Review of literature for exploration of waste plant oils for production of biodiesel

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Abstract

Global energy demand is increasing due to exponential increase in world population and rapid industrialization. The world energy demand is increasing due to expanding population and better living standards. Energy supply reliability and economy will enhance with the availability and consumption of renewable energy sources. Biodiesel is an attractive alternative to conventional petroleum-based diesel fuel because of its renewable and environment friendly nature. This article extensively reviews the importance of different waste plant oils feedstocks, biodiesel manufacturing processes and physical and chemical characteristics of waste plant oils. Feedstock and catalyst selection are key steps in biodiesel production because these determines two-third of the total biodiesel production cost. In this review, it has been concluded that waste plant oils are considered as promising alternative feedstocks for biodiesel production. The biodiesel production from waste plant oils is an effective way to minimize all the problems because the use of pure plant oils as biofuel is inappropriate due to their low volatility and high viscosity.

Keywords: Biodiesel, catalyst, feedstock, volatility, viscosity, waste plant oils

1. Introduction

Energy is the basic human need and a particularly important factor for economic and social development. There are different reasons to seek out the alternative fuel, which is readily available, environment friendly, economically viable and technically feasible. The primary reason is the ever-increasing fossil fuels demand in all the human life sectors, industrial processes, transportation, residential consumption, and power generations. This ever-increasing demand gives rise to global warming and carbon dioxide as well as greenhouse gas emissions [1-2]. Some reports claimed that if the consumption rate remains constant, oil and gas reserves will be depleted in between 41 to 63 years. Several hydro, wind, nuclear, solar, biofuel and biodiesel as alternatives have been suggested and are all still in progress in research studies. Furthermore, with the current consumption rates, petroleum supply will last only 65 years and fossil fuels emissions will also cause global warming and air pollution. Due to the international pressure on global warming, the demand of renewable, clean alternative fuels have gained increasing attention for future consumption [3-4].

On the other hand, energy crisis has gained attention of researchers to fulfill the future energy needs

with a renewable and clean energy source. Fossil fuels, consisting of petroleum reserves, natural gas and coal etc. are the main energy sources, meeting 80 % of the world's energy demands. In transportation, gasoline and diesel are widely used to run aircrafts, trucks, cars, and military vehicles etc. Due to the lack of conventional fossil fuels, generation of pollutants in terms of emission, and the increasing petroleum fuel prices will bring more attraction in the use of biomass source having carbon neutral properties [5-6].

In the early 1800s, the production of fuel with biomass feedstock started through the same method, as used now-a-days. The automobiles were generally powered with the gasoline fuel in 20th century and the crude oil is refined to supply maximum gasoline that was an excellent diesel fuel for the engines and are less expensive in comparison to vegetable oils. The production of biodiesel by using vegetable oils is not a new process. Transesterification is the most widely used method in which animal fats or vegetable oils are converted into fatty acid alkyl esters. In 1853, Patrick and Duffy used transesterification method in which triglycerides were converted into biofuels [7]. In 1893, Diesel engine was first invented by Dr. Rudolf Diesel, a famous Germen inventor. A paper entitled "The theory and

construction of a rational heat engine" was published by Dr. Rudolf Diesel. Several types of fuel and vegetable oils had been used to run this diesel engine. The Paris Exposition introduced a new diesel engine fueled with peanut oil. Due to the availability of cheap petro based fuels, many people were interested in this newly featured engine. In early 1930s, due to the splitting of fatty acids present in vegetable oil glycerin, a thin product like petroleum-based diesel was produced [8]. In 1938, the first traveler bus was run with palm oil ethyl esters and practiced the route between Brussels and Louvain. During the World War II, vegetable oils were used as a fuel by several countries due to interruption of petroleum fuel such as cottonseed oil by Brazil and soybean oil in France and Argentina. However, when war came to an end, the supply of petroleum based fuels was started and the use of vegetable oil fuels was forgotten [9]. Biodiesel is defined as a fuel composed of mono alkyl esters of long fatty acids obtained from renewable vegetable oils, waste cooking oils or animal fats meeting the requirements of international standard (ASTM D6751). Biodiesel is an alternative to petroleum fuels used in diesel engines owing to the dwindling reserves of petroleum and increasing environmental issues. The chemical combustion of natural oils results in the biodiesel production. Chemically, combining any natural oil with an alcohol usually methyl alcohol produces biodiesel. Biodiesel is more efficient fuel, exhibiting greater potential for compression-ignition engines and has relatively higher heating values in comparison to gasoline. HHVs of some fuels are given in Table 1 [10].

Mostly methanol is used for the commercial scale biodiesel production. Many researchers have successfully shown the use of vegetable oils as a fuel in diesel engines with energy density closer to the regular diesel fuel. The transesterification reaction of soybean oil and methyl alcohol in the presence of an acid catalyst results in the biodiesel production. Biodiesel is the most promising renewable and sustainable fuel for diesel engines having properties similar to petroleum diesel [11]. Huge increase in the use of petro diesel and the fuel shortage in near future stimulated the initiation of a dual fuel project at The Ohio State University. During this project, conventional diesel blends were mixed with corn oil and cottonseed oil to study their relative effectiveness. In 1970's, the depletion of petroleum oil resources caused many states to think about the sources. Many scientists in Austria, South Africa, Brazil, United States and other countries rediscovered that in order to run the diesel engine, vegetable oils can be used directly but it also damage the engines due to the poor fuel quality. Vegetable oils at that time were thin and of low quality so the experiments were conducted to convert these vegetable oils into biodiesel [12]. The total world biodiesel production between 1991 and 2009 is represented in Figure1. After 2000's, the biodiesel production raised sharply [13].

Table 2 shows the production of biodiesel in European countries and among which France and Germany are the leading biodiesel producers. About 75% of the world biofuel is produced by European Union with 65% of biodiesel output worldwide. Different methods are used to produce biodiesel which include: blending, pyrolysis, micro emulsion as well as transesterification.

Biodiesel is an attractive alternative to conventional diesel fuels because it has number of environmental benefits, competitive economically, possesses high biodegradability and positive net energy balance ratio. Biodiesel was accepted as the second largest biofuel in 2014, and its production increases upto 10.4% in order to meet the global 29.8 billion level around the world [14].

Different types of feedstocks are used for biodiesel production which includes edible oils, non-edible oils, waste cooking oils, animal fats and microalgae. About 80 % of the total biodiesel production comes from these countries, including Brazil, Malaysia, Germany, Indonesia, Spain, Argentina, Netherland, Belgium, Philippines, and USA. The most important feedstocks used for the production of biodiesel in these countries are: 28% soybean oil, 20% animal fats and 22 % palm oil [15]. Biodiesel can be generally produced by using different feedstocks which include: soybean oil, karanja, sunflower oil, jatropha oil, cottonseed oil, tobacco oil, linseed oil, canola oil, palm oil, olive oil, peanut seed oil, animal fats, waste cooking oils and algal oils [16]. About 90% of total biodiesel production cost depends on the type of feedstock. Literature reports that agricultural wastes, waste frying oils, soap stocks and algal oils are the cheap raw materials used for biodiesel production [17]. Biodiesel industry due to first generation feedstocks would possibly have an adverse impact on the global food market which includes: capital cost, soil degradation, food insecurity, deforestation, ecological imbalance, loss of biodiversity and water shortage. Thus, non-edible waste feedstocks have become more promising for the sustainable biodiesel production [15]. The majority of biodiesel is produced from soybean, sunflower, mustard seed, rapeseed, sunflower and palm oils. About 90 % of the biodiesel in United States is produced from soybean oil whereas in European countries rapeseed oil accounts 58 % of world total biodiesel. However, palm oil and coconut oil are being used in Indonesia and Malaysia for biodiesel production [18]. Microalgae which is recognized as third feedstock generation, has received great attention due to significant decrease in global warming and greenhouse effects. In comparison to edible oils, such as palm oil, microalgae are very economical and give up to 25 times highest oil yield. Microalgae which contains 70 % oil content by weight, requires 0.1 m^2 area to produce biodiesel (121,104 kg) per year [19].

