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Review article

A review on feedstocks, production processes, and yield for different generations of biodiesel

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ABSTRACT

Continuous increase in world's population, rapid industrialization, urbanization, and economic growth force for continuously increase in fossil fuel consumption to meet growing energy demand. Continuous emissions from burning of fossil fuel will create the need to find the appropriate and sustainable replacement for fossil fuels. Biodiesel is appropriate alternate solution for diesel engine due to its renewable, non-toxic and eco-friendly nature. According to EASAC biodiesel evolution is classified into four generations. Cultivation in arid and semi arid land or water, crop yield, effect on food supply, yield of biodiesel, energy content, carbon-neutral economy, easy availability, and economic viable are the main factors behind the evolution of biodiesel generations. This article highlights a comprehensive assessment of various feedstocks used for different generation biodiesel production with their advantages and disadvantages. Different production methods for biodiesel with yield calculation are also explained. Algae based third generation feedstocks are better in comparison with first and second generation due to their high energy content, high oil content and less polluting nature. Forth generation of biodiesel produced from synthetic biology, which will enhance the various physiochemical properties of biodiesel to achieve carbon neutral economy. Among the all biodiesel production processes; transesterification is the most suitable process, because it produces biodiesel of high yield, comparable properties with diesel. This process is also feasible as per economic point of view. The energy demand of future can be met by the blending of different generation oil feedstocks.

1. Introduction

Conventional energy sources like fossil fuel, petroleum, coal and methane are non renewable sources. These are main sources of energy at present time and due to larger consumption shortage is about to happen [1]. From 1970 to 2015 energy supply has increased from 6 Gtoe to 15 Gtoe and the consumption of fossil remains high for the primary energy supply. The consumption of fossil fuel was around 86% for production of primary energy in 1973 and in the year 2015, this consumption is about 78%. Oil production will reach to a maximum limit by 2020 and also the consumption will continue to rise, pulled primarily by China and India. Rapid industrialization leads to decrease of fossil fuel reserves [2]. Petroleum, nuclear, wind, coal, solar etc. produced major part of energy for different sectors (agriculture, transport and industry) [3–5]. For these sectors oil consumption in year 1973 is 42% and in 2014 it is 64.5% of total world's oil consumption. The consumption of fossil fuel is increased by 43.33% from last 41 year. [6]. Solar, wind, organic, hydrothermal are renewable energy resources and has great importance at present [1]. Less pollution potential and less contribution in global warming are the key factors that force to switch towards alternate solution. 20% population of European Union faces the problem of high noise production by rail and road traffic [7]. To meet the energy requirements biofuels grabbing the attention of researchers as an alternative of conventional fuel [8,9]. Other factor like high price of energy import, high cost and environmental issues have also created more interest in biofuels. The important properties that an alternative fuel should have the economically feasible, easily available, less environment issues as compared to conventional fuels

Abbreviations: CI, compression ignition; BP, brake power; BT, brake torque; IP, injection pressure; FAME, fatty acid methyl esters; PFCE, photon to fuel conversion efficiency; GCMS, gas chromatography–mass spectroscopy; GCFID, gas chromatography-flame ionization detector; ASTM, American Society of Testing and Materials; HPLC, high-performance liquid chromatography; EASAC, European Academies Science Advisory Council; GHG, Green House Gas; BSFC, brake specific fuel consumption; BTE, brake thermal efficiency; IT, injection timing; MES, microbial electro-synthesis; TG, Triglyceride

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[10]. Rudolf Diesel (inventor of diesel engine) also tested peanut oil in diesel engine as a fuel initially. During the research on alternative fuels this point was notice that the vegetable oils can also used in diesel engines without modifications.

Various harmful matters are emitted from engine exhaust (smoke, un-burnt hydrocarbons, carbon mono oxide, particulate matter and nitrogen oxides), which are very dangerous for human being and environment also. Most harmful pollutants are nitrogen oxide and smoke [11–15]. Accumulation of carbon mono oxide and other gases in the environment are also responsible for change in climatic condition [16]. From 2007 to 2030 the level of CO_2 has been estimated to increase by 80% approximately [17]. Due to reduction in fuel reserves and rising environmental issues has increased the attention of researcher towards the alternative fuels in place of conventional fuels [18–20]. Nowadays several countries have emphasized and encourage the use of alternative fuel like biodiesel fuel by governmental and regulatory pathways by means of both incentives and prescriptive volumetric necessities. From economic and emission quality point of view vegetable oil is the good source of energy as alternative fuels [21–23]. Mono alkyl ester that produced from fatty acid esters of edible oil, non edible oil and waste oils are called biodiesel [24]. Biodiesel can be used directly in engine in pure form or blend with diesel in various proportions to provide alternative solution of fuel in compression ignition (CI) engines. Biodiesel is renewable source of energy, sulfur free, oxygenated, sustainable and biodegradable. In diesel engine no modification is required while using biodiesel as fuel [25–28]. Biodiesel shows less regulated and unregulated emissions as compare to diesel fuel [28,29]. Various reasons for biodiesel used as alternative fuel are focus on reduction of greenhouse gas (GHG) emissions, less effect on global climate, sustainable and renewable energy solution and to get more promising alternate fuel supply to meet the current energy demand. With the help of biodiesel emissions of particulate matter, carbon monoxide, unburned hydrocarbon and carbon dioxide can be reduced [17,18,30]. The parameters of diesel engine performance like brake power (BP), brake torque (BT), brake thermal efficiency (BTE), break specific fuel consumption (BSFC) are also improved [18,21,31]. Fuel economy and emissions from engine is greatly affected by fuel injection system. The parameters of fuel injection systems are injection pressure (IP), injection timing (IT), fueling and injection duration [32,33]. The performance of engine can be improved by recirculating the exhaust gases and it can also reduce the engine emission [34]. Biodiesel produced from raw vegetable oil has its properties almost similar to diesel, so that it can be used as an alternate fuel. The main drawback of biodiesel as compared to diesel are high pour and cloud point, high viscosity, augmented nitrogen oxides emission, less volatility, lower energy content and poor spray characteristics [35]. Many researchers have been done to resolve all the problems of biodiesel fuel by changing feedstocks types, using additives and engine modifications.

The main advantages of biodiesel as compared to diesel fuel are eco-friendly, renewability, high flash point, biodegradability and non-toxicity [36]. Biodiesel has similar properties to petroleum diesel and lower emissions so it can be used in the transport sector as alternate solution to diesel fuel [37,38]. With increase in use of biodiesel could reduce the pollutants and movable carcinogens [39]. Different source of feedstocks like vegetable oils, algal oils, animal fats, microbial oils and waste oils can be used for production of biodiesel [40]. Transesterification, pyrolysis and supercritical fluid method etc are the procedures for the production of biodiesel. From all of these methods the most adoptive method of biodiesel production is transesterification, which produce biodiesel and glycerol as secondary product from the oil [41]. This review article covers different aspects of biodiesel produced from different generation of oil feedstocks. This article discusses about various feedstocks used for biodiesel production and also describes the different production processes and calculation for yield of biodiesel. This review will help researchers to analyze and compare different generations of biodiesel.

2. Generations of biodiesel

All biodiesels have the equal renewable origin and basic. They are produced from photosynthetic conversion of solar energy to chemical energy, which make them isolated from early photosynthesis. In accordance to ASTM, term biodiesel assigned for monoalkyl esters of long-chain fatty acids resulting from edible oils, non-edible oils and waste oils, which produced from transesterification process of triglycerides using methanol and catalyst [42]. Glycerol (glycerin) is formed as by-product during transesterification process. Generally methanol is used to produce biodiesel due to low cost and easy availability. The term B100 means 100% of FAME, while lesser amount, like B20 designate as ‘biodiesel blends’. Production of biodiesel depends on solar energy and it is the base of sustainable bioeconomy. Mainly in the transport sector biodiesel is still of primary significance in current societies (in spite of enormous improvement in technology to convert solar energy to electricity with photovoltaic cells).

Major issue regarding renewable fuel is about struggle of land for food and development of fuel. Scientific steps taken for biodiesel development are of covering the feedstocks development, optimum production method, quality and quantity improvement for biodiesel and carbon–neutral economy [43]. According to the EASAC report 2012 biodiesel are usually classified as the first, second and third generation of biodiesel that primarily based on the origin of biodiesel, whereas the fourth generation biodiesel drawn from man-made biological tools and is at infancy level of fundamental research [24]. The production processes used for different generations of biodiesel are shown in Fig. 1.

