Promising evolution of biofuel generations. Subject review

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Biofuels have attracted a lot of attention due to the increasing demand on energy resources as well as elevated concerns about greenhouse gas emissions. In contrast to other green energy resources, biofuels can provide liquid fuels which are essential for transportation. This review reports recent advances in liquid biofuels, focusing on their generations and types. Generally, biofuels are classified into four generations based on the type of the feedstock that is used. First generation biofuels utilize edible biomass which sparked controversy because it competes with global food needs. Second generation biofuels use non-edible biomass but there are still some limitations related to the cost-effectiveness involved in scaling the production to a commercial level. Third generation biofuels use microorganisms as feedstock, while fourth generation biofuel focuses on modifying these microorganisms genetically to achieve a preferable hydrogen to carbon (HC) yield along with creating an artificial carbon sink to eliminate or minimize carbon emissions. These last two generations of biofuel are still in early development stages. This article reviews and summarizes 124 papers, 77% of which were published within the last three years. The aim of this work is to provide an overview of the four liquid biofuel generations as well as the latest development efforts in this field. This review concludes that the current production methods of biofuel in the first and second generations will soon fail to satisfy the increasing demand on biofuel. Therefore, development efforts should be focused on third and fourth generations, specifically the genetic engineering of algae.

Introduction

In the twentieth century, change in the global climate was identified as one of the most serious issues that the world faces. The main reason for this problem is high consumption of fossil fuels which represent about 80% of the global energy usage [1]. The combustion of fossil fuels results in the emission of greenhouse gases, especially CO_2. There are several techniques that are used to capture CO_2 such as adsorbing by chemicals like amines, carbonates, and ammonia or by pre-combustion techniques such as chemical looping combustion processes [2,3]. However, these techniques are insufficient to suppress the rapid increase in the environmental CO_2 concentration resulting from fossil fuel combustion. Also, the high demands on fossil fuels leads to another problem which is a severe depletion of this important source of energy.

Although there are several ways to create clean energy from the wind, sun, and water, the use of biomass is very important because unlike the other energy sources it provides liquid fuels for transportation. The United States (USA) is at the forefront of the biofuel market with a target of substituting 20% of transportation fossil fuels with biofuel by 2022 [4]. Based on feedstocks and method of production, biofuels are classified in different groups named as first, second, third, and fourth generation biofuels [4].

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Nomenclature

ETBE	Ethyl tertiary butyl ether
GHG	Greenhouse gas
DDGS	Distillers' dried grains and soluble
CGM	Corn gluten meal
CGF	Corn gluten feed
TAEE	Ter-amyl ethyl ether
ASTM	American Society for Testing and Materials
CoA	Coenzyme A
FAME	Fatty acid methyl ester
DME	Dimethyl ether
MTBE	Methyl teritiary-butyl ether
DEE	Diethyl ether
TAME	Ter-amyl methyl ether
VOC	Volatile organic compound
FA	Fatty acids

First-generation biofuels use edible biomass such as starch and sugar [5] which increases the cost of production and causes inefficient utilization of resources and energy spent in cultivating crops. Specifically, using edible biomass competes with food crops, requires significant amounts of fertilizer and water, and large areas of cropland [6]. The second generation of biofuels are based on more efficient renewable alternatives by utilizing inedible lignocellulosic biomass such as switch grass, sawdust, low-priced woods, crop wastes, and municipal wastes [7]. While this generation overcomes the drawbacks of the first generation, more steps are required to produce adequate biofuels at a competitive cost [6]. The last few years have seen several studies aiming to achieve this goal by using thermal, biological, enzymatic or chemical processes. Obstacles have been encountered with all these conversion techniques. However, chemical processes are identified as the most flexible [8]. Combinations of multiple processes have also been investigated such as the production of sugar solution from biomass using a chemical method followed by an enzymatic or biological step [8].

Aquatic feedstock such as alga biomass is used in third-generation biofuels [9]. Algae, which are photosynthetic plants such as seaweed, capture high quantities of CO_2 and generate O_2 as well as oil [6]. However, this kind of biomass has some disadvantages such as its high cost and the fact that biofuel produced from algae is less stable than that produced from other sources. The main reason for this is that the oil generated by algae is highly unsaturated, which means it is more volatile especially at high temperatures, and therefore more likely to degrade [10]. Fourth-generation biofuels, which are still in an early developmental stage, use bioengineered microorganisms such as bioengineered algae or crops that are genetically altered to consume more CO_2 from the environment than they emit when they are consumed (burning). Biofuels are used to produce different fuels including ethanol, butanol, hydrogen, methane, vegetable oil, biodiesel, isoprene, gasoline, and jet fuel [11,12].

This article provides a comprehensive review of the four generations of biofuels including their advantages, limitations, technologies, and evaluations. This work summarizes the most recent contributions, criticisms, and evaluations that have done in this field. Particularly, this article reviews and summarizes 124 papers, 77% of which were published between 2015 and 2018. The main objectives of this work are (a) to summarize and systematize the peer-reviewed data; (b) to provide details illustration about the production arts of biofuels and their evolution; and (c) to illustrate the advantages and drawbacks of each biofuel's generation and production method. Thus, this manuscript is written as a broad review covering all biofuel production aspects which is lack in the recent review articles in this field.

Generations of biofuels

First generation

First-generation biofuels produced from edible biomass such as starch (from potato, wheat, barley, and corn) or sugars (from sugarcane and sugar beet), initially showed a promising capability in minimizing the fossil fuels combustion and lowering atmospheric levels of CO_2 which is consumed by crops as they grow [13]. However, concerns arose about using edible crops as feedstocks and the impacts on croplands, biodiversity, and food supply. First-generation biofuels, which are produced commercially today at around 50 billion liters per year, include biodiesel (bio-esters), and bioethanol, as well as bio-gas. Unlike the other two types of biofuels, bio-gas, which is derived from anaerobic processing of manure and other biomass sources, has limited utilizing the transportation sector [14]. The fuels are evaluated either by their abilities to be blended with petroleum-based fuel for use in internal combustion engines or by their utility in alternative vehicle technology such as natural gas vehicles or flexible fuel vehicles [14]. Several points must be considered in the evaluation of edible biomass to produce biofuel. These are (a) the biomass chemical composition, (b) energy balance, (c) availability of croplands and the contribution to biodiversity and cropland value losses, (d) competition with food needs, (e) cultivation practices, (f) emission of pollutant gases, (g) impact of mineral absorption on water resources and soil, (h) use of pesticides, (i) cost of the biomass and its transport and storage, (j), soil erosion, (k) economic evaluation considering both the coproducts and feedstocks, (l) creation or maintenance of employment, and (m) resource availability such as water [15].

First generation bioethanol

Bioethanol fuel is liquid ethyl alcohol (C_2H_5OH or EtOH) produced from feedstocks such as wheat, sugar beet, and corn through fermentation. Its primary application is in motor vehicles. It can be used as a transportation fuel in its pure form or by blending it with gasoline in traditional combustion engines especially in flex-fuel vehicles. It is most commonly blended with gasoline at a low percent (10% bioethanol) which known as E10. It can be also used as a feedstock to produce ethyl tertiary butyl ether (ETBE) which is blended with gasoline to increase its oxygen content for pollution control [16].

Historically, bioethanol was utilized industrially in Germany and France as early as 1894 [17]. In 1925 Brazil started to use it as a transportation fuel. Its use as fuel was common in Europe and the United States until the early 1900s. However, due to its high production cost, it was ignored especially after World War II until the oil crisis of the 1970s [18]. In the last three decades, the use of bioethanol has gotten more attention as an alternative transportation fuel. Several countries such as Brazil and the USA have long promoted domestic production of bioethanol.

Shifting to the use of bioethanol as a green energy source could decrease CO_2 concentrations in the atmosphere in two ways. First it reduces dependence on fossil fuels, and second it consumed CO_2 in the atmosphere to grow the feedstock crops. Global bioethanol production reached about 93 billion liters in 2014 which is approximately four times more than its production a decade earlier [19]. A recent investigation showed that most bioethanol production is based on sugarcane and maize followed by wheat, sugar-beet, and sorghum. These crops could have fed 200 million people [5], thus concerns arose about competition of fuel with food needs.

In term of edible biomass, sugarcane is the highest crop used in bioethanol production and requires less water than maize and wheat [5]. The USA is at the forefront of the bioethanol market with about 47% of the global bioethanol production [20].

To produce high bioethanol equality from crops with reference to greenhouse gas (GHG) benefits, two important requirements should be considered. These are the wise choice of croplands and fertilization strategies to avoid increasing the carbon concentration in/on ground and minimize nitrous oxide emissions [21,22]. In addition, by-product production should be emphasized and utilized efficiently to maximize the cost effectiveness.

Several carbohydrate-containing crops have been utilized as feedstocks for ethanol production using a fermentation process. These feedstocks are classified in two major categories: (a) Sugar-containing crops, such as palm juice, sugar cane, beet root, wheat, fruits. (b) Starch-containing crops including grain, such as wheat, barely, sweet sorgum, rice, and corn. The direct conversion of starch to ethanol cannot be done using conventional fermentation technologies due to the long chain polymer structure of glucose [23]. Therefore, a practical approach involves breaking down the macromolecular structure first into simpler and smaller glucose molecules. In order to do this, starch feedstocks are converted to a mash typically containing 15–20% starch. The process involves starch grinding, mixing with water, and then cooking at or above its boiling point. The process also requires using two enzymes. The first enzyme, amylase, breaks down starch molecules to short chains and releases dextrin and oligosaccharides. These components are hydrolyzed in a process known as saccharification which uses enzymes such as pullulanase and glucoamylase. This process converts all dextrans to glucose, maltose and isomatose. The next step is cooling the mash to 30 °C and yeast is added for fermentation [24].

Bioethanol production from corn can be classified into wet & dry mill processes [25]. The wet mill ethanol process has usually a higher production capacity than the dry process and produces some valuable coproducts such as nutraceuticals, pharmaceuticals, organic acids and solvent [26]. In addition to ethanol, the dry milling process produces distillers' dried grains and soluble (DDGS) which is an excellent livestock feed because it contains protein, fats and carbohydrates. On the other hand, in addition to ethanol the wet milling process produces corn oil, and two types of animal feed which are corn gluten meal (CGM) and corn gluten feed (CGF) [27].

First generation biodiesel

Diesel fuel, which has a chemical formula range between $C_{10}H_{20}$ to $C_{15}H_{28}$ with an average molecular weight 168 (amu), is an important liquid petroleum fuel that is widely used in transportation. Several technologies have been well established to produce biodiesel (fatty acid esters) from different feedstocks.

Biodiesel fuel depends mainly on oil crops and 75% of its production cost is due to the feedstock production cost [28]. More than 350 oil-bearing crops, both edible and non-edible, have been suggested as promising feedstock for biodiesel manufacturing [29]. The most common food crop sources are rapeseed, soybean, palm, sunflower, peanut, safflower, corn, rice bran, coconut, olive, castor, milkweed seed, and linseed. *Jatropha curcas*, *Pongamia glabra*, *Madhuca indica*, *Salvadora oleoides*, cotton seed oil, Tobacco, Calophyllum Eruca Sativa Gars, *inophyllum*, terebinth, rubber seed, desert date, Jojoba, neem oil, leather pre-fleshings, apricot seed, *Pistacia chinensis* Bunge Seed, sal (*Shorea robusta*) and fish oil, Moringa oleifera and croton *megalocarpus* are common non-edible oil sources.

Several technologies have been established to produce high quality biodiesel such as direct use and blending, pyrolysis of vegetable oil micro-emulsions, and transesterification. The direct use of vegetable oils blended with diesel fuel is used to overcome the drawbacks of using the high viscous pure vegetable oil. These drawbacks include coking and trumpet formation on the engine injectors after long-term use, as well as carbon deposits, thickening and gelling of the lubricant, and oil ring sticking [28]. Another common solution is decreasing the vegetable oil's viscosity by preheating it and that also improve the atomisation and mixing process to achieve better combustion [30].

Micro-emulsification can be used to solve the high viscosity issue of vegetable oils. Micro-emulsion is defined as clear thermodynamically stable isotropic liquid mixtures of oil with dimensions range between 1–150 nm created spontaneously from two normally immiscible fluids and one or more ionic or non-ionic amphiphiles [31]. Microemulsions consists of three phases, which are surfactant, oil, and aqueous phase. Methanol and ethanol are the common solvents used in this process. The standard viscosity limitation for diesel engines can be achieved by all micro-emulsions with butanol, hexanol and octanol [32,33]. The pyrolysis process is also used to enhance the quality of biodiesel by thermal and catalytic means. In pyrolysis a conversion of one substance into another can be achieved by using heat or with the assistance of a catalyst in the absence of oxygen. Compared with other cracking processes, pyrolysis is very simple, waste-free, pollution free, and very efficient [34].

Transesterification of oils (triglycerides) with alcohol is the most developed and promising method of biodiesel production which produces glycerine as a by-product. Figure 1 which is adapted from Ghazali et al. shows the transesterification reaction of triglycerides [31]. Transesterification, or alcoholysis, is replacing alcohol from an ester with another alcohol in a similar way to hydrolysis, but using alcohol instead of water [35]. Figure 2 shows the process diagram of biodiesel produced by the transesterification reaction using alkali catalyst [36]. Catalysts usually speed the completion of the transesterification reaction. Several operating variables such as reaction temperature, time, and pressure, as well as the molar ratios of alcohol to oil, catalyst concentration and type, mixing intensity and kind of feedstock can affect the transesterification process [37].

Albayati and Doyle recently reported using the incipient wetness impregnation method to manufacture nonporous catalyst, SBA-15, from encapsulated of alkali metals and their hydroxides to produce biodiesel from sunflower oil [38]. Specifically, they used

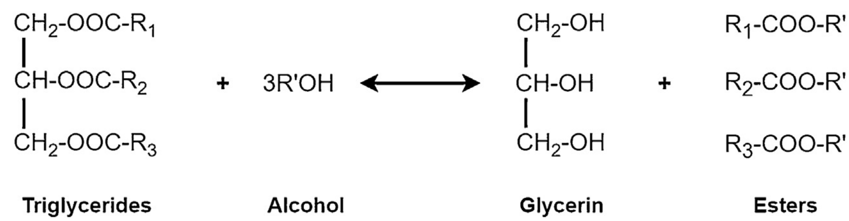

FIGURE 1
Transestrification reaction of triglycerides with alcohol.

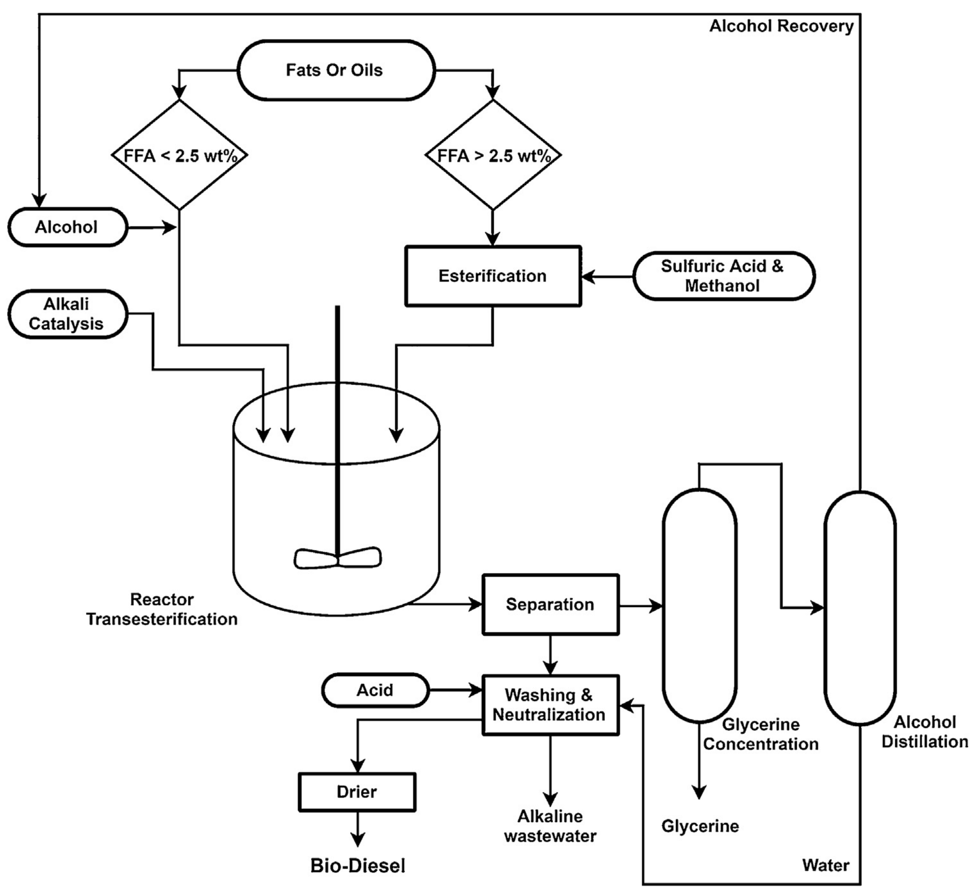

FIGURE 2
A schematic diagram of biodiesel production according to the transesterification process.

Na, NaOH, Li, and LiOH to prepare the catalyst which showed promising results with yields of fatty acid methyl ester (FAME) in the range between 96 to 99% at moderate process conditions (1 atm and 65 °C). The catalyst also showed high production stability and easy recovery through seven production cycles under the same conditions with better fuel properties than those of fossil fuels.

Also, Doyle et al. reported that using zeolite Y, with a Si/Al ratio 3.1 for the biodiesel production from oleic acid esterification with ethanol increased the oleic acid conversion to 85% comparing with 76% using commercial catalyst of HY zeolite [39]. Later, the same research group reported that using FAU-type zeolites showed similar oleic acid conversion to that reported for commercial HY zeolite [40], while addition of Co-Ni-Pt to the FAU-type zeolites enhanced its efficiency in biodiesel production in the same process to achieve 93% and 89% for batch and continuous reactors, respectively [41].

First generation bioethers

Bioethers (also known as fuel ethers) are used to enhance the octane number of fuels. They can replace petro-ethers and improve engine performance [42]. Furthermore, bioethers can greatly reduce engine wear and toxic exhaust emissions [42]. They are produced by the reaction of bioethanol with *iso*-olefins, such as *iso*-butylene. The usual source of bioethers are wheat and sugar beet [43]. However, their main drawback is low energy density. There are six ether additives that are commonly used to enhance transportation fuel quality: dimethyl ether (DME), methyl teritiary-butyl ether (MTBE), diethyl ether(DEE), ter-amyl methyl ether

(TAME), ethyl ter-butyl ether (ETBE), and ter-amyl ethyl ether (TAEE) [44]. Ethers have been used in Europe since the 1970s to replace highly toxic compounds such as lead especially MTBE and ETBE. However, bioethers are no longer used in the USA as fuel additives [45].

Second generation

In this generation, a more sustainable protocol is used to produce biofuels. The net carbon (emitted–consumed) from combusting second-generation biofuels is neutral or even negative. The feedstock is lignocellulosic material which include the inexpensive and abundant nonedible biomass available from plants [46]. The cost-effectiveness of this generation of biofuels still needs development because there are several technical barriers that need to be overcome [47]. The use of waste plant biomass has attracted researchers for a wide variety of uses such as feedstock to generate heat and electricity by direct burning [14,48] or as a raw material for wastewater treatments [49]. However, utilizing it as an inexpensive source of biofuel is very attractive [50]. A wide variety of abandoned materials can be used as biofuel feedstock such as agriculture waste, poplar trees, willow and eucalyptus, miscanthus, switchgrass, reed canary grass, and wood and they mostly consist of plant cell walls whose primary components is polysaccharides (75%) [50,51]. These polysaccharides have a high sugar content which is preferred for biofuel production. However, agricultural by-products can provide only a limited proportion of the increased demand for biofuels [14].

The feedstock is also known as lignocellulosic material because it is derived from lignin, cellulose, and hemicellulose [52]. These three components are characterized by their large and complex structures which consist of repeating cyclic units with different functional groups. Figure 3 which is adapted from Sadeck et al. [53], shows the three component structures. Figure 3A shows the carbohydrate polymer structure of cellulose which consists of D-glucose monomers connected by b-1,40-glycosidic bonds. This rigid structure is usually found in the primary cell wall of plants. Figure 3B shows that hemicellulose consists of a variety of carbohydrate monomers with a branched random structure which varies by plant type. Finally, Figure 3C shows the noncarbohydrate irregular polymer structure of lignin which is more complex than the other two components. Three essential types of monomeric subunits are found in lignin, each derived from an aromatic alcohol. These are the syringyl group which is derived from sinapyl alcohol, the guaiacyl group derived from coniferyl alcohol, and the p-hydroxyphenyl group which is derived from p-coumaryl alcohol.

Second generation bioethanol

Bioethanol can be produced from lignocellulosic biomass through hydrolysis and subsequent fermentation. It can also be produced by thermochemical processes which include gasification followed by either fermentation or a catalyzed reaction [54]. However, these processes are complicated due to (1) the difficulty of biomass breakdown, (2) the release of different types of sugars after hemicellulose and cellulose polymers breakdown and the need to ferment these sugars with suitable organisms which can require genetic engineering, and (3) the cost of collection and storage of low density lignocellosic feedstocks [55].

There are four main operational steps in the lignocellosic conversion process to ethanol: (1) pretreatment, (2) hydrolysis, (3) fermentation, and (4) product separation/ distillation [56]. The hydrolysis step increases the complexity of the fermentation of sugar which is released from the cellulosic part of the biomass, and fermentation converts these sugars to bioethanol. To promote the hydrolysis step, a pretreatment step is required that softens the biomass and breaks down its cell structures. An efficient pretreatment must meet the following standards: (1) enhance the formation of sugars by hydrolysis, (2) avoid the degradation or loss of carbohydrate; (3) avoid the formation of undesired by-products that reduce the hydrolysis and fermentation process efficiencies, and (4) be economically feasible [57].

Fermentation is the metabolic process in which an organic substrate is converted due to the activities of enzymes excreted by micro-organisms. Generally, there are two main methods of fermentation (a) aerobic and (b) anaerobic according to whether oxygen is involved in the process or not [58]. Thousands of micro-organisms in nature have been identified as fermentative agents. Some of these are used to convert sugar and starch to ethanol. The use of micro-organisms for ethanol production relies on three main types which exist in nature and are very selective in their fermentation characteristics. These types are yeast (*saccharomyces* species), bacteria (*zymomonas* species), and mold (mycelium) [59]. Some of these micro-organisms are specific to hexoses or pentose, or mixtures of both [14]. Developing ideal micro-organisms, which can convert any carbohydrate to ethanol has attracted a lot of attention [14].

Second generation biodiesel

Several kinds of second-generation feedstocks can be utilized to produce biodiesel such as energy crops, agricultural remains, and wood residual wastage. The most common energy crops for this purpose are Jatropha, *Aleurites moluccana*, salmon oil, Rubber tree *Madhuca longifolia*, tobacco seed, sea mango, and jojoba oil. In addition, waste from cooking oils, non-edible oil crops, restaurant grease, beef tallow, animal fats, and pork lard can also be utilized as biodiesel feedstocks [60]. Animal fats are preferable over first generation feedstocks due to properties such as higher-octane numbers, non-corrosiveness, lack of waste and sustainability. However, the main drawback of this generation of feedstocks is the lack of active technologies for the commercial exploitation of waste generated by biodiesel production. Furthermore, most animal fats possess a high concentration of saturated fatty acids, which increases the transesterification complexity [10]. The main limitation of biodiesel is its comparatively low performance in cold temperatures which hinders their ability to fully replace petroleum transport fuels [61]. Furthermore, bio-safety issues can present in cases of contaminated animal feedstocks [10].

Second generation butanol

Butanol alcohol ($C_4H_{10}O$) consists mainly of hydrogen and carbon, so it can be easily blended with gasoline and other hydrocarbon products [62]. Butanol has more heat energy than ethanol, which increases the harvestable energy gains (around 25%) [63,64]. The gross heat value of butanol is 110,000 BTU per gallon which is closer to that of diesel fuel (115,000–138,700 BTU per gallon) [64]. Butanol is safer to handle than gasoline and ethanol due to its low Reid Value of 0.33 psi. The Reid Value is a measurement indicator of a fluid's rate of evaporation, and it has values of 8–15 and 2.3 psi, for gasoline and ethanol, respectively [65].

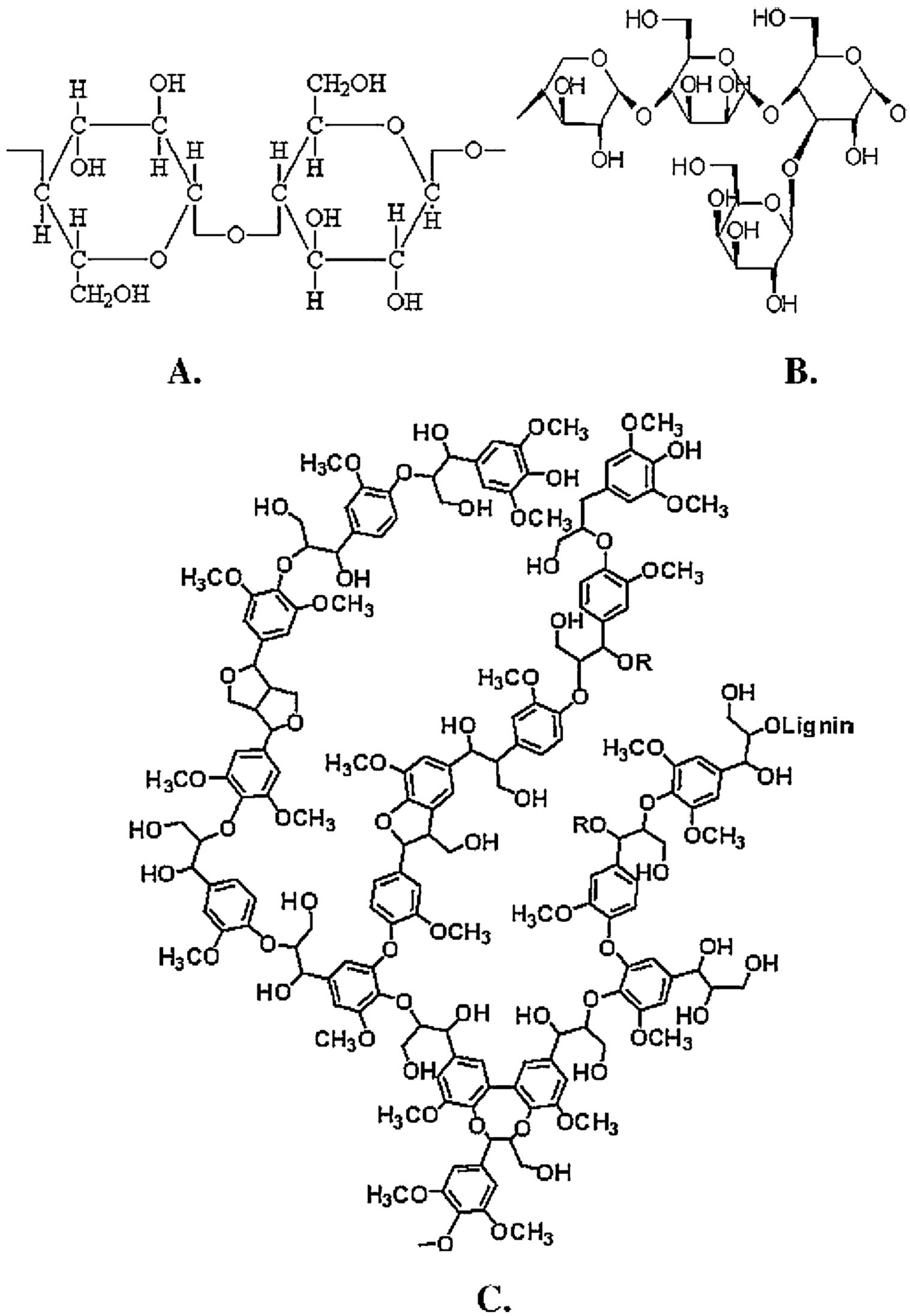

FIGURE 3

Chemical Structures of A- cellulose, B- hemicellulose, and C- lignin.

Another reason why butanol is considered safer than ethanol and gasoline is its low production of volatile organic compound (VOC), which is also due to its low evaporation rate. In addition, the corrosiveness of butanol is less than that of ethanol which helps with shipping and distribution it through existing pipelines and filling stations [65].

The relatively high oxygen content of butanol, 21.6%, makes it a great fuel extender that is cleaner than ethanol [65]. It has also been reported that burning butanol in an internal combustion engine releases only CO_2 and H_2O, which makes it more the environmentally friendly choice [64]. There are four isomers of butanol with similar energy and which are identical in blending with gasoline and in combustion. These are normal-butanol $CH_3CH_2CH_2CH_2OH$ (*n*-butanol), secondary-butanol $CH_3CH_2CHOHCH_3$ (2-butanol), *iso*-butanol $(CH_3)_2CH_2CHOH$ (*i*-butanol) and ter-butanol $(CH_3)_3COH$ (*t*-butanol). However, their manufacturing processes are very different [66]. *t*-Butanol is limited to petrochemical manufacturing and there is still no biological technique to produce it [67]. *n*-Butanol, which is a toxic alcohol, was manufactured using a fermentation process with sugar or starch even before the rise of the petroleum industry. This complicated fermentation process involves the anaerobic conversion of carbohydrates into acetone, butanol and ethanol (known as ABE process) with a product ratio of 3:6:1, respectively [68].

The production of *iso*-butanol, which is less toxic than *n*-butanol [69], has attracted several organizations' attention such as, DuPont, BP, GEVO [64]. Wine manufacturing yeast cultures generate small amounts of *iso*-butanol. However, to produce high quality wine, careful distillation is needed to remove *i*-butanol and methanol. The manufacturing of 2-Butanol involves, first, a bacterial fermentation that help to convert glucose (from starch or cellulose) and all kinds of sugars resulting from hemicellulose to a nontoxic intermediate product. Then this intermediate product is converted to 2-butanol through a chemical conversion step. The overall conversion rate of the raw materials to 2-butanol is higher than that with other butanol isomers [64].

Third generation

Several kinds of microorganisms are used as feedstocks in the third generation of biofuels [70]. Promising microalgae are the most common type for biodiesel production. There are two main classifications for algae based on their size and morphology: macroalgae and micro-algae. One of the most commonly used marine macro-algae is kelp which has multiple cells, resembling the roots, stem and leaves of higher plants. In contrast, microalgae which are classified as autotrophic, heterotrophic, and mixotrophic microscopic organisms, exist in both fresh and marine water [71].

Microalgae organisms have excellent potential to produce special chemicals and nutritional products due to their photosynthetic ability [72]. Autotrophic and heterotrophic microalgae differ in the source of the carbon they consume, where autotrophs use inorganic carbon while heterotrophs use organic carbon sources [73]. Mixotrophic algae can simultaneously drive autophototrophy and heterotrophy to use both inorganic and organic carbon substrates, which increase the productivity and enhance the capability of microalgae to grow in wastewaters [74]. This kind of algae could overcome issues associated with the growth of autotrophic algae regarding light limitation at high cell densities and dark colored wastewaters [75]. The mixotrophic growth of Chlorella protothecoides can provide 69% higher lipid than that of heterotrophic yield on glucose with a reduction CO_2 releasing by 61.5% [74]. Despite the high biomass and lipid productivities, the cost of glucose represents around 80% of the total fee penalty of growth medium which making mixotrophic algae cultivation unattractive economically [75]. However, utilizing inexpensive carbon sources offers excellent promise for the cultivation of mixotrophic algae. Example sources of carbon are sugars from industrial and agricultural waste, crude glycerol from biodiesel industry, cellulosic materials and cane molasses [74].

Microalgae have several important properties such as requiring less space to grow, high oil content, the ability to grow in both artificial and natural environments, and being ecofriendly [76]. They also possess a unique advantage which is the capability for both oxygenic photosynthesis and hydrogen production [10]. In addition, their growth requirements are simple and limited to light, carbon dioxide and other inorganic nutrients [77]. Microalgae also assist to decrease the CO_2 level in the environment because the production of 1 kg of algal biomass consumes around 1.8 kg of CO_2 [78]. Historically, in the 1950s Oswald and Golueke from California in the USA were the first researchers who investigated microalgae anaerobic digestion. They used different microalgal biomass types such as high rate ponds and harvested the biomass for biogas production. [10].

The oil content of microalgae biomass varies widely. In some types oil composes more than 80% of the dry weight of algal biomass while in other types it is about 15–40% [10]. In comparison with crops, the oil content of palm kernel, copra, and sunflower is between 50 to 60%. In general, microalgae are considered the best oil provider among various plants. The production capacity of oil from microalgae is up to 100,000 l/hectare/year, whereas the capacity of palm, coconut, castor and sunflower is between 1000 and 6000 l/hectare/year [79]. Microalgae can be used in the production of several biofuels including bioethanol and biodiesel as well as CH_4 and H_2 using different processes. Biofuels produced from microalgae are compatible with presenting fuel engines which eliminate the need for further modification [80]. Microalgae-based biodiesel fuels have similar properties to petroleum-based biofuels such as density, viscosity, flash point, heating value, cold filter plugging point, and solidifying point. Thus, they are compatible with the standards of both the American Society for Testing and Materials (ASTM) and the International Biodiