosphorous content	%(m/m)	0.001 max	0.01 max	D4951	pr EN 141101
Carbon residue					
ASTM D6751 (100% sample)	%(m/m)	0.050 max	-	D4530	-
EN 14214 (10% bottoms)		-	0.3 max	-	EN ISO 10370
Cloud point	°C	Report customer	-	D2500	-
Density at 15 °C	kg/m^3	-	860–900	-	EN SIO 3675 EN SIO 12185
Distillation T90 AET	°C	360 max	-	D1160	-
Sulfur (S 15 Grade)	ppm	0.0015 max	-	D5453	-
Sulfur (S 500 Grade)	ppm	0.05 max	-	D5453	-
Sulfur content	mg/kg	-	10 max	-	-
Water and sediment	%vol.	0.050 max	-	D2709	-
Water content	mg/kg	-	500 max	-	EN ISO 12937
Total contamination	mg/kg	-	24 max	-	EN 12662
Oxidation stability at 110 °C	h	-	6 min	-	pr EN 14112
Iodine value	-	-	120 max	-	pr EN 14111
Linolenic acid methyl ester	%(m/m)	-	12 max	-	pr EN 14103d
Polyunsaturated (≥4 double bonds) methyl esters	%(m/m)	-	1 max	-	pr EN 14103
Ester content	%(m/m)	-	96.5 min	-	pr EN 14103d
Methanol content	%(m/m)	-	0.2 max	-	pr EN 141101

2.3 Glass reactor with heating plate and magnetic stirrer

Alkali catalyzed transesterification process was used for this work. The reaction was carried out on a single stage batch reactor

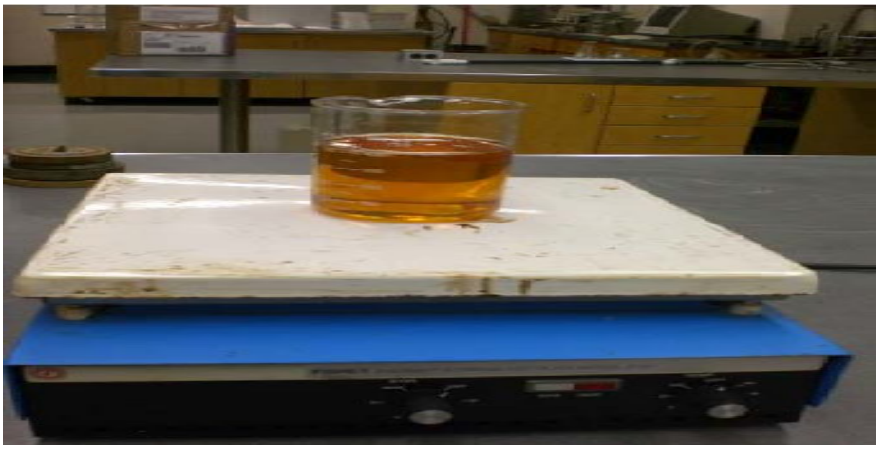

Figure (2-7) Glass reactor with heating plate and magnetic stirrer.

The reactor used was a 500 ml glass beaker in a heating plate with magnetic stirrer for mixing.

2.4 Biodiesel ester and glycerin layer

Shows two phase of biodiesel ester and glycerin layer. The complete separation was achieved after 20 hours.

Figure (2-8) Biodiesel ester and glycerin layer

2.5 Biodiesel using NaOH catalysts

Shows the glycerin biodiesel separation by gravity method the biodiesel was separated in another vessel for washing

Figure (2-9) Biodiesel using NaOH catalysts

2.6 Biodiesel washing using distilled water

It was washed using a separating funnel creating a fine mist of water from the top.

Figure (2-10) Biodiesel washing using distilled water

2.7 Freshman academy & the green school initiative

The students in the freshman academy & the green school initiative are proud to present the following on line tutorial about biodiesel production at Highland Park High School (HPHS) biodiesel laboratory.

Figure (2-11) Producing the biodiesel fuel using waste Vegetable oil from the school cafeteria.

2.8 Biodiesel advantages & disadvantages

From the literature, numbers of technical advantages of biodiesel fuel are reported by researchers; they are:

- Portability, availability and renewability of biodiesel.
- It prolongs engine life and reduces the need for maintenance.
- Safer to handle, more biodegradable, and having a higher flash point.
- An efficient, clean, 100% natural energy alternative to petroleum fuels.
- Safe for use in all conventional diesel engines.
- Offers the same performance and engine durability as petroleum diesel fuel.
- Non-flammable and non-toxic.
- Reduces tailpipe emissions, visible smoke and noxious.
- Higher thermal efficiency.
- Higher flash point, leading to safe handling and storage.
- Biodiesel can make the vehicle perform better as it has a cetane number Range between (40-60). Moreover, it prolongs engine life

and reduces the need for maintenance (biodiesel has better lubricating qualities than fossil diesel).

In contrast there are some problems associated with biodiesel when used in diesel engines; they are summarized as follows:

- Relatively high cost of investment.
- Higher NOx emission.
- Higher PM emission.
- The high viscosity (about 11-17 times greater than diesel fuel) due the large molecular mass and chemical structure of vegetable oils leads to problems in pumping, combustion and atomization in the injector systems of a diesel engine.
- Biodiesel lower engine speed and power. The biodiesels on the average decrease power by 5% compared to that of diesel at rated load.
- Degradation of biodiesel under storage for prolonged periods.
- Coking of injectors on piston and head of engine.
- The high viscosity, in long term operation introduces the development of gumming, formation of injector deposits, plugging of filters, lines and injectors, ring sticking as well as incompatibility with conventional lubricating oils.
- Biodiesel causes excessive engine wear. Higher pour and cloud point fuel freezing in cold weather causing a cold weather starting.
- Biodiesel has a corrosive nature against copper and brass.