Waste cooking oils and animal fats have been considered as a promising option for biodiesel production

with relatively cheaper price in comparison to vegetable oils [20]. The use of animal fats for production of biodiesel has not been used widely but it eliminates the disposal problem as compared to vegetable oils. Since many meats processing and rendering companies collect large amount of waste animal fats in order to produce biodiesel from these cheaper raw materials [21].

The physicochemical properties of used cooking oils that affect the biodiesel production are moisture contents, impurities, calorific and free fatty acid contents. Various plant oils with different fatty acid composition can be used while palm, soybean, sunflower, jatropha, rapeseed, pongamia and cottonseed oil are mostly used for production of biodiesel [16-22]. With the increasing availability of natural oil resources from agriculture, there is a conflict between the productions of crops for use as energy, contrast to food [23].

This review article explains the importance of using waste plant oils as an alternative leading feedstock for the sustainable biodiesel production. Several aspects related to feedstocks including an overview of the waste oil resources, different oil extraction techniques, biodiesel production mechanisms and characteristics of waste plant oil biodiesel as alternative fuel are critically described in this review.

2. Techniques to produce biodiesel from waste plant oils

Some major advantages of using vegetable oils as a diesel fuel are renewability, eco-friendly nature, high heat contents, easy availability, lower sulfur, and aromatic contents. Despite the several advantages, some major disadvantages of plant oils are low volatility, high viscosity, and the reactivity of unsaturated hydrocarbons [24]. Table 9 explains the fuel properties of various waste plant oil methyl esters [25].

2.1. Waste plant oils (WPO)

Waste plant oils are the oily substances used in cooking of foods consisting of vegetable matter and inappropriate for human consumption. The United States was producing more than 2.9 billion gallons annually of waste plant oils, mainly from snack food factories, industrial deep fryers and fast food restaurants [26]. The utilization of the waste plant oils as an alternative fuel would reduce the gasoline price by preserving the petroleum supply. On the other hand, generation of the large amount of waste plant oil annually has become a challenging issue in many countries because WPO cannot be discharged into drains and pollutes watercourses leading to wildlife problems [27]. The generation of waste plant oils is huge worldwide and differs according to the consumption amount of edible oils. Hence, waste plant oil is a leading feedstock used for the production of biodiesel [28]. Currently, the price of waste plant oil obtained from soybean in the market is around $1.21/US gallon and by the year 2020, it is expected to rise upto

$1.39/US gallon [29]. The physicochemical characteristics of waste plant oils are like edible oils and vary from source to source. For example, the properties of rapeseed waste oil might be different from palm oil due to difference in oil composition. Apart from that, the free fatty acid and water content in waste plant oils are relatively higher than edible oils. During frying, the edible oil is heated at 160–200ºC temperature in the presence of light and air for a moderate time. After frying, some changes observed in edible oil are: change in surface tension, increase in viscosity, fat formation and specific heat. All these physical changes are due to the hydrolytic, thermolytic and oxidative reactions during frying process [30].

2.1.1. Thermolytic reaction

The thermolytic chemical reaction takes place at high temperature in the absence of oxygen. The fatty acids, alkanes, ketones, alkenes, and carbon dioxide are the series produced mainly from the saturated fatty acids present in oil. Since from unsaturated fatty acids, mostly diametric compounds are formed which include polycyclic compounds, dehydrodimers and saturated dimers. In addition, when the unsaturated fatty acids react with other fatty acid then possibly trimers and dimers are formed through Diels–Alder reaction [10].

2.1.2. Oxidative reaction

The oxidative reaction occurs when fats or oil reacts with unsaturated acyglycerols in the presence of oxygen. It eventually results in the formation of oxidation products like alkylperoxyl radicals. Finally, due to hydroperoxides (ROOH) decomposition, alkoxyl radicals are formed which produce different unsaturated or saturated aldehydes, hydrocarbons, esters, acids, lactones, ketones and alcohols [31]. Most of the polymeric, dimeric acids and polyglycerols as the products of the radical reaction will remain in fat or oil increases the cooking oil viscosity [32].

2.1.3. Hydrolytic reaction

The triglycerides hydrolysis take place as steam formed in food preparation. The fraction of water evaporates quickly, while certain fraction dissolved in fats or oil and induces its cleavage to form monoglycerides, higher fatty acids, diglycerides and glycerol concentration [33]. If the oil is repeatedly used, then the above three chemical reactions will cause the formation of harmful and undesired components. Although waste cooking oils are the potential leading feedstock for the production of biodiesel, but the amount of free fatty acids must be considered because it will affect the transesterification method to a greater extent. Waste cooking oils contain free fatty acids in the range between 0.5 and 15 wt% whereas in refined oil, free fatty acid content is less than 0.5 wt% [34].

2.2. Biodiesel from waste oil seeds

Different types of waste plant oils which include: karanja (*Pongamia pinnata*), jatropha (*Jatropha curcas*), tea seed, Mahua (*Madhuca indica*), tomato seed, castor bean (*Ricinus communis*), neem (*Azadirachta indica*), rubber seed (*Hevea brasiliensis*), rice bran, tobacco seed (*Nicotiana tabacum*) and corn germ can be used as a promising feedstock for biodiesel production. The list of waste oil seeds used to produce biodiesel is shown in Table 8. The biodiesel production from different crops has been investigated widely over the last few years. The oil contents of non-edible feedstock is shown in Table 3 [35].

2.2.1. Jatropha curcas

Jatropha belongs to the family (Euphorbiaceae), is a large size shrub, 5–7 m in length, and drought resistant. *Jatropha curcas* is found in Brazil, Africa, Bolivia, India, Paraguay, America, Peru, Pakistan and Argentina. *Jatropha curcas* oil is found to be a leading feedstock having an oil content range between 30%-40%. Jatropha contains moisture content (5.54%), crude protein (24.60%) and approximately (47.25%) of crude fat [15]. The oil content of *Jatropha curcas* consists of both unsaturated (linoleic acid 32.8% and oleic acid 44.7%) and saturated fatty acid (stearic acid 7.0% and palmitic acid 14.2%) [36].

2.2.2. Pongamia pinnata

Pongamia pinnata is a medium size rapidly growing tree belongs to family (*Papilionaceae*) and grows naturally in Bangladesh, India, New Zealand, China, Pakistan, Australia, USA and some south-east Asian countries [22]. The seeds of *Pongamia pinnata* contain 30-40 wt % oil content and a yield of oil seed per tree is between 9-90 kg, which indicates a high yield potential (900-9000 kg) seed/hectare [37]. In recent years, *Pongamia pinnata* has been recognized as a versatile resource provides an environmentally acceptable liquid fuel and expanding the biodiesel industry [38].

2.2.3. Azadirachta indica

Azadirachta indica, also called neem is a tropical forest tree that grows to a height of about 25 m and belongs to the family (*Meliaceae*). *Azadirachta indica* is found in at least 30 countries of the world, much in Asia, South America and Africa [39]. *Azadirachta indica* oil contains linoleic acid (38.27 %) as a major fatty acid and then followed by oleic (34.04 %), stearic (12.96 %) and palmitic acids (12.21 %). An average neem tree annually yields about 40-50 kg seeds. The seed of neem fruit contains an oil content of about 25-35 wt% while kernels contains 50–60 % oil [40-41].

2.2.4. Aleurites moluccana

Aleurites moluccana is a candle nut tree belonging to the family (*Euphorbiaceae*). *Aleurites moluccana* grows between (0−1200 m) altitudes at an optimal (18-28 ˚C) temperature with a soil 5-8 pH and average rainfall of about 640-4400 mm [42]. An average yield of 5-20 ton per hectare can be expected in a nut tree plantation each year. Each nut tree gives 30-85 kg seeds per year and contains approximately 16 %-24 % oil.

2.2.5. Aleutites fordii

Aleutites fordii, commonly called Tung tree, widespread in Paraguay, China, India, United States, Argentina, and Africa. The oil yield differs from 300-470 kg per hectare. The kernel contains 54-60% oil and the seeds have an oil content ranges from 30-40% [43]. The Tung seed oil contains palmitic (4%), stearic (1%), oleic (15%) and alpha-stearic acid (75-80%).

2.2.6. Calophyllum inophyllum

Calophyllum inophyllum, also recognized as polanga, is a large sized tree which grows 8-20 m in height and belongs to the family (Clusiaceae), Polanga tree with broad spreading irregular branches, grows best in sea sands and deep soils. *Calophyllum inophyllum* is most widely grown in Australia, Africa, and India. Each polanga tree yields whole fruits an average of 25-100 kg per year. The mature tree gives an oil yield of (1–10 kg) per year while the kernel contains (50-70 %) oil content and of it depends upon the mechanism of extraction [44].

2.2.7. Crambe abyssinica

Crambe abyssinica, commonly known as hochst, is an oil bearing plant with an average height of about (1-2 m) belongs to the family (*Cruciferous*). The white or yellowish flowers held the seeds into capsules and each capsules contains spherical greenish brown (0.8-2.6 mm) seeds. The oil content of crambe seeds is 36-43% which can be used for biodiesel production [45].

2.2.8. Hevea brasiliensis

Hevea brasiliensis, usually called rubber, is a large sized tree that belongs to the family *Euphorbiaceae*. It is most widely cultivated in tropical areas worldwide and produces naturally 99% rubber [46]. The rubber tree grows upto 35 m in height, and produces 2-4 g seeds. The normal rubber tree yields annually (70 to 500) kg/hec seed while in India, the production of *Hevea brasiliensis* seed is about 150 kg/hec per year. Rubber plant is a non-edible feedstock, contains 50-60 wt% oil content used for biodiesel production. The rubber seed oil contains high percentage of both unsaturated (16.3 wt.% linolenic, 39.6 wt.% linoleic and 24.6 wt.% oleic) and saturated acids (8.7 wt.% stearic and 10.2 wt.% palmitic) [47]. Table 6 shows the yields of various waste plant oil feedstocks.

2.2.9. Madhuca indica

Madhuca indica, also known as mahua, a middle-size tree, belongs to Sapotaceae family which grows at a height of about (10-15 m). Madhuca indica grows mainly in Sri Lanka, China, India, Pakistan, and Bangladesh. Madhuca indica tree has a potential to produce approximately 60 million tons waste oilseeds annually in India [15]. An average yield of about 800 kg per hectare could be expected after 10 years Madhuca indica plantation. Madhuca indica seed contains approximately about 70 % of kernel with 16 % protein and 50 % oil content [48].

2.2.10. Moringa oleifera

Moringa oleifera, commonly called drumstick tree, belonging to (Moringaceae) family, is a softwood fast growing perennial tree. Moringa is widely cultivated in Pakistan, Ethiopia, India, Philippines, Florida, Sudan, Algeria, America, Pacific Islands and South Africa [49]. In comparison to soybean seeds of about 3000 kg/hectare, drumstick tree gives approximately 3000 kg seeds per hectare annually. Depending upon the climate, Moringa oleifera have oil content ranges from 30-40 % [50].

2.2.11. Nicotiana tabacum

Nicotiana tabacum, also called tobacco, belonging to family (Solanaceae), is an herbaceous plant most widely grows in India and America. The tobacco tree produces approximately 1171 kg/hectare seeds, giving an oil content of 432.9 kg with an estimated 15,000 tons yield per year. The Nicotiana tabacum oil contains following fatty acids (3.2 % stearic acid, 70.7 % linoleic, 7.8 % palmitic and 17.3 % oleic acid). In comparison to edible oils, the non-edible Nicotiana tabacum oil can be considered as a new leading feedstock for production of biodiesel [39].

2.2.12. Rice bran

Rice bran is a non-edible plant, most widely cultivated in Pakistan, China, Southern Asia, and contains oil content about 15-23 % [51]. The rice bran oil contains unsaturated (42.5 wt. % oleic and 39.1 wt. % linoleic) and saturated fatty acids, (15.1 wt. % palmitic and 1.9 wt. % stearic) [42].

2.2.13. Ricinus communis

Ricinus communis, generally called castor, is a medium sized tree belonging to family (Euphorbiaceae). Ricinus communis is found throughout the tropics including Australia, Brazil, United States, Africa, China and India. Due to Ricinus communis seeds high 45 % - 60 % oil content, it is considered to a leading feedstock for biodiesel production [46]. The main advantage of using Ricinus communis oil is its growth rate which is shorter to a great extent than Pongamia pinnata and Jatropha curcus. While some major disadvantages of using castor oil is its high

viscosity which cause ring carbonization, incomplete combustion and poor atomization [52].

2.2.14. Simmondsia chenensis

Simmondsia chinensis, well-known as jojoba, is a flowering shrub belongs to the family (Simmondsiaceae). Jojoba is native to Sonoran and Mojave deserts of Arizona, Mexico, and California. Simmondsia chinensis shrub gives an average yield of about 400 kg per hectare and its seed contains 50 % oil content by weight, which is greater than other oil seed crops. Its oil is colorless, odorless and composed of monoesters chain of C_{22} along with C_{20} acids [53-54].

2.2.15. Schleichera oleosa

Schleichera oleosa, commonly called kusum is a medium size evergreen tree, belonging to family (Sapindaceae) which grows at a height of about 40 m and native to South Asia. The Schleichera oleosa seed contains about (51-62 %) oil content although the yield is upto 25-27 % half in village mills. The total fatty acid content of Schleichera oleosa oil is 91.6% and its Iodine value content is between 215-220 [44].

2.2.16. Thevettia peruviana (Yellow Oleander)

Thevettia peruviana, commonly called yellow oleander is an evergreen shrub of various names and found mainly in Brazil, America, West Indies, and Mexico. Thevettia peruviana grows between 4.5 and 6 m in height with green linear sword or funnel shaped flowers and leaves. Depending upon the age and the average rainfall, the yellow oleander plants give 400-800 fruits per year. Thevettia peruviana kernel contains high oil content up to 67% in its seeds and about 52.5 tons/hec and 1750 L of oil can be produced from a hectare of waste land [55].

2.3. Biodiesel production from waste plant oils
2.3.1. Pretreatment of waste oils

The variety of feedstock consisting of waste plant oils recovered from different resources like restaurant is continuously fed into vessels along with metal filter in order to eradicate the unwanted substances. Then the oil which collects from the vessel is transferred to feed tank equal to about (80 %) tank level. The feed tank is heated at a temperature of about 500-600 and a crude glycerin (5-10 %) along with pre-treatment agent is added to prevent the oil precipitation, solidification as well as sedimentation. The mixture is agitated gently for about 20 min and one hour. The pre-treated oil is fed into the esterification reactor and the soap sediments are removed from the bottom of the tank [16-56].

2.3.2. Esterification process

During the esterification process (Figure 2), the catalysts such as caustic soda and methanol are

simultaneously mixed in methanol tank. Because the reaction is exothermic, so caution is necessary to ensure the catalyst amount. Usually, the methanol and caustic soda ratio is 4.7 %, which increases the mixture temperature up to 500 ˚C in tank. In esterification reactor, where the temperature and the retention time are kept around (600 ˚C and 30 minutes), this mixture is continuously pumped to react with the pre-treated feedstock oil [57]. Before the feed oil pass through the esterification reactor, it is firstly preheated up to 700 ˚C from a tube coil. The products of the reaction are transferred to the (Glycerin Separator) where separation of glycerin occurs, which contains methanol and soap residues. Then biodiesel is sent towards the warm water wash tank for further refining and treatment [58]. The zinc sulphate is added to crude biodiesel in tank which is equipped with an agitator, to remove the soap residues and suspension.

This crude product is sent towards the (settling tank) in order to eliminate further contaminants and recovered water obtained is then recycled back towards the warm water tank [59]. The crude biodiesel is further treated through sedimentation and de-watering agent by adding activated white earth (0.3 %) and glycerin (0.5 %) in the crude biodiesel tank. The solution is agitated gently for about 15 minutes and settled overnight. The treated supernatant is refined further through the process of filtration in the filtration tank and the sediments are removed from the bottom [60].

2.3.3. Glycerin recovery

The glycerin which is obtained from the (glycerin separator) is heated under normal pressure and temperature in the neutralization tank to distill out the methanol. The glycerin left behind is neutralized by adding HCL and the soap residues are converted into oil, which is easily removed. The glycerin concentrator is also equipped with vacuum ejector and steam-heated jacket in order to eradicate excess water from the glycerin [61]. Then the crude glycerin is transferred towards a (vacuum distillation unit) where at the first stage, light-yellow color (99.5 %) glycerin is produced as well as dissolved solids such as NaCl are removed. Then the activated carbon is mixed with glycerin in activated carbon tank for about 15 minutes at (900-1000 ˚C) temperature. Finally, the mixture is passed through the glycerin filter to produce the final (99.5 %) glycerin product [62].

2.3.4. Wastewater treatment

The wastewater obtained from the warm water separating tank which contains, biodiesel residues and sodium soap, are collected in the wastewater storage tank. The wastewater is automatically propelled towards the (acid treatment tank) when the level reaches a certain point in the tank, where dilute HCl is added to maintain 2-3 pH. After 10 min mixing, the mixture is allowed to rest in order to

separate the two layers (aqueous and oily phase). The treated water is sent towards the pH control tank where the dilute caustic soda is added to maintain the pH around 9 automatically before being discharged out [63].

2.4. Different techniques of biodiesel production
2.4.1. Transesterification (alcoholysis)

Transesterification is the chemical reaction between oil and fats with a short chain alcohol in the presence of catalyst to produce fatty acid methyl esters along with glycerol as a side product shown in scheme 1. Transesterification is a reversible reaction, so excess alcohol is used to shift the equilibrium towards the product side. Commonly methanol, propanol and ethanol are used in transesterification, mainly methanol is used commercially because of its low price and it reacts quickly with NaOH and triglycerides [64-65].

2.4.1.1. Homogenous base catalyzed production

The most common homogenous alkali catalysts being employed are KOH, CH₃OK, NaOH and CH₃ONa. These catalysts are cheap, pure and easily available but its major disadvantage is its prohibitive cost and high energy consumption. Furthermore, this presence of fatty acids and water leads to soap formation which reduces the biodiesel yield and affects the product quality [66]. Different experiments were performed to check the effect of homogeneous alkaline (NaOH or CH₃OH) catalysts on yield by using coconut oil, with (6:1) methanol/oil ratio, (0.5 %) catalyst concentration and (60-65 ˚C) temperature. These catalysts achieved 94% biodiesel yield at 65 ˚C. In another study, the transesterification reaction of waste cooking oil with ethanol by using NaOH as a catalyst gave 94.5 % biodiesel yield at optimum reaction conditions (60°C temperature, catalyst concentration (0.08 %) and 20 min reaction time) [67]. A previous study [78] investigated the biodiesel production from used cooking oil with methanol by using NaOH as a catalyst. Different experiments were performed to check the effect of different operating parameters on biodiesel yield. These include oil/methanol ratio (3:1, 5:1, 6:1, 7:1 and 8:1), temperature (30, 40, 45, 50, 60 and 70 ˚C), catalyst concentration (0.5, 0.7, 1, 1.1, 1.2 wt. %) and the reaction duration (30, 50, 60, 70, 90 and 110 min). These catalysts achieved a biodiesel conversion of 86 % at the optimum (0.7 %) catalyst concentration, molar ratio (6:1), 50 ˚C and 1.5 h of reaction duration. Tomasevic and Siler-Morinkovic (2003) investigated the production of biodiesel from waste sunflower oil by using two different catalysts (NaOH and KOH) having different methanol/oil ratio (9:1, 4.5:1 and 6:1) and check their effect on biodiesel yield. The results showed that highest biodiesel yield was achieved at 25 ˚C by using KOH concentration (1.0 %), molar ratio (6:1) and 30 min time duration. Another study [79] reported the effect of transesterification reaction of soybean oil on biodiesel yield by using different catalyst

concentration such as (9-14 g/l) KOH, NaOH (30-40 %) and 30 min time duration. The results showed that 78.5 % biodiesel yield at the optimum reaction condition of 30 % ethanol and 12 g/l catalyst amount. Waste palm oil [80] used to produce biodiesel using (KOH catalyst) with different methanol/oil (6:1, 8:1 and 10:1) ratio, catalyst concentrations (0.5, 1 and 2 wt.%) and reaction temperature (45, 55 and 65 ˚C). The results showed that highest 96 % biodiesel yield was achieved at 55 ˚C by using KOH concentration (2 %), methanol/oil ratio (8:1) and 3 hr time duration. Leung and Guo (2006) also used NaOH as a catalyst and canola oil to produce biodiesel. The results showed that biodiesel yield achieved was 90.4 % at 70 ˚C with methanol/oil ratio (7:1), (1 %) catalyst concentration and 20 min time duration.

2.4.1.2. Homogenous acid catalyzed production

The most common acidic catalysts used in transesterification reactions are sulphuric acid, sulfonic acid, phosphoric acid and hydrochloric acid Although acidic catalysts are insensitive to free fatty acids, shown better results and provide higher yield but the reaction rate is many times slower than basic catalysts [81]. [82] investigated the effect of different homogenous acid catalysts (THF and $AlCl_3$ or $ZnCl_2$) on biodiesel yield having different optimum reaction parameters. The results showed that highest 98% biodiesel yield was achieved at 110°C temperature by using $AlCl_3$ concentration (5%), alcohol/oil ratio (12:24) and 18 h reaction duration. However, $ZnCl_2$ gave 48% biodiesel yield in 24 h time duration. Hence, it is concluded from the results that in comparison to $ZnCl_2$ and $AlCl_2$ are stronger and more effective acid catalyst.

[89] also investigated the effect of soybean oil transesterification on biodiesel yield by using methanol and sulfuric acid. The catalyst achieved a biodiesel conversion of 90 % at the optimum (1wt. %) catalyst concentration, molar ratio (30:1), 65 ˚C and 69 h of reaction duration. One major advantage of using homogenous acid catalyzed transesterification is that this method does not need any pretreatment and independent of free fatty acids [90].

[70] confirmed that homogenous acid catalysts are most promising in transesterification of waste plant oils. Different experiments were performed to check the effects of homogeneous acidic catalysts (HCl or H_2SO_4) and waste palm oil on the biodiesel yield with different catalyst concentrations (0.5 %) and 100 % alcohol. The results showed that high acid concentration produce fatty acid methyl esters in shorter reaction time and with lower specific gravity. The results showed that in comparison to HCl, H_2SO_4 gives high biodiesel yield.

2.4.1.3. Heterogeneous base catalyzed production

Researchers reported that calcium oxide, a solid alkaline catalyst obtained from calcinations of limestone, showed great potential in the transesterification reaction of soybean oil. The biodiesel yield obtained was 93 % with methanol/oil ratio (12:1) in 1 h. It is clear that strong adsorption of free fatty acids on the catalyst surface, poisoned the basic sites of calcium oxide. Furthermore, it is observed that calcium concentration in reaction product was about 3065 ppm which increases the biodiesel standard, while the concentration of mineral matter should be below (200 ppm) [91-92].

2.4.1.4. Heterogeneous acid catalyzed production

[99] reported that the transesterification reaction of coconut oil and palm oil with methanol and SO_4^{2-}/ZrO_2 acts as a catalyst gave high (86.3 % and 90.3 %) biodiesel yield. On the other hand, only 49.3 % (crude coconut) and 64.5 % (palm kernel oil) biodiesel yield was obtained when instead of SO_4^{2-}/ZrO_2, ZrO_2 was used as a catalyst.

[100] investigated the effect of sulfated and tungstated zirconia alumina in soybean oil transesterification at about (200-300 ˚C) temperature with methanol under the atmospheric pressure. The tungstated zirconia was found to have a high biodiesel yield in transesterification reaction in comparison to sulfated zirconia. Nevertheless, the long reaction time (20 h) and high temperature (250 ˚C) were required to achieve conversion about 90 %. Similar results were investigated by [27] where the catalyst was prepared by the method of impregnation with ZrO_2–Al_2O_3 on 10 wt. % of WO_3. Comparatively low about 65% fatty acid methyl ester yield was obtained at 200 ˚C temperature and 10h time duration.

Recently, [101] had estimated the catalytic activity of SO_4^{2-}/TiO_2 and SO_4^{2-}/ZnO_2 on the transesterification reaction of cotton oil. The results showed that in comparison to SO_4^{2-}/ZnO_2, the highest 90% yield was obtained using SO_4^{2-}/TiO_2 as a catalyst with (99.5 m^2/g) surface area. While SO_4^{2-}/ZnO_2 can only achieve 85 % biodiesel yield with (91.5 m^2/g) specific surface area. It was proposed that addition of a secondary metal SiO_2 to SO_4^{2-}/TiO_2, the reactivity and surface area of the catalyst (SO_4^{2-}/TiO_2-SiO_2) increased to 258 m^2/g [102] and this synthesized catalyst SO_4^{2-}/TiO_2-SiO_2 was used in transesterification reaction of cotton seed oil blend with (50 %) oleic acid. The results showed that 90 % biodiesel yield was achieved at 200 ˚C temperature by using catalyst concentration (3 wt. %), alcohol/oil ratio (9:1) and 3 h reaction duration. However, in comparison to homogeneous basic catalysts temperature which is in the range between 60-100 ˚C, the reaction temperature of SO_4^{2-}/TiO_2-SiO_2 catalyst is very high.

2.4.1.5. Enzyme catalyzed production

Enzymatic transesterification reactions were carried out with the biocatalysts which can overcome the limitations of the chemical catalysts. Most biodiesel production processes lead to the generation of large amount of wastewater and glycerol that increase the overall biodiesel production cost. In contrast, biocatalysts appear as

a good alternative because the reaction proceeds without the generation of by-products as well as biodegradability, selectivity, eco-friendly, thermal stability, high efficiency, recyclability and insensitivity towards high free fatty acid are the factors that make biocatalysts very efficient than other catalysts [25]. However, high cost, enzyme deactivation and slow rate of reaction are the drawbacks when implemented this method on industrial scale [106].

[107] reported that methanol addition during transesterification avoid the enzyme deactivation and extend its durability. Waste cooking oil as a feedstock and the enzyme (immobilized Novozym 435) was used. The transesterification reaction was carried out in three different ways: one-step flow methanolysis, three-step batch (fixed flow rate) and three-step continuous flow methanolysis.

The methanol amount was equally divided in three-step batch reactions and after the third step, 90.4% biodiesel yield of waste cooking oil was achieved. In contrast, for three-step flow methanolysis, the methanol was introduced into the first, second and third reactor at a flow rate of (6.1, 6.3 and 4.2 ml/h) and biodiesel conversion of (90.9%) was achieved. While in one-step flow reaction, biodiesel yield achieved was 90% when waste cooking oil was diluted with methanol/oil molar ratio of (3:1) and the mixture was continuously fed into a reactor having (4 ml/h) flow rate and 3 g of (Novozym 135) biocatalyst.

2.4.1.6. Oscillatory flow reactor for transesterification

[111] first introduced the oscillatory flow reactor for biodiesel production through some improvements in mixing intensity. Oscillatory flow reactor is a novel continuous tubular reactor, having several tubes consisting of equally distanced orifice baffles. Each orifice baffle plates behave as a stirred tank by creating vortices between the oscillating fluid and baffles that lead to suspension and excellent mixing. Thus, in comparison to conventional batch stirred tank reactor, some improvements in mixing intensity and catalyst suspension tend to produce high biodiesel yield in shorter time duration. [112] used oscillatory flow reactor for biodiesel production from rapeseed and used cooking oils. Pure (32.4 g) NaOH was initially dissolved in methanol at 40 °C temperature for 1 h duration. The results showed that 99 % biodiesel yield was achieved at 50 °C temperature by using methanol/oil ratio (3:2) and 30 min reaction duration.

2.4.1.7. Microwave reactors

Microwave reactors uses electromagnetic radiation of 0.01 to 1 m wavelengths and 0.03 to 300 GHz frequency ranges. In recent years, through many researchers, the electromagnetic energy development and utilization has gained much attention [113]. The main advantages of using microwave reactors are simplicity, easy to control, higher yields of cleaner product, less down streaming and thermal efficiency when compared with conventional heating methods. The production of biodiesel from waste plant oils using continuous microwave reactor was investigated by [116]. The process of transesterification was done through commercialized microwave (CEM MARS) apparatus. Firstly, a (10L) mixture of used cooking oil, catalyst and methanol were prepared having methanol/oil ratio (1:6) and KOH (1 wt. %) and placed in a holding tank. Then it was pumped into the reactor vessel and heated up to 50 °C at (2 L/min) rate and (1600 W) microwave power. The products were propelled out from the reactor and obtained 97.9 % biodiesel yield after 10 min reaction time. Furthermore, 98.9 % biodiesel yield can be obtained by increasing the flow rate to (7.2 L/min) [109].

2.5. Fuel properties of waste plant oils

Due to the rapid increase in alternative fuels, the criteria for determining the waste plant oil biodiesel properties are now becoming incredibly significant. The properties of waste plant biodiesel may differ depending upon the chemical and fatty composition, which shows a noticeable effect on emission and engine performance. Therefore, careful measurements of properties are required while considering WPO biodiesel. Table 9 shows the physicochemical properties of different waste plant oils biodiesel [117].

2.5.1. Cloud point and pour point

The Cloud point and pour point are the most important properties of biodiesel. The cloud point can be chemically defined as the temperature at which a cloud of crystals first visible in a liquid when cooled under optimum conditions. The pour point refers to the lowest temperature where biodiesel due to gel formation can no longer be poured. Usually biodiesel has higher pour and cloud point than other diesel fuels. Table 13 shows the pour point of waste plant oil methyl esters.

2.5.2. Flash point

Flash point of oil is the lowest temperature at which the produced fuel will ignite upon exposure to an ignition source i.e. flame. The conventional diesel fuel has a low flash point about (55-66 °C) while for biodiesel, the highest flash point is more than 150 °C. The flash point can be usually measured according to the EN ISO 3679 and ASTM D93 standards. The lowest (109 °C) flash point of biodiesel produced from waste palm oil is presented in Table 13 [97].

2.5.3. Cetane number

The cetane number is used as an indicator that describes the ignition quality of diesels for compression engines. Cetane number provides information about the ignition delay; the time elapsed since the fuel inject into the combustion chamber. The cetane number makes sure the proper functioning of diesel engine. If the cetane number is

low, it will cause incomplete combustion, diesel knocking and will also increase particulate exhaust emissions, especially hydrocarbons. In comparison to conventional diesel fuels, the cetane number of biodiesel is generally high. The cetane number of biodiesel according to EN ISO 5165 and ASTM D613 standard is 51 and 47 min. Table 13 shows the cetane number values of biodiesel produced from various plant oils feedstock. It has been found that waste olive oil biodiesel has highest (58.7) cetane number while waste linseed biodiesel has the lowest (37.66) cetane number [124].

2.5.4. Calorific value

The calorific value is another important property in evaluating the quality of biodiesel fuel. The calorific value of biodiesel is lower than that of diesel fuel because of higher oxygen content. Table 9 shows the highest (45.4 MJ/kg) calorific value of waste linseed oil and the lowest (39.26 MJ/kg) calorific value of waste corn oil [125].

Table 1: Higher heating values of different fuels

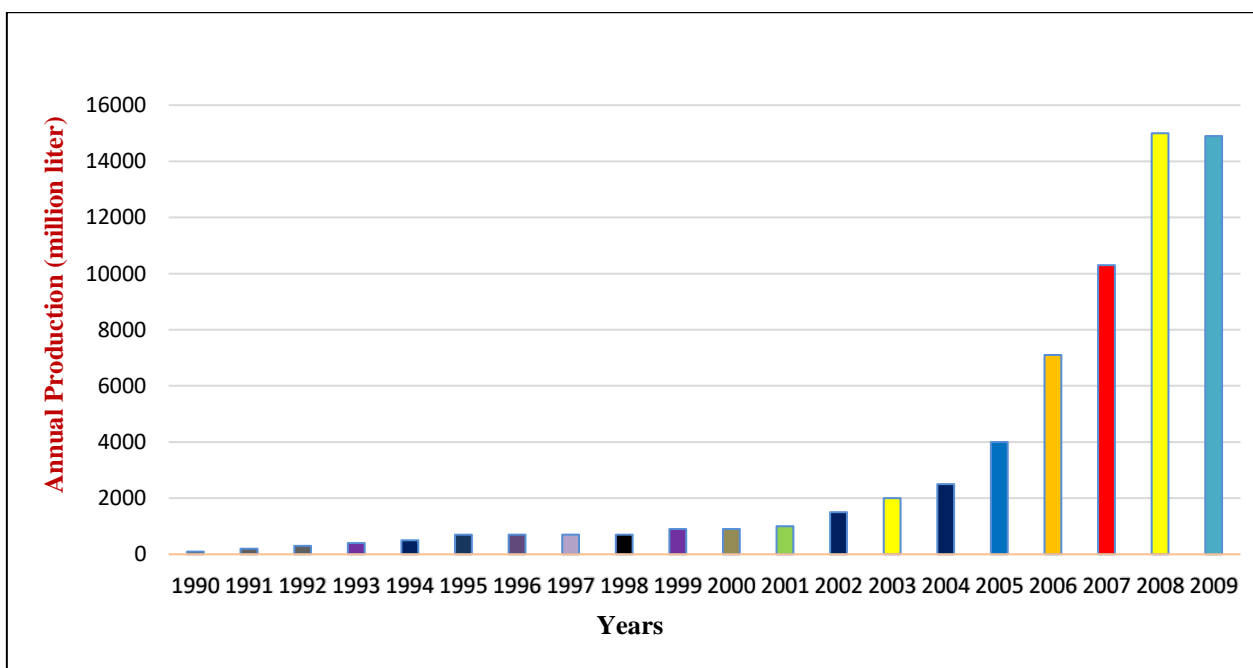| Types of Fuels	High Heating Values
Biodiesel	39─41 MJ/Kg
Gasoline	46 MJ/Kg
Petroleum	42 MJ/Kg
Diesel	43 MJ/Kg
Coal	32─37 MJ/Kg

Figure 1: World biodiesel production between 1991 and 2009

Table 2: Production of biodiesel in European countries (2008)

Country	Biodiesel Production (1000 Ton)	Country	Biodiesel Production (1000 Ton)
Austria	310	Belgium	416
Italy	737	Cyprus	9
Germany	2539	Malta	1
Sweden	233	Portugal	250
Spain	859	France	1959
Finland	220	Netherland	323
Greece	77	Ireland	17
Romania	29	Hungary	133
UK	137	Slovenia	9

Table 3: FAME yield obtained from *Jatropha curcas* with different catalysts

Plant Oil	Catalyst	Solvent	Molar Ratio	Conditions	Yield
Jatropha curcas	*Rhyzopusoryzae*	4 % (w/w) Methanol	Methanol/Oil (3:1)	30 ˚C, 60 hr	80 %
Jatropha curcas	(H$_2$SO$_4$, KOH and MeOCH$_3$)	0.8 % (w/w) Methanol	Methanol/Oil (9:1)	45 ˚C, 120 min	90-92%
Jatropha curcas	1wt.% NaOH	Methanol	Methanol/Oil (3:10)	50 ˚C, 2 hr	90.1 %
Jatropha curcas	4wt.% SO$_4^{2-}$/TiO$_2$	Methanol	Methanol/Oil (20:1)	90 ˚C, 2 HR	>98 %
Jatropha curcas	KOH	0.55 wt. %	Methanol/Oil (5:10)	60 ˚C, 24 min	99 %
Jatropha curcas	1wt.% H$_2$SO$_4$	Methanol	0.60 % (w/w)	50 ˚C, 1 hr	90 %
Jatropha curcas	*Pseudomonas cepacia*	Ethanol	-	50 ˚C, 8 h	98 %
Jatropha curcas	H$_2$SO$_4$	Methanol	0.28 % (v/v)	60 ˚C, 88 min	>99 %

Table 4: FAME yield obtained from waste plant oils with different catalysts

Plant Oil	Catalyst	Molar Ratio	Reaction Conditions	Yield
Pongamia pinnata	1–1.5wt.% NaOH	Methanol/Oil (6:1)	65 ˚C, 3h	90.4 %
Pongamia pinnata	1wt.% KOH	Methanol/Oil (6:1)	65 ˚C, 3h	97–98 %
Cerbera odollam	1wt.% NaOH	Methanol/Oil (6:1)	65 ˚C, 1h	83 %
Cerbera odollam	5wt.% sulfated zirconia alumina	Methanol/Oil (8:1)	180 ˚C, 3h	83.8 %
Cerbera odollam	4wt.% morillonite KSF	Methanol/Oil (10:1)	150 ˚C, 2h	48.32 %
Calophyllum inophyllum	Pretreatment acid catalyzed (H$_2$SO$_4$, KOH) KOH 1.5%	Methanol/Oil (6:1)	65 ˚C, 240min	85 %
Croton megalocarpus	SiO$_2$ (SO$_4^{2-}$/SnO^{2-}SiO$_2$) 3%(w/w)	Methanol/Oil (15:1)	180 ˚C, 2h	95 %
Croton megalocarpus	1wt.% KOH	30% (w/w)	180 ˚C, 1h	88 %

Table 5: FAME yield obtained from waste plant oils with different catalysts

Plant Oil	Catalyst	Reaction Time	Molar Ratio	T (°C)	Yield
Hevea brasiliensis	1wt.% NaOH	1 hr	Methanol/Oil (6:1)	60	84.5 %
Hevea brasiliensis	H_2SO_4 1.0% (v/v)	60 min	0.75% (v/v)	65	98.5 %
Hevea brasiliensis	KOH 0.5% (w/v)	45 min	0.3% (v/v)	55	-
Madhuca indica	Pretreatment acid catalyzed (H_2SO_4, NaOH) NaOH 0.7 wt.%	3 hr	Methanol/Oil (6:1)	60	98 %
Madhuca indica	0.7wt.% KOH	5 hr	Methanol/Oil (6:1)	60	98 %
Moringa oleifera	1wt.% $NaOCH_3$	1 hr	Methanol/Oil (6:1)	60	-
Rice bran	0.75wt.% NaOH	1 hr	Methanol/Oil (9:1)	55	90.2 %
Rice bran	Two steps catalyzed H_2SO_4	-	Methanol/Oil (10:1)	60	<96 %

Table 6: FAME yield obtained from waste plant oils with different catalysts

| Plant Oil	Catalyst	Molar Ratio	Reaction Conditions	Yield
Brassica carinata	1.2 wt.% KOH	Methanol/oil (6:1)	25 °C, 1 hr	97 %
Brassica carinata	1.4 wt.% KOH	Methanol/oil (4.6:1)	45 °C, 5 hr	91.9 %
Camelina sativa	1.5 wt.% NaOH	Methanol/oil (6:1)	25 °C, 1 hr	97.4 %
Camelina sativa	1.5 wt.% KOH	Methanol/oil (6:1)	1 hr	98 %
Terminala catappa	CH_3CH_2ONa	Methanol/oil (6:1)	-	93 %
Melia azedarach	1 wt.% NaOH	Methanol/oil (9:1)	36 °C, 40 min	63.8 %
Aslepias syiraca	1.1 wt.% CH_3ONa-KOH	Methanol/oil (6:1)	60 °C, 1 hr	>99 %
Jojoba	1.35 wt.% KOH	Methanol/oil (6:1)	25 °C, 1 hr	83.5 %
Cerbera odollam	NaOH 1%(w/w)	Methanol/oil (6:1)	65 °C, 1 hr	83 %
Raphanus sativus	0.6 wt.% NaOH	Ethanol/oil (11.7:1)	38 °C, 1 hr	99.1 %
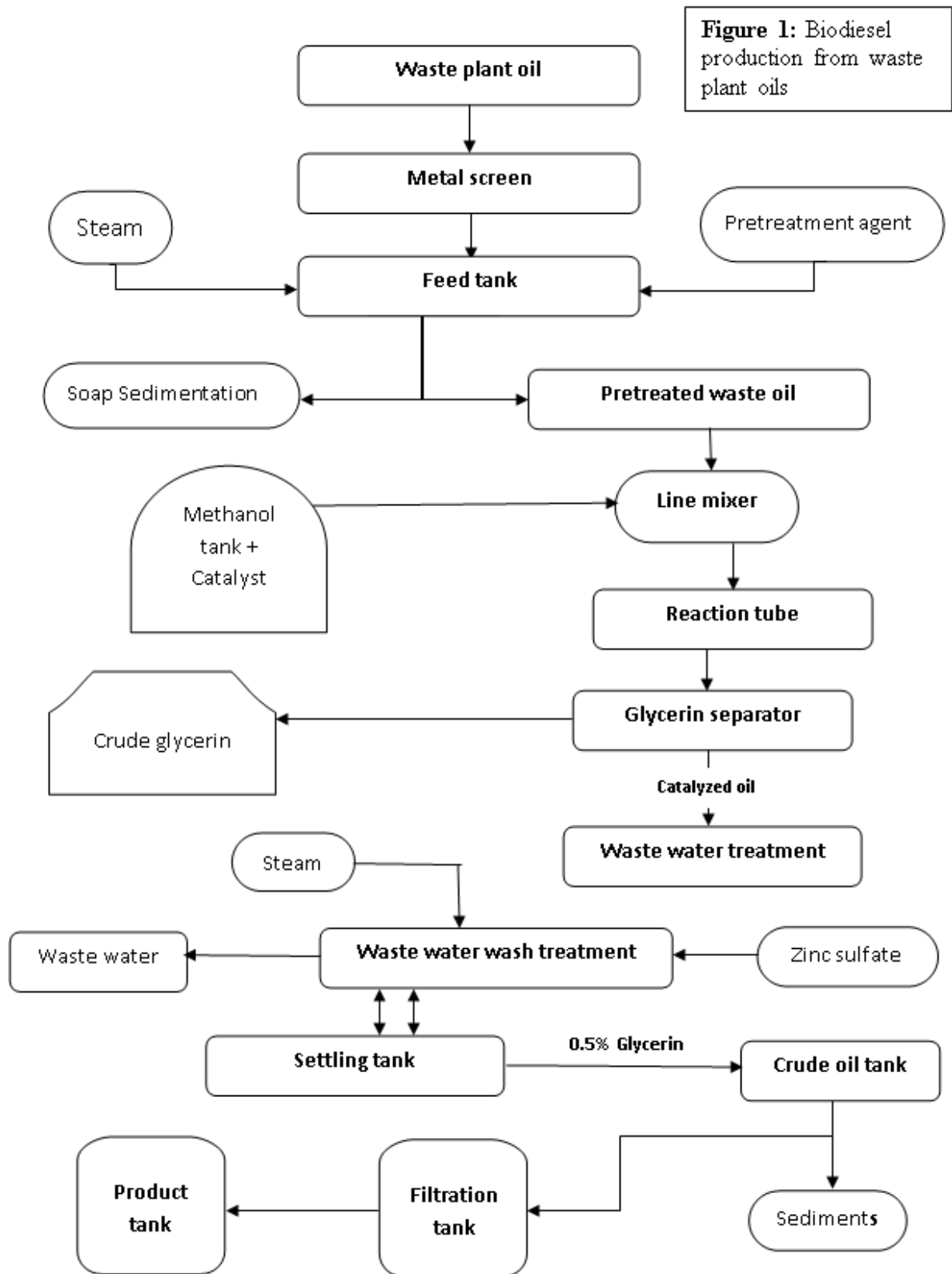
Figure 1: Biodiesel production from waste plant oils

Figure 2: Esterification Process
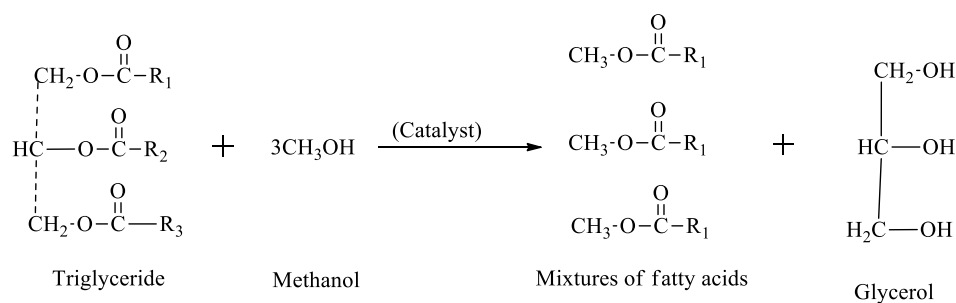
Scheme 1 explains mechanism of transterification process

Table 7: Homogenous base catalyzed waste plant biodiesel production

Feedstocks	Reagent	Catalyst	Ratio	Catalyst	Time	T (˚C)	Yield	Ref
Waste cooking oil	Ethanol	NaOH	-	0.08wt. %	20 min	60	94.5 %	[26]
Waste cooking oil	Methanol	NaOH	3:1	0.5 wt.%	30 min	30	86 %	[68]
	Methanol	KOH	6:1	1 wt.%	60 min	45	98.2 %	
Used coconut oil	Methanol	NaOH	6:1	0.5 wt.%	-	60-65	94 %	[69]
Waste palm oil	Methanol	KOH	8:1	2.0 wt.%	180 min	55	96 %	[70]
Waste soybean oil	Ethanol	KOH	30% wt.	12g/l	35 min	50	78 %	[71]
Waste canola oil	Methanol	NaOH	7:1	1.0 wt.%	60 min	43	93.5 %	[72]
Waste rapeseed oil	Methanol	NaOH	6:1	1.0 wt.%	65 min	45	84.1 %	[73]
Waste cottonseed oil	Methanol	NaOH	6:1	1.0 wt.%	45 min	65	87 %	[74]
				2.0 wt.%			96 %	
Waste olive oil	Methanol	KOH	4:1	1.26 wt.%	30 min	25	90 %	[75]
Waste linseed oil	Methanol	KOH	8.24:1	1.45 wt.%	40 min	36	92 %	[76]
Waste castor oil	Ethanol	KOH	20:1	2% w/w	30 min	80	96 %	[77]

Table 8: Homogenous acid catalyzed waste plant biodiesel production

Feedstocks	Reagents	Catalyst	Ratio	Catalyst	Time	Temp (˚C)	Yield	Ref
Waste palm oil	Methanol	HCl	24:1	1 wt.%	3h	90	87 %	[83]
Waste sunflower oil	Methanol	H_2SO_4	-	-	4h	-	51.1 %	[84]
Waste soybean oil	Methanol	H_2SO_4	30:1	1 wt.%	69h	65	90 %	[85]
Waste canola oil	Methanol	$ALCl_3$	24:1	5 wt.%	18h	110	98 %	[81]
Waste rapeseed oil	Methanol	H_2SO_4	30:1	1 wt.%	69h	65	99 %	[86]
Waste cottonseed oil	Methanol	H_2SO_4	20:1	4 wt.%	20h	95	99 %	[87]
Waste olive oil	Methanol	H_2SO_4	3:1	1 wt.%	68h	65	89 %	[88]
Waste linseed oil	Methanol	H_2SO_4	8:1	-	45h	45	85 %	[37]

Table 9: Heterogeneous base catalyzed waste plant biodiesel production

Feedstocks	Reagent	Catalyst	Ratio	Catalyst	Time	T (°C)	Yield	Ref
Used coconut oil	Methanol	Mg-Al hydrotalcite	12:1	5 wt.%	5h	65	97.98 %	[69]
Waste palm oil	Methanol	CaO	18:1	5.35 wt.%	0.5h	60	71.7 %	[93]
Waste sunflower oil	Methanol	CaO	6:1	1 wt.%	5.5h	80	91 %	[84]
Waste soybean oil	Methanol	CaO	12:1	2	1.5 h	900	93 %	[71]
Waste canola oil	Methanol	Dolomite	6:1	3 wt.%	3h	67.5	91.78 %	[72]
Waste rapeseed oil	Methanol	KNO$_3$/CaO	6:1	1 wt.%	3h	65	98 %	[94]
Waste cottonseed oil	Methanol	CaMgO and CaZnO	15:1	4 wt.%	6h	65	78 %	[95]
Waste olive oil	Methanol	Sodium silicate	7.5:1	3 wt.%	1h	60	~100 %	[96]
Waste linseed oil	Methanol	CaO	12:1	0.85 wt.%	1h	63	66 %	[97]
Waste castor oil	Methanol	K$_3$PO$_4$	6:1	2 wt.%	2h	60	97.3 %	[98]

Table 10: Heterogeneous acid catalyzed waste plant biodiesel production

Feedstocks	Reagent	Catalyst	Ratio	Catalyst	Time	T (°C)	Yield	Ref
Used coconut oil	Methanol	SO$_4^{2-}$/ZnO$_2$	7:1	4.8 wt.%	11h	70	86.3 %	[103]
Waste palm oil	Methanol	SO$_4^{2-}$/ZnO$_2$	5:1	3 wt.%	17h	110	90.3 %	[70]
Waste sunflower oil	Methanol	WO$_3$/ZnO$_2$	19.4:1	-	20h	75	85 %	[84]
Waste soybean oil	Methanol	SO$_4^{2-}$/SnO$_2$-SiO$_2$	15:1	3 wt.%	3h	150	92.3 %	[104]
Waste canola oil	Methanol	Zeolite	6:1	-	0.37h	460	26.6 %	[72]
Waste rapeseed oil	Methanol	Carbon based catalyst from starch	30:1	10 wt.%	8h	80	92 %	[94]
Waste cottonseed oil	Methanol	SO$_4^{2-}$/TiO$_2$-SiO$_2$	9:1	3 wt.%	3h	200	>90 %	[87]
Waste olive oil	Methanol	H$_3$PW$_{12}$O$_4$. 6H$_2$O	70:1	3.7 wt.%	14h	65	87 %	[96]
Waste linseed oil	Methanol	ZrHPW	20:1	2.1 wt.%	-	65	98.9 %	[97]
Waste castor oil	Methanol	ZS/Si	18:1	3 wt.%	5h	200	98 %	[105]

Table 11: Enzyme catalyzed waste plant biodiesel production

Feedstock	Reagent	Catalyst	Ratio	Catalyst	Time	Temp (°C)	Yield	Ref
Used coconut oil	Methanol	PS 30	6.6:1	13.7 wt.%	2.47h	38.4	96 %	[103]
Waste palm oil	Methanol	Novozym 435	3:1	4 wt.%	50h	30	90.4 %	[108]
Waste sunflower oil	Methanol	Novozym 435	3:1	4 wt.%	50h	30	90.9 %	[26]
Waste soybean oil	Ethanol	Novozym 435	25:1	10 wt.%	50h	-	89.1 %	[104]
Waste canola oil	Methanol	Novozym 435	4:1	4 wt.%	12h	40	88 %	[109]
Waste rapeseed oil	Methanol	*Bacillus subtilis*	1:1	3 wt.%	72h	40	90 %	[94]
Waste cottonseed oil	Methanol	*Rhizopus oryzae*	4:1	30 wt.%	30h	40	88.90 %	[95]
Waste castor oil	Ethanol	Novozym 435	1:1	10 wt.%	4h	40	57.4 %	[98]
Waste cooking Oil	Methanol	Novozym 435	3:1	3g	4h	40	90 %	[110]

Table 12: Microwave assisted waste plant biodiesel production

Feedstock	Reagent	Catalyst	Ratio	Catalyst	Time	Temp(°C)	Yield	Ref.
Waste palm oil	Methanol	NaOH	10:1	1 wt.%	6 min	55	98.4 %	[70]
Waste sunflower oil	Methanol	NaOH	7:1	1.2 wt.%	2 min	60	95 %	[114]
Waste soybean oil	Methanol	NaOH	7:1	3.2 wt.%	5 min	-	37.1 %	[115]
Waste canola oil	Methanol	K$_2$SO$_4$	30:1	24 wt.%	1.5h	65	96.7 %	[109]
Waste rapeseed oil	Methanol	CaO	6:1	2 wt.%	15min	58	92 %	[94]
Waste cottonseed oil	Methanol	KOH	6:1	1.5 wt.%	30min	65	91 %	[95]
Waste olive oil	Methanol	CaO	7:1	3 wt.%	30min	69	96.6 %	[96]

Waste linseed oil	Methanol	CaO	7:1	5 wt.%	44min	56	93 %	[97]
Waste castor oil	Methanol	CaO	8:1	1.2 wt.%	50min	72	89 %	[98]
Waste cooking oil	Methanol	KOH	6:1	1 wt.%	20min	50	98.9 %	[110]

Table 13: Fuel related properties of waste plant oils

Feedstocks	Viscosity	FP ($^\circ$C)	HV	CN	CP ($^\circ$C)	PP ($^\circ$C)	Ref
Petroleum Based Diesel	3.25 (cSt)	75	43.73 Kg/J	54.5	-	-3.0	[110]
Used coconut oil	3.62 mm^2/s	-	-	53.4	-2	-5	[110]
Waste palm oil	14.94 (cSt)	109	39.31 Kg/J	52.91	-	-	[117]
Waste soybean oil	6.24 mm^2/s	175.4	36.7 Kg/J	46.3	-	-3	[118]
Waste canola oil	6.02 mm^2/s	109	42.3 Kg/J	57.2	-	0	[119]
Waste rapeseed oil	6.35 mm^2/s	-	42.59 Kg/J	45	-3	-9	[120]
Waste cottonseed oil	5.94 (cSt)	198	39.31 Kg/J	56.9	-	-	[121]
Waste olive oil	5.29 mm^2/s	169	39.67 Kg/J	58.7	-2	-6	[122]
Waste linseed oil	4.8 (cSt)	151	45.34 Kg/J	37.66	2	-4	[97]
Waste peanut oil	6.98 mm^2/s	-	39.48 Kg/J	56.8	-	-	[123]
Waste corn oil	8.72 mm^2/s	166	39.26 Kg/J	47.0	-	-	[124]
Waste pumpkin oil	7.70 mm^2/s	-	39.55 Kg/J	58.3	-	-3	[125]

3. Conclusions

The depletion of fossil fuels and their associated environmental problems has increased the awareness to seek for alternative renewable and sustainable resources for biodiesel production. Transesterification appears to be the best method for biodiesel production. Regardless of other feedstocks, waste plant oils have several advantages including elevated calorific value, ecofriendly, high stability towards oxidation, easily available, and technically acceptable. Furthermore, biodiesel production from waste plant oils also plays an important role to overcome the problems of biodiesel transportation and unavailability at local resources. Different types of waste plant oils used for the production of biodiesel include used coconut oil, waste soybean oil, waste palm oil, waste sunflower oil, waste rapeseed oil, waste soybean oil, waste olive oil, waste cotton oil, waste linseed oil, waste corn oil, and waste peanut oil etc. Such waste oils are produced throughout the world in an exceptionally large quantity. Hence, these waste oils can be converted into methylated esters through different transesterification methods, having properties similar to biodiesel pure plant oil. Moreover, the physicochemical properties beside the engine performance and emission are covered in this review which indicated that it is economical to produce biodiesel from waste plant oil sources.

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