2.1. First generation biodiesel

First generation biodiesels are produced from the edible feedstocks, example of edible feedstocks are Rapeseed oil, Soybean oil, Coconut oil, Corn oil, Palm oil, Mustard oil, Olive oil, Rice oil, etc. [44]. Various feedstocks used for first generation biodiesel are illustrated in Table 1. Use of edible feedstock for the production of biodiesel is quite popular at beginning of biodiesel era. Availability of crops and comparatively easy conversion procedure are the main benefits of the first generation feedstocks. The risk of limitation in food supply is the main disadvantage in use of these feedstocks that increase the cost of food products [45]. Adaptability to environmental conditions, high cost, and limited area of cultivation are also the obstacles for the production of biodiesel from edible feedstock. These drawbacks constrained users to shift on the further alternate sources for the biodiesel production [46].

2.2. Second generation biodiesel

Second generation biodiesels are produced from the non-edible feedstocks, example of non-edible feedstocks are Neem oil, Jatropha oil, Nagchampa oil, Karanja oil, Calophyllum inophyllum oil, Rubber seed oil, Mahua indica oil etc. [47,48]. Different non-edible feedstocks used for biodiesel production are discussed in Table 1. Drawbacks of first generation feedstocks attract researchers to work on non edible feedstocks. Eco-friendly, less production cost, eradicates food inequality, less requirement of land for farming are the main benefits of second generation biodiesel [44–46]. These oils contain the main benefits of using second generation biodiesel are, no requirement to relay food plants and no requirement of agricultural land only. Disadvantages of second generation fuels is yields of plants, where yield falls for main non-edible plants like Jatropha oil, Jojoba oil and Karanja oil. These feedstocks can cultivate in unimportant lands. That’s why it is forced to farm non-edible crops at farming lands; it directly influences economy of society and the food production. To beat the socioeconomic issues of nonedible oil, the researchers paying attention on new alternate solution, which are economically feasible and simply accessible at greater extent. Requirement of additional alcohol amount is also the drawbacks for second generation biodiesel [46].

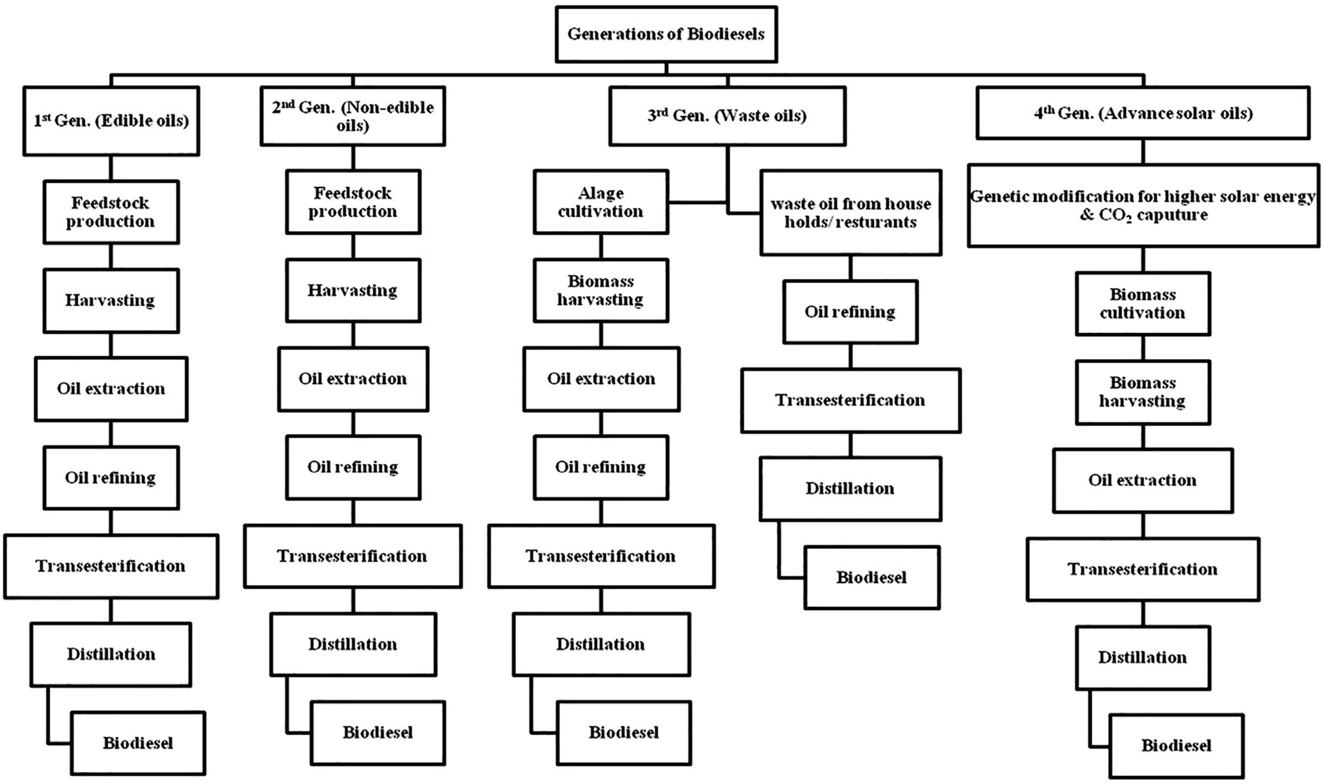

Fig. 1. Biodiesel production process for different generations.

2.3. *Third generation biodiesel*

The biodiesel produced from microalgae and waste oils are termed as third generation biodiesel [46]. The major benefits of third generation biodiesel are lesser greenhouse effect, elevated growth rate and productivity, lesser struggle towards farming land, higher amount of oil percentage and lesser influence on food supply. The main disadvantages are requirement of large amount of investment, necessity of sunlight, issue of production at larger scale, and difficulties in oil extraction [46,49,50]. At present the production of biodiesel from algal biomass is under research to enhance the production rate of biodiesel and also extraction process. The main sources for third generation biodiesel are fish oil, animal fat, micro algae, waste cooking oil etc. [51]. All these feasible resources of third generation biodiesel beat the issues faced by earlier generation feedstocks that influence the food chain, availability, flexibility with environmental parameters, economic feasibility. In severe situation some algal species have capability to survive and high lipid content that's why microalgae can be a possible future source for third generation biodiesel [52]. In case of waste oils, used cooking oil, waste fish oil, waste animal tallow oil are also sources for the third generation biodiesel. It also diminishes load of waste handling plant and decrease of water pollution. At present animal fats like pork, beef, goat and poultry rising as a possible and dependable source for biodiesel production [53]. Various feedstocks for third generation biodiesel are shown in Table 1.

Table 1
Feedstocks used for different generation of biodiesel production.

Edible oil (1st generation)	Non-edible oil (2nd generation)	Waste oils (3rd generation)	Solar biodiesel (4th generation
Cashewnut [55]	Aleutites fordii [64]	Animal tallow [67]	Photobiological solar biodiesel [74]
Coconut [86]	Babassu tree [55]	Biomass pyrolysis [68]	Electrobiofuels [74]
Corn [44]	Calophyllum inophyllum [65]	Botryococcus braunii [69]	Synthetic cell [74]
Cotton seed [56]	Castor [66]	Chicken fat [70]	
Hazelnut [57]	Cerbera odollam [64]	Chlorella vulgaris algae [69]	
Mustard [58]	Crambe abyssinica [64]	Dunaliella salina algae [69]	
Olive [191]	Jatropha curcus [64]	Poultry fat [71]	
Palm [142]	Jojoba [55]	Fish [72]	
Pistachio [55]	Karanja [55]	Waste cooking oil [73]	
Raddish [58]	Mahua indica [64]		
Rapeseed [59]	Milk bush [55]		
Rice bran [60]	Nagchampa [55]		
Soyabean [61]	Neem [64]		
Sun flower [62]	Nicotiana tabacum [64]		
Tigernut [63]	Petroleum nut [55]		
Walnut [55]	Rubber seed [64]		
	Sapindus mukorossi [64]		
	Silk cotton tree [55]		
	Tall [55]		
	Thevettia peruviana [64]		

Table 2
Benefits and limitations of alternative fuel options for different generations [75–81].

	First generation	Second generation	Third generation	Fourth generation
Benefits	Easy biodiesel conversion process, easy availability of crops	Not affect on food supply, Feedstocks can be grow on non-arable land, less production cost	Waste food oil can be use for biodiesel production, growth rate of algae is high, not affect on food supply, can be use seawater or waste water for algae growth	More lipid content, more CO_2 absorbing ability, high energy content, rapid growth rate
Limitations	Affect food supply, Low crop yield, Limited area of cultivation, less adaptability of crop to environmental conditions	Less cost-effective conversion technology, low crop yield for some feedstocks	High energy consumption for algae cultivation, low lipid content in open pond system, expensive oil extraction process from algae	High intial investment, research on infancy level

2.4. Fourth generation biodiesel

Photobiological solar fuels and electro-fuels are considered in fourth generation of biodiesels. Solar biofuels are produced by conversion of solar energy into biodiesel using raw material, this method of conversion is a new field of research. Raw materials are widely available, inexhaustible and cheap. Different solar energy based biodiesel for fourth generation biodiesel are shown in Table 1. Synthetic biology is an enabling technology for such a transformation [54]. For sustainable development, new-to-nature solutions must be find out, which make synthetic living firms and stylish microorganisms for efficient and direct change of solar energy to fuel. Similarly, a mixture of photovoltaic or inorganic water-splitting catalysts with metabolically engineered microbial fuel development is a rising methodology for efficient development and liquid fuel storage. Table 2 describes the benefits and limitations associated with different generations of biodiesel.

3. Feed stocks for biodiesel production

Biodiesel can be obtained from different feedstocks like vegetable, algae, microbial oil and animal fats. Biodiesel obtained from different feedstocks have various purity and composition [44]. The main step for the biodiesel production is selection of feedstock, which influence various factors, like purity of biodiesel, cost, composition and yield. Availability and type of feedstocks source are the main parameters for classification of biodiesel into edible and non-edible and waste based origins [82]. Selection of feedstocks for biodiesel production is also reliant on regions. Availability and economic aspect of country is mainly considered before selecting feedstock. Canola oil is used as feedstock in Canada and Soyabean oil is used as feedstock in Brazil and USA. Coconut and Palm oils are used in Indonesia and Malaysia as biodiesel feedstock and Rapeseed oils used in Italy, Germany, Finland and UK as biodiesel feedstock. Karanja and Jatropha have considered as future feedstocks for biodiesel in India. Among them, Sunflower oil, Rapeseed oil, Soybean oil and Mustard oil have been used previously as biodiesel feedstock but due to unfavorable result on food plants slowed down their utilization as biodiesel feedstocks. The utilization of edible oils as biodiesel feedstocks have big issue because this directly affect food chain [43]. From various research it is concluded that consumption of nonedible oil as biodiesel feedstock have many benefits like bio degradable, low sulphur amount, no effect on food chain, Low aromatic content and availability. There are certain growing feedstocks for biodiesel such as tallow oil, animal fats, fish oil and micro algae etc., which can also be used to produce biodiesel.

3.1. First generation feedstocks

3.1.1. Coconut (Cocos nucifera)

For the production of biodiesel Coconut is one of feedstock source. This feedstock is accepted in Philippines for biodiesel production. Height of Coconut tree is about 15–18 m [86,94]. Coconut oil is a triglyceride having less percentage of monounsaturated fatty acids (6%), polyunsaturated fatty acids (2%) and high percentage of saturated fatty acids (86%). It have mainly three acids e.g. lauric (45%), palmitic (8%) and myristic acid (17%). It has totally seven various type of saturated fatty acids. It has less amount of monounsaturated fatty acid is oleic acid and it also has only polyunsaturated fatty acid is linoleic acid. Coconut oil has high biodiesel yield [83]. Some of physical properties like density, viscosity, and heating value of Coconut oil are 914 kg/m^3 (at 15 °C), 27 mm^2/s (at 40 °C), and 37.806 MJ/kg respectively [24]. Automobiles operated on coconut biodiesel enhance mileage by 1–2 km due to enhance oxygenation, even with 1% minimum blend and decrease in emission level by 60% [84].

3.1.2. Palm oil (Arecaceae)

The two main palm oil producer countries from last decade are

Malaysia and Indonesia. Nigeria and Brazil have high potential for Palm oil production. In Europe the demand of Palm biodiesel oil increases rapidly. Major benefits of Palm oil are very high yield of oil per hectare and economic, compared to other edible oils. Height of Palm tree varies from 10 to 15 m. Density, viscosity, and heating value of Palm oil are 897 kg/m^3 (at 15 °C), 40.65 mm^2/s (at 40 °C), and 39.867 MJ/kg respectively [24]. Palm oil has monounsaturated fatty acids and high amounts of medium-chain saturated. It contains palmitic acid (39–48%), oleic acid (36–44%), linoleic (9–12%), and stearic acid (3–6%) [83]. One issue associated with Palm oil is alkali catalyzed biodiesel production because, Palm oil has high amount of saturated fatty acids. The solution of this problem is follow acid catalyzed pre-esterification method [85].

3.1.3. Soyabean (Glycine max)

Soybean is the leading oilseed crop cultivated globally. In USA Soybean oil is very trendy biodiesel production source. Soybean oil have same iodine number with Sunflower oil (121–143). Height of Soyabean tree varies from 0.5 to 1.2 m. As compared to others, Soybean produces less yield of oil per hectare [86–89]. Soybean have nitrogen fixing ability that why it can cultivate in both temperate and tropical conditions. Soybean also recharges soil nitrogen. The requirement of fertilizer is less for Soybean which develops positive fossil energy balance. Physical properties like density, viscosity, and heating value of Soyabean oil are 916 kg/m^3 (at 15 °C), 31.83 mm^2/s (at 40 °C), and 39.6 MJ/kg respectively [24]. Soyabean oil contains linoleic acid (50–60%), oleic acid (20–30%), palmitic acid (6–10%) and linolenic acid (5–11%) [90].

3.1.4. Sunflower (Helianthus annuus)

Fifth largest oilseed crop all around the world cultivated is Sunflower. In Europe after Rapeseed, Sunflower oil is used for production of biodiesel. Sunflower tree can grow up to 3 m. The yield of oil production for Sunflower seeds is higher than Soybean and Rapeseed per hectare. It is much productive as Rapeseed, Sunflower is more used by the people because it need a smaller amount of fertilizer and water [41,86,91–93]. Density, viscosity, and heating value of Sunflower oil are 918 kg/m^3 (at 15 °C), 34.01 mm^2/s (at 40 °C), and 39.56 MJ/kg respectively [24]. It contents high amount of linoleic acid (30–70%), which is an obstacle in utilization of it as biodiesel feedstock. It also contains oleic acid (15–40%), palmitic acid (5–8%) and stearic acid (2–6%). High value of iodine number and less oxidation stability are the main reasons for pure Sunflower is not suitable as fuel [83].

3.2. Second generation feedstocks

3.2.1. Cotton seed (Gossypium)

The main producer countries of Cotton crop are Europe, China and United States. The main species of Cotton plants are Gossypium herbaceum and Gossypium hirsutum, which are used for the production Cotton seed oil. Cotton plants can reach up to height of 1.2 m. This oil has various kinds of non-glyceride things, like sterols, carbohydrates, gossypol, resins, phospholipids, and connected pigments [95]. This oil has density in the range of 917–933 kg/m^3(at 15 °C). Viscosity and heating value of Cotton Seed oil are 34.79 mm^2/s (at 40 °C), and 39.5 MJ/kg respectively [24]. Seeds of Cotton plant have oil in the range of 17–25%. The cotton seed oil has fatty acid, like oleic of 19.2–23.26%, palmitic of 11.67–20.1%, and linoleic acid of 55.2–55.5% [16,96].

3.2.2. Jatropha (Jatropha curcas)

Jatropha is an oilseed plant and it cultivated on semi arid, marginal areas. Scrub can be collected two times in a year, are not often looked by cattle, and stay productive for 30–50 years. Seeds can obtain from plant after 1 year of plantation and its productivity is highest after 5 years of plantation [97]. Plant of Jatropha belongs to the family of Euphorbiaceae and maximum height of plant is up to 5–7 m [98,99]. Jatropha plant requires approximate rain 100–150 cm per year. India, Argentina, United States, Paraguay Brazil, Africa, Bolivia and Mexico countries are the home for the Jatropha crop [98,100,101]. In India Jatropha tree has been recognized as one of important sources for biodiesel, where about 64 million hectares of area is classify as uncultivated or waste area. Seed of Jatropha plant have approximate 20–60% oil. Heating value, density, and viscosity of Jatropha oil are 38.96 MJ/kg, 916 kg/m^3 (at 15 °C), and 37.28 mm^2/s (at 40 °C) respectively [24]. Jatropha have mostly unsaturated components, like oleic (34.3–44.7%) and linoleic acid (31.4–43.2%), certain saturated components, like palmitic acid (13.6–15.1%) and stearic acid (7.1–7.4%) [102].

3.2.3. Jojoba (Simmondsia chinensis)

Mexico, California, Arizona and India are the main producers of Jojoba plant. Jojoba plant belongs to the family of Simmondsiaceae. The main important products obtained from Jojoba plant are liquid wax ester and oil obtained from its seeds. In India Plant of Jojoba used to stop desert growth. The maximum height of plant is up to 1–2 m. The profile of leaves of Jojoba plant is oval and width of leave is about 1.5–3 cm and long about 2–4 cm, they are grayish green in color [103,104]. Density, viscosity, and heating value of Jojoba oil are 868 kg/m^3 (at 15 °C), 24.89 mm^2/s (at 40 °C), and 46.47 MJ/kg respectively [24]. Seeds of Jojoba plant have fatty acid approximate linoleic 25.2–34.4% and oleic acid 43.5–66% and oil content from Jojoba seed is about 40–50% [105–107].

3.2.4. Karanja (Millettia pinnata)

The main producer countries of Karanja are South-east Asia, Australia, China, and US [108]. It is belongs to the family of legumnosae. The maximum height of Karanja plant is up to 15–25 m. After 3–4 year plantation blossoming initiates and it ripens 4–7 years after plantation. Plant of Karanja has 9 to 90 kg seeds from a single plant. It has huge inconsistency of oil amount in Karanja seed (25–40%) [100,109,110]. Heating value, density, and viscosity of Karanj oil are 35.992 MJ/kg, 933 kg/m^3 (at 15 °C), and 39.9 mm^2/s (at 40 °C) respectively [24]. Karanja oil has stearic acid (2.4–8.9%), linoleic acid (10.8–18.3%) and oleic acid (44.5–71.3%) [111–113].

3.2.5. Linseed (Linum usitatissimum)

The main producer countries of Linseed are Argentina, India, Europe and Canada. It is an herbaceous type crop. Physical properties like density, viscosity, and heating value of Linseed oil are 924 kg/m^3 (at 15 °C), 26.24 mm^2/s (at 40 °C), and 39.3 MJ/kg respectively [24]. It has huge unsaturated fatty acids like linolenic acid (46.10–51.12%), oleic acid (20.17–24.05%) and linoleic acid (13.29–14.93%) and saturated part contains palmitic acid (5.85–6.21%) and stearic acid (5.47–5.63%) [114,115].

3.2.6. Mahua (Madhuca longifolia)

The largest producer country of Mahua is India. It is evergreen tree and belongs to the Sapotaceae family [116,117]. Warm and humid climate is best environmental condition for the cultivation of Mahua plant. From single Mahua plant approximately 20 to 200 kg seeds are produced yearly. For production of soap and beauty items and for skin treatment its oil fat is used. The average age of Mahua plant is approx 60 years and after 10 years of plantation seeds starts developing and it have 35–50% of oil amount. The maximum height of Mahua plant is approximately 20 m [105,117]. Heating value, density, and viscosity of Mahua oil are 36.85 MJ/kg, 942 kg/m^3 (at 15 °C), and 32.01 mm^2/s (at 40 °C) respectively [24]. It has large amount of unsaturated part like 41–51% of oleic acid (41–51%), stearic acid (20.0–25.1%), palmitic acid (16.0–28.2%) and linoleic acid (8.9–18.3%) [118].

3.2.7. Neem (Azadirachta indica)

The main producer countries of Neem are some parts of Bangladesh, Australia, India, Japan, Burma, Sri Lanka, Indonesia and Pakistan. Neem is belongs to the family of Meliaceae. Neem can be cultivated in all type of sand like calcareous, dry, alkaline, saline, shallow, stony soil, and clay soil. Plant of Neem has reach maximum height up to 12–18 m. For the cultivation of Neem plant 140–120 cm rain required yearly. The age tenure for Neem plant is about 150 to 200 years and after 15 year of plantation, it has highest productivity. Oil amount is 20–30% in the seed of Neem [100,105]. Some of physical properties like density and viscosity and heating of Neem oil are 929 kg/m^3 (at 15 °C) and 38.875 mm^2/s (at 40 °C) respectively [24]. Neem has mainly large amount of unsaturated part like oleic acid (25–54%) and linoleic acid (6–16%) and saturated parts have stearic acid (9–24%) [119,120].

3.2.8. Rubber seed (Hevea brasiliensis)

The main producer country of Rubber seed is Brazil and some other producer countries are Indonesia, Malaysia, Thailand and India. It belongs to the family of Euphorbiaceous. The tree of rubber is so tall and its height is up to 34 m [121]. For the growth of Rubber plant non frost environment and high rain is essential. Copra or kernel of it has 40–50% brown oil (by weight) and its seed have 50–60% oil content [105,122]. Density, viscosity, and heating value of Rubber seed oil are 917 kg/m^3 (at 15 °C), 42.54 mm^2/s (at 40 °C), and 38.64 MJ/kg respectively [24]. Rubber seed oil has high amount of unsaturated fatty acids, like linolenic acid (16.3%), linoleic acid (39.6%), and oleic acid (24.6%) [90].

3.2.9. Tobacco (Nicotiana tabacum)

The main producer countries of Tobacco are Russia, Turkey, India, Macedonia, South America and North America. It belongs to the family of Solanaceae [123,124]. Mainly Tobacco plant is cultivated for the collection of leaves. The main characteristics of Tobacco is quite similar to vegetable oils like physical and chemical properties that's why Tobacco is recognized as future source for development of biodiesel [66–68]. Heating value, density, and viscosity of Tabacco oil are 39.4 MJ/kg, 918 kg/m^3 (at 15 °C), and 27.7 mm^2/s (at 40 °C) respectively [24]. Seeds of Tobacco plant have 35–49% of oil amount and also have unsaturated fatty acids like linoleic acid (69.49–75.58%) [125].

Probability of development of biodiesel from various plants is high in India. India is the house of more than 300 unlike plant from which seeds are obtained for the production of oil. The expected possible obtain-ability of non-edible oils volume is around one million tons per annum that include Mahua oil (180,000 tones), Sal (180,000 tones), Neem (100,000 tones) and Karanja (55,000 tones), as the plentiful oil feedstocks. The advantages of these non-edible plants are not only compatibility with engines but also it can be cultivated in arid to semi-arid areas that are less suitable for food plants. Non-edible feedstocks are not presently cultivated on a large area. These feedstocks can be main constituents of local economies [126].

3.3. Third generation feedstocks

3.3.1. Animal fat

The co-product of fishery and meat industry is animal fat. It can be obtained from fish, cattle, chicken and hog. At present co-products from animal fat are mainly used for biodiesel production because it has low retail prices, particularly in turn to substitute fuel for automobile fleets, companies developing these raw materials. Due to numerous animal scandals and infections the possibility of using sources of animal fats is not permitted to be utilized as food any longer. It is verified for its use for biodiesel development. Tallow obtained from diseased livestock is also found as an important feedstock for biodiesel development. Irregular supply is biggest issue for all these feedstock, because animal fat has not been produced only for biodiesel.

Beef tallow or mutton, yellow grease, lard and residues after omega-3 fatty acids are used for producing third generation biodiesel [50]. These are main products from leather and meat industry. These sources provide food security, economic, and environmental benefits over edible oils. However, animal waste fats with higher saturated fatty acids and free fatty acids required complex development methods. Animal waste fats with lesser saturated fatty acids have numerous benefits like containing shorter delay in ignition, good stability to oxidation, and elevated calorific value [127]. These feedstocks have high degree of saturation which provides high heating value and Cetane number. Large volume of saturated fatty acids create problem of low temperature operability. Due to this the biodiesel obtained from animal fats are less suitable in cold countries.

3.3.2. Micro algae

Algae cultures are defined in which micro algae farming is done. Algae culture is a type of aquaculture concerning cultivation of algae to generate food or other stuffs that can be obtained from algae. These are aquatic plants having one cell, with possibility to generate huge amount of lipids that are suitable for production of biodiesel [128]. For the cultivation of algae two systems are used. First one is open pond system and other one is closed system. In open pond system algae are susceptible of being attack by other species and bacteria. The development of lots of species is comparatively small for open system. Water temperature and lighting are not controlled in open system. The rising period is dependent on the environmental location and is restricted to warmer months. The benefits of these systems are lesser price, and the larger production capacity [129]. Closed system or pond system is the other system of cultivating algae which is enclosed by greenhouse. These systems are smaller due to economic reasons in spite of this they have many benefits. These systems permit cultivation of additional species which are sheltered from other species from outer. It also enlarges the growing period. The closed system has photo bioreactor which connected to source of light. Photobioreacter is an enclosed pond that contains a light source, polyethylene bags, and plastic or glass tubes. As light simply penetrates 7–11 cm from top in algae culture, so for thick development of algae, blend of algae and water has to moved to permit that light spreads in blends. Many other system also use plastic or glass sheets [130]. These sheets are inserted into the pond and provide light directly to the algae for accurate concentration. Algae can be harvested by flocculation or centrifugation techniques, with the help of these systems algae can be grown in poor conditions of like arid and semi arid area. In addition per hectare yield is predictable to be higher than that of tropical oil plants. Algae can also cultivate in saline water, for example water from ocean or polluted aquifers. This water has few opposing uses in industry, forestry, agriculture, or municipalities [131]. At present probability of growing algae next to power plants is high. The algae can be nourished by CO_2 emissions because the main nutrients for algae growth are carbon dioxide and nitrogen oxides [132].

3.3.3. Waste oil

For the production of biodiesel a wide range of waste oils are available. Generally waste oils are cheap and present an extra ecological force by consuming materials of such types which would have to be disposed [133]. Waste oils can classify into three categories; waste oil from food industry, non food industry and from household and restaurants. Waste oil from rape seed, coconut, soybean, palm oils and other edible oils are utilized in biodiesel development. Utilization of these waste oils needs extra processing to handle obtained acid at high temperatures and clean out residues. In the food factory also so many co-products produced, which can be used for biodiesel production. Waste oils from non food industry use waste plastic oil, waste tyre oil etc to produce biodiesel through pyrolysis process [134].

3.4. Fourth generation feedstocks

High energy content, inexhaustible, easily availability and less cost are the key parameters behind fourth generation biodiesel feedstocks development. Artificial photosynthesis [135] and direct solar biodiesel production are the main technologies those use photosynthetic water splitting into its constituents by the use of solar energy. Fourth generation biodiesel based on synthetic biology technologies. Second and third generation biodiesel feedstocks are improved to increase photon to fuel conversion efficiency (PFCE) with the help of improvement in biomass processing technology. Future photobiological solar fuel production system harvests the solar energy and uses it to production of high quality fuel with improved yield. The microorganism will be making it possible to collect the fuel continuously in a photo-bioreactor. Direct solar fuel production technology is independent on harvested biomass. In an ideal system the production of biomass stopped when the system is shifted to direct photobiological solar fuel production. So, the microorganism's growth targeted to be provisionally separated from the production process of fuel. Immobilisation of algae and cyanobacteria could provide a solution for this. In comparison with ordinary biomass harvesting system PFCE of a photobiological fuel production process is higher. Presently research on these "designer organisms" target at 10% PFCE, with the necessity for appropriate bioreactors configuration. The future technologies, based on microbial electrosynthesis (MES) [136], hybrid systems (electrobiofuels), and synthetic cell are used to reach even higher PFCEs.

4. Steps for biodiesel production

The production of biodiesel; oils from plant feedstocks, microalgae, animal fats, and waste oils are used. The yield of biodiesel from oil crops mainly depends on the crop species. The yield of biodiesel produced from oils of third generation feedstocks is less in comparison with oil from first and second generation feedstocks [86]. The production of biodiesel involves two major steps. First one is production of oil from seeds or algae biomass, than conversion of oil in biodiesel using different major techniques like pyrolysis, micro-emulsification, dilution, transesterification etc. Transesterification process is the one of the most economic process with high biodiesel yield so, it is the most adaptive method for commercial biodiesel production.

4.1. Extraction of oil from feedstocks

The production of oil is done from its extraction from seeds of first and second generation feedstocks. Third generation feedstocks content microalgae, waste oils and animal fats so extraction of oil for these feedstocks is different from first and second generation. For the production of biodiesel, extraction of oil from seeds of oil crops (first and second generation) is the first step. There are two methods of oil extraction on the basis of infrastructure and amount of production. First one is small scale pressing and another one is large scale or industrial pressing. In small scale pressing first step is cleaning of oil seeds, and next step is mechanical pressing of seeds at 40 °C (highest). Next step is filtration in which suspended impurities are removed. The residual oil has some amount of press cake (approximately 10%). Press cakes formed as side product and it is full of protein so it can be utilized as protein fodder [137]. Presently small scale pressing is not commonly used due to greater production prices; while it provides opportunity for extra profits and also press cake that is side product can be directly used as feeder for animals. In large scale production the requirement of temperature is more than 80 °C to disable bacteria growth and spreading of press through proteins. In the beginning crushing of press cake is done and then solvent is mixed in it. The requirement of specific amount of water is essential because high amount of water creates issue for diffusion of solvent, while less amount increase compactness. Furthermore, the diffusion of solvent is better in crushed seeds. As a solvent generally hexane is used, which can remove oil at 80 °C temperature [137]. The mixture of hexane and oil is obtained at the end of procedure known as extraction grist and miscella. Recycling of hexane is done and removed from the mixture. Afterward maintaining the temperature and water amount, next step is pressing of seeds at 80 °C temperature. Thus about 75% of entire oil amount can be obtained [42]. After this process obtained oil further processed for refining. From various literatures it is found that edible oils and non edible oils have wide range of oil content percentage from feedstocks like Canola (40–45%) [86,143,144], Coconut (63–65%) [86,94], Linseed (40–44%) [86], Palm (30–60%) [86,142], Peanut (45–55%) [86,145], Rapeseed (38–46%) [86,140,141] Soybean (15–20%) [89], Sunflower (25–35%) [41,86,91-93], Castor (45–50%) [42,86,152,153], Chinese tallow seed (44.15%) [150,151], Jatropha (30–40%) [86,148,149], Karanja (27–39%) [86,147], Neem (20–30%) [38,139], and Rubber seed (53.74–68.35%) [154]. The main reason behind the variation of oil content is varying climate conditions throughout the globe [86]. In case of third generation feedstocks, waste oils only required refining process while; in case of microalgae different approach is used. Algae that are collected from pond spread under the sunlight for 48 h to evaporate the water content. The dried algae are grinded and the fine powder was passed through different micron sieves to get different mesh size algal biomass. Hexane as a solvent was mixed with the dried algae powder to extract oil. Then the mixture was kept for 24 h for settling and two layers are separated in the funnel. The Algal oil was separated from Algae biomass by filtration. The extracted oil evaporated in a water bath to release hexane [38]. From literature it is found that third generation feedstocks have high oil contents e.g. Algae, Boiler chicken waste, Micro algae, Microbial, Pine and kapok have 30–70% oil content [155–160]. The Percentage of oil content from different feedstocks are given in Table 3.

4.2. Oil refining

Refining process is used to eliminate unwanted components like colorants, phosphatides, tocopherols and free fatty acids. These components influence further steps of processing and also affect storage life of oil. Physicochemical properties of oil and type of feedstock resources influence the refining process. Degumming is initial purification stage of refining, in which elimination of phosphatides is done. Elimination of phosphatides is essential because it makes oil muddy and also they support accumulation of H_2O [138]. Acid and water degumming are the two methods used for elimination of Phosphatides. In acid degumming

Table 3
Percentage of oil content from different feedstocks.

Edible oils	Oil content (%)	Non edible oils	Oil content (%)	Animal Fat & other sources	Oil content (%)
Soybean [86–89]	15–20	Neem [38,139]	20–30	Algae [155,156]	
Sunflower [41,86,91–93]	25–35	Karanja (Pongamia pinnata) [86,147]	27–39	Broiler chicken waste [155]	
Rapeseed [86,140,141]	38–46	Jatropha [86,148,149]	30–40	Micro algae [38,42,157]	
Palm [86,142]	30–60	Chinese tallow seed (stillingia) [150,151]	44.15	Microbial [158,159]	30–70
Linseed [86]	40–44	Castor [42,86,152,153]	45–50	Pine and kapok [160]	
Canola [86,143,144]	40–45	Rubber seed [154]	53.74–68.35		
Peanut [86,145]	45–55				
Coconut [86,94]	63–65				

acidic components are mixed with oil and this method is used for insoluble phosphatides elimination i.e. not hydrated. Water degumming is used for removal of soluble phosphatides. In water degumming, water is mixed with oil at temperature 60–90 °C and then with help of centrifugal separation, oil and water phase are separated [139].

De-acidification is the next stage of refining. It is the essential stage for first generation edible oils because it prohibits production of rancid flavors of free fatty acids (FFA). De-acidification approach is also used for elimination of heavy metals, phenol, phosphatides and oxidized fatty compounds. Elimination of these components is not only essential for edible oil but also essential to fuel development because these components directly affect transesterification process and storage life. The approach of de-acidification includes distillation, de-acidification and removal of pigments and smells by many solvents like propane, ethanol, and furfural, neutralization with alkali, and de-acidification. Bleaching is the next step of refining in which colorants are eliminated. Storage time is improved with bleaching. In this approach adsorbing materials are used like activated carbon, bleaching earth, silica gel. Deodorization is the next stage of refining in which odorous components like aldehydes and ketones are eliminated. Dehydration is the last stage of refining in which water content is eliminated. Elimination of water is performed by distillation process at low pressure [138].

Microalgae have highest oil content up to 70%. In case of non-edible feedstock Rubber seed has maximum 68.35% oil content whereas in edible feedstocks coconut has 65% oil content. The oil content is about 15–20% in soybean, which is lowest.

4.3. Refined oil to fuel conversion techniques

For the production of biodiesel there are numerous methods which are investigated by researchers. Table 4 briefly describes about the pro's and con's of different production technologies used for biodiesel production. Among these techniques, there are four methods which are most favorable for production of biodiesel from different generation oil feedstocks.

4.3.1. Pyrolysis

Pyrolysis is one method which is used for biodiesel production. In this method thermal decomposition of material occur at high temperature in absence of air or in inert atmosphere. This process affected with variation in chemical composition of material. When oil is used as raw material during heating it will break and features of its liquid portion is like as diesel fuel. The characteristics of fuel obtained from pyrolysis process have calorific value similar to diesel fuel; pour point, viscosity and flash point are less than diesel. Cetane number is lesser than diesel of biodiesel produced through pyrolysis process. Biodiesel produced through this process has adequate quantity of water and sulfur, but it has in adequate amount of residual carbon and ash content [161]. High installation cost is the major drawback of this process.

Based on operating parameters pyrolysis method is classify into three sub categories-

(a) flash pyrolysis,
(b) conventional pyrolysis, and
(c) fast pyrolysis

Flash pyrolysis process is a high heating rate (> 1000 °C/s) thermal cracking process. It takes very less vapour residence time to minimize cracking at secondary stage to provide high liquid yield. Fast Pyrolysis reduces the yield of bio-oil in comparison to conventional pyrolysis. Physiochemical properties of fast pyrolysis and conventional pyrolysis bio-oils were tested by ASTM 7554-10 [162].

4.3.2. Micro-emulsification

The issue of viscosity for vegetable oil can be eliminated by making of micro emulsion. It is the stable, transparent and isotropic mixture of water, oil and surfactant. It is colloidal dispersion that is thermodynamically stable. The range of droplet diameter varies from 100 to 1000 Å. For preparing micro-emulsion of oils; co-solvent, alcohol, Cetane improver and surfactant are added. The maximum viscosity requirement for fuel can be met by making micro-emulsion with butanol, hexanol and octanol. The process of micro-emulsion is easy. Less volatility, stability and high viscosity are some issues with micro-emulsification [163].

4.3.3. Dilution

Dilution is the method in which amount of solute decreased in solution by increasing the amount of solvent. Ethanol and diesel fuel can be used as solvent for dilution of oils. The outcomes from this process are decrement in density and viscosity of oil. If 4% amount of solvent (ethanol to diesel fuel) is added to oil than brake power, brake thermal efficiency and brake torque increases and brake specific fuel consumption decreases. The value of boiling point for diesel fuel is higher than ethanol that's why ethanol could promote progress of combustion procedure over an unburned blend spray. The process of dilution is easy but there are some problems are associated with it like carbon deposition in engine cylinder and incomplete burning.

4.3.4. Transesterification

Biodiesel produced from transesterification process have comparable properties with diesel fuel and this process is favorable for commercial production as per economic point of view. In transesterification process glycerol and esters are formed when triglyceride reacts with alcohol. Fig. 2 shows the transesterification reaction for biodiesel production. Three fatty acids are connected to triglycerides (organic fats and oils) base and it has molecule of glycerin. Free fatty acids are formed by hydrolyzing triglycerides. After this these free fatty acids are reacts with alcohol and formed ester or biodiesel (methyl or ethyl fatty

Table 4
Pro's and con's of various biodiesel production technologies [164–166].

Production technologies	Pro's	Con's
Catalytic distillation	Easy separation of products	Usage of solvent and rate of conversion rate after treatment depends on recovery of catalyst
Dilution	Process is easy	Carbon deposition in engine cylinder and improper burning
Micro-emulsion	Process is easy	Less volatile and stable and higher viscosity
Microwave technology	Fast rate of reaction and less heat loss	After the process catalyst is required to remove, catalyst activity highly influences the conversion process
Pyrolysis	Easy process with less emissions	High installation cost, high carbon residue creates lower purity, clinker high temperature is required
Reactive distillation	High free fatty acid content feedstocks can be processed, Process is easy, methanol requirement is less, easy separation of Products	Requirement of high energy, catalyst efficiency affects the conversion process
Super fluid method	Fast rate of reaction, high efficiency of conversion, no requirement of catalyst	High energy requirement and installation cost
Transesterification	Produced biodiesel properties are comparable with diesel, favorable for industrialized production	Less efficiency of conversion, catalyst can't be reuse.

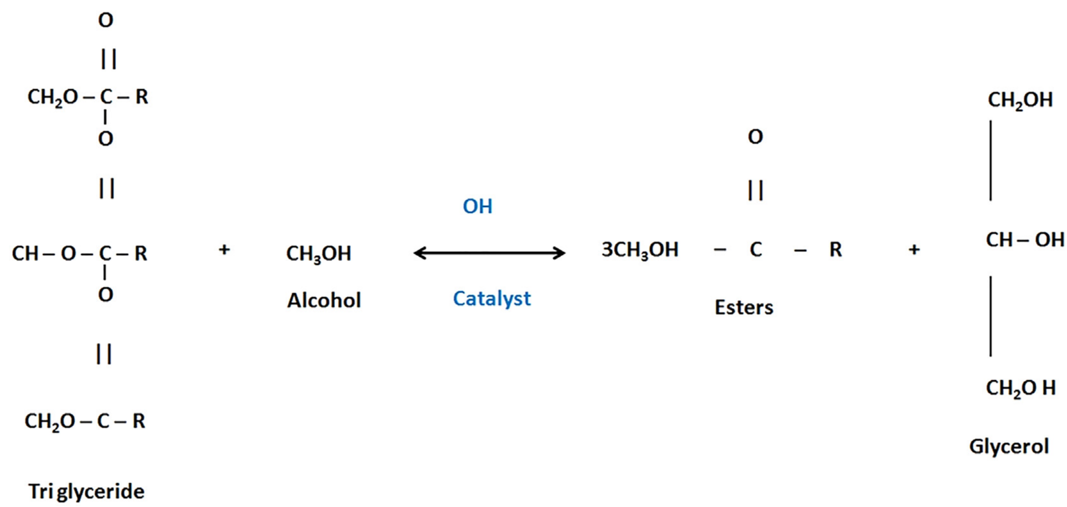

Fig. 2. Transesterification reaction for biodiesel production [138].

acid ester) and glycerol. Transesterification is also known as alcoholysis, due to reaction of free fatty acid with alcohol. The end products of transesterification process are separated, biodiesel settles on the top and due to high weight glycerol settles down. The process of separation should be very fast to avoid reverse process [164]. Usually in transesterification process methanol and ethanol are used. If methanol is used to react with free fatty acids than this transesterification process is known as methanolysis. In methanolysis process heat is applied to the mixture of oil (80–90%) and methanol (10–20%) and very less quantity of catalyst. The solubility of methanol in oil is less that's why proper mixing is essential. The produced biodiesel after the process is fatty acid methyl ester (FAME) [165].The methanol has higher reactivity and cheaper in price than other alcohols due to this reason it is preferred for transesterification.

If ethanol is used to react with free fatty acid than this transesterification process is known as ethanolysis. As compared to other alcohol ethanol slightly enhances cetane number and heat content of fuel and also ethanol has less toxic content [166]. The main issues associated with ethanolysis are high energy requirement for the reaction and issue in separation of ester and glycerol [138]. That's why price of biodiesel produced through ethanolysis is increased. Biodiesel produced from the ethanolysis process is fatty acid ethyl ester (FAEE) [167]. Produced biodiesel from transesterification process have many benefits as compare to pure plant oil (PPO). One important property of fuel is viscosity which directly effects engine performance. PPO has higher viscosity than biodiesel. Like high viscosity inversely influence the atomization, fuel injection time, and injection pressure for diesel engine. Biodiesel can be used in diesel engines with small variations in engine because its characteristics are quite similar to fossil diesel.

For the production of biodiesel from transesterification two approaches are followed-

(a) Catalytic Transesterification.
(b) Supercritical Methanol Transesterification.

In catalytic transesterification approach glycerol and ester is formed when triglyceride reacts with alcohol in the presence of catalyst. Due to presence of catalyst this approach is known as catalytic transesterification. The nature connected fatty acids define the features of triglyceride or fat/oil that means nature of fatty acid directly influence the behavior or feature of biodiesel [163].

To eliminate water content from oil, heat is applied to oil in a container. After removal of water, oil taken inside container and again heat is applied and continuously subjected to stirring. The oil reacts with catalyst and form a mixture at 60 °C temperature of oil, and stirring process is continued till glycerol separation initiates. After this mixture is taken into a separate vessel and kept it in for 8 h. After the completion of reaction glycerol settles down slowly due to high weight. It may be purified for further use in cosmetic and pharmaceutical industries. The separation of end products i.e. glycerol and ester indicates effectiveness of transesterification process. These catalyst transesterification processes are usually classified on the basis of nature of catalyst.

- Acid catalyzed transesterification
- Alkaline catalyzed transesterification
- Lipase catalyzed transesterification
- Transition metal compound catalyzed transesterification
- Silicates catalyzed transesterification.

The selection of catalyst depends on the fatty acids content of oil [165]. The main challenges faced by catalyst transesterification process are comparatively higher time required for completion of reaction and extra process is required for separation of catalyst. These issue arises because phase separation of mixture (alcohol and oil). This mixture may faces the forcefully stirring for formation of mixture and require more time. Alkaline catalyzed transesterification have several benefits like reaction rate is fast, so less time consuming and simple setup is required as compare to acid catalyst. In Table 5 various types of catalyst, their amount, alcohol type, reaction time and yield of biodiesel are given for different generation feedstocks. In super critical transesterification instead of this two phase mixture, single phase mixture is formed at supercritical state (pressure- 43 MPa, temperature- 340 °C). At these conditions dielectric constant of alcohol reduces. At supercritical state reaction time is very less and it is approximately 2 to 4 min. In this process purification of biodiesel is very easy because catalyst is not used [166]. High cost of production is the main drawback of super critical transesterification process.

For the production of biodiesel, nanocatalyst technology is a new approach with high catalytic efficiency, which grabs all the attention at present [184]. As compared to traditional catalyst, nanocatalysts have high surface area that's why they have improved activity rate [185]. The important characteristics of nanocatalyst are high opposition to saponification, high stability, and efficient volume to surface ratio, reusability and high activity [38,151]. The one type nanocatalyst is prepared by help of oxides, zeolites and carbon [184]. Various nanocatalysts have been used for the transesterification reaction, as summarized in Table 6. For example biodiesel production from Soybean oil using transesterification process with nanocatalyst (potassium tartrate) which is prepared by impregnation. Highest yield of biodiesel is

Table 5
Biodiesel production parameters in transesterification reaction for different feedstocks.

Feed stock/Oil type	Alcohol type	Catalyst used	Catalyst Amount	Molar ratio of alcohol to oil	Reaction Conditions	Biodiesel yield (%)	Reference
Animal tallow oil	Methanol	NaOH	2 g	6:1	60 °C/180 min	–	[168]
Canola, corn Karanja and jatropha, Oil	Methanol	H_2SO_4	0.5 %w/v	9:1	60 °C/120 min	80	[169]
Canola, corn Karanja and jatropha, Oil	Methanol	KOH	2 %w/v	9:1	55 °C /60 min	90–95	[169]
Honne oil	Methanol	H_2SO_4	0.5 ml	8:1	45–65 °C/ 30–150 min	89	[170]
Honne oil	Methanol	KOH	0.75–1.5%w/v	4:1	45–65 °C/ 30–150 min	89	[170]
Karanja oil	Methanol	H_2SO_4	1 ml	6:1	54.5–55.5 °C/60 min	98.6	[171]
Karanja oil	Methanol	NaOH	28.5 g	–	70 °C/60 min	84	[172]
Karanja oil	Methanol	H_2SO_4/NaOH	1%w/v	–	50 °C/60 min	97	[173]
Mahua oil	Methanol	H_2SO_4	1%w/v	–	60 °C/30 min	98	[116]
Mahua oil	Methanol	KOH	0.7%w/v	4:1	–	–	[116]
Mahua oil	Methanol	KOH	0.7%w/v	6:1	60 °C/30 min	98	[174]
Mahua oil	Methanol	KOH	1%w/v	8:1	54.5–55.5 °C/60 min	95.71	[171]
Hybrid (or) Mixture of Karanj and Mahua oil	Methanol	KOH	–	–	–	94	[171]
Restaurant waste oil	Methanol	NaOH	0.3 g	35% by vol	55 °C/90 min	85.5	[175]
Waste cooking oil	Methanol	Copper doped zinc oxide nano composite	12% w/w	–	55 °C/50 min	97.71	[176]
Waste cooking oil	Methanol	KBr/CaO	3% w/v	12:1	65 °C/180 min	–	[177]
Waste cooking oil	Methanol	Calsinide scallop shell	5%w/v	6:1	65 °C/120 min	86	[178]
Waste frying oils	Methanol	NaOH	0.6%w/v	4.8:1	60 °C/40 min	98	[179]
Palm oil by using waste obtuse horn shells	Methanol	CaO	5%w/v	12:1	360 min	86.75	[85]
Rubber seed oil	Methanol	H_2SO_4	0.5%w/v	6:1	40–50 °C/120 min	–	[180]
Rubber seed oil	Methanol	NaOH	5 g	9:1	–	–	[180]
Palm oil	Methanol	H_2SO_4	5%v/w	40:1	95 °C/540 min	97	[181]
Palm kernel oil	Ethanol	NaOH	1%w/v	20%	60 °C/90 min	95.8	[182]
Jatropha Curcas Oil	Methanol	KOH	2.09%w/w	7.5:1	60 °C/60 min	80.5	[183]

Table 6
Various nano catalyst used for biodiesel production in transesterification reaction.

Feedstock	Catalyst	Alcohol to oil ratio	Temp. (°C)	Reaction time (min)	Catalyst wt%	Catalyst Size (nm)	Biodiesel yield %	Reference
Algal lipids	$(Ca(OCH_3)_2$	30:1	80	150	3	–	99	[187]
Algal oil	CaO	9:1	55	–	1.25	–	96.3	[188]
Jatropha curcas oil	$CaO\text{-}Al_2O_3$	5:1	100	180	–	29.9	82.3	[185]
Jatropha oil	Li-CaO	12:1	65	120	5	–	> 99	[40]
Karanja oil	Li-CaO	12:1	65	60	5	–	> 99	[40]
Mahua indica oil	Heteropoly acid coated ZnO	–	50–60	300	–	5–29	98	[189]
Mutton fat	Li/MgO	12:1	65	40	5	17	–	[190]
Neem oil	Cu-ZnO	10:1	55	60	10	–	97.18	[146]
Olive oil	Cs-MgO	30:1	90	1440	2.8	12.2–22.8	93	[191]
Palm oil	TiO_2-ZnO	6:1	60	300	–	34.2	92.2	[142]
Palm oil	ZnO	6:1	60	300	–	28.4	83.2	[142]
Pongamia oil	Fe/ZnO	10:1	55	55	12	–	93	[192]
Rapeseed oil	MgO	4:1	70–310	40–120	–	50–200	98	[184,193]
Rapeseed oil	KF/CaO-MgO	–	70–310	40–120	–	50–200	95	[184,193]
Soybean oil	$ZrO_2/C_4H_4O_6HK$	16:1	60	120	6	10–40	98.03	[186]
Soybean oil	Nano MgO supported on Titania	18:1	150–225	60	0.1–7	–	95	[184,194]
Soybean oil	$Sr_3Al_2O_6$	25:1	–	61	1.3	–	95.2–96.2	[195]
Soybean oil	Sr-Ti nanocomposite	15:1	–	15	1	–	98	[39]
Soybean oil	lipase on Fe_3O_4 @polydopamine nanoparticles	1:1	37	720	–	50	93	[196]
Stillingia oil	KF/Ca-Fe_3O_4	12:1	65	180	4	50	95	[151]
Sunflower oil	Cs/Al/Fe_3O_4	14:1	58	120	4	30–35	94.8	[184]
Sunflower oil	$MgO/MgAl_2O_4$	12:1	110	180	3	21.3	95.7	[197]
Sunflower oil	$CsH_2PW_{12}O_{40}$ /$FeSiO_2$	12:1	60	240	4	38–42	81	[198]
Sunflower oil	CaO nanoparticles/NaX Zeolite	6:1	60	360	10	–	93.5	[92]
tallow seed oil	KF/CaO	12:1	65	150	4	30–100	96	[150]
Vegetable oil	Cs-Ca/SiO_2-TiO_2	12:1	60	120	–	45	98	[199]
Waste cooking oil	$TiO_2/PrSO_3H$	15:1	60	540	4.5	8.2–42	98.3	[200]
Waste cooking Oil	CaO-MgO	7:1	–	360	–	–	98.95	[201]
Waste cooking oil	CZO	8:1	–	50	12	–	97.71	[202]
Waste cooking oil	$Ti(SO_4)O$	9:1	75	180	1.5	25	97.1	[203]

obtained by Li-CaO nanocatalyst. The dimensions for nanocatalysts are in the range of 10 to 200 nm. The highest yield of biodiesel is more than 99% were obtained for Karanja oil and for this the ratio of methanol to oil was 12:1 at temperature of 65 °C with amount of catalyst was 5 percentage by weight and for completion of reaction time required will be one hour [186].

5. Biodiesel yield

Biodiesel yield is defined as the amount of biodiesel obtained from raw oil that includes the percentage of fatty acid methyl esters. Chromatographic or spectroscopic analysis is used for the characterization of biodiesel. Thin layer chromatography is used for qualitative analysis of biodiesel. For the evaluation of glycerides (mono-, di-, and tri-) and fatty acids, this was taken as main approach. It contains restrictions like sensitivity to humidity and very less accuracy. Gas chromatography is new process used for biodiesel classification and it is used along with a gas chromatography-flame ionization detector (GC-FID) or gas chromatography-mass spectroscopy detector (GCMS). Precise quantity of major and minor components in biodiesel can be found using gas chromatography [187,204]. This systematic method offers distribution zone consequent to every element in produced sample. Analysis of produced biodiesel is carried out by find out the approximate percentage of fatty acid methyl esters. It can be find out from distribution zone outcome from gas chromatography investigation. Percentage of fatty acid methyl esters for a feedstock is prime requirement to find out biodiesel yield using equation-1 [205]:

$$\text{Percentage of biodiesel yield} = (\text{FAME percentage result from GC}) \times (\text{Volume yield}) \quad (1)$$

The volume yield of biodiesel obtain from oil feedstock can be find out using equation (2).

$$\text{Percentage of Volume yield} = \frac{\text{Volume of product}}{\text{Volume of feed}} \times 100 \quad (2)$$

Apart from biodiesel yield the entire amount of mono, di, and triglycerides can be find out by high-performance liquid chromatography (HPLC) and it can also be used to distinguish biodiesel from more than one feedstocks [187,204]. Eq. (3) describes the percentage translation of triglyceride (TG) [184]:

$$\text{Triglyceride}(\%) = \frac{[\text{TG(oil)} - \text{TG(sample)}]}{[\text{TG(oil)}]} \times 100 \quad (3)$$

Here,

TG (sample) signifies the total HPLC peak area of triglyceride in biodiesel sample (diluted), and
TG (oil) is the total triglyceride HPLC peak area in oil (diluted) [206].

The chemical classification of biodiesel can also be done by nuclear magnetic resonance (NMR) technique. It is used to find out the blend value and analyze the peaks of different range in parts per million, which provides the biodiesel yield that produced from transesterification method [187,204]. Equation (4) is used to find out the percentage translation of triglycerides to fatty acid methyl esters (C %) [207]:

$$C(\%) = \frac{[2 \times \text{integration value of protons of methyl ester}]}{[3 \times \text{integration value of methyl protons}]} \times 100 \quad (4)$$

The details of biodiesel and triglycerides can be analyzed by infrared spectroscopy. ASTM D6751 (USA), EN 14213 (European Union), IS 15607 (India) etc. standards are used to maintain the quality of produced biodiesel. These standards are used for biodiesel (B100), not for biodiesel blends. For biodiesel blends standards are only given by ASTM.

6. Conclusion and future scope

Biodiesel is the sustainable appropriate replacement of fossil fuel. This review article covers all four generations of biodiesel in terms of feedstocks used for biodiesel production, various biodiesel production technologies, and calculation of biodiesel yield. Each generation of biodiesel have its own benefits and limitations. The evolution of generations of biodiesel primarily focused on the biodiesel quality enhancement with less deterioration to environment. The first generation of biodiesel produced from edible oil feedstocks and the conversion process for this generation is easy. The crop yield of this generation is also low. The first generation of biodiesel is not suitable for commercial biodiesel production due to food-fuel competition. In context of this issue second and third generations of biodiesel provide an alternate solution. Second generation of biodiesels are produced from non-edible oil feedstocks, while third generation of biodiesels are produced from waste oil or algae oil. Feedstocks of these two generations can be grow on non-arable land. Algae feedstocks can be grow on waste water or sea water. High energy content is required for algae cultivation so research should be focus on reduction in cost of cultivation. The oil content obtained from algae feedstock is high (30–70%) in comparison with edible and non-edible feedstocks. Research for fourth generation of biodiesel feedstocks is on infancy level. Fourth generation of biodiesel uses synthetic biology technology, which is the future of biodiesel generations. Metabolic engineering is used in this generation to add biological tools to improve the quality and quantity of biodiesel from different feedstocks. Fourth generation biodiesel have high energy content, rapid feedstock growth rate and more CO_2 absorbing capacity during the feedstock production. Biodiesel is produced from oil using different techniques i.e. catalytic distillation, dilution, micro-emulsion, pyrolysis, transesterification etc. Among these conversion techniques transesterification is the most economic and the biodiesel produced from this technique have comparable properties with diesel. The present review summarizes that the energy demand of future cannot be met by single generation so; blending of different generation of biodiesel will be preferred. On the basis of present literature review it is found that various research opportunities are available in the area of biodiesel production process, economic feasibility, performance enhancement, and emission reduction. In future research should focus on the identification of non-edible feedstocks for biodiesel production with high yield. There are wide research opportunities are available in the area of reduction in cost of biodiesel production without affecting the quality of fuel. Improvement in photon to fuel conversion efficiency (PFCE) for biodiesel production will be the main area of future work.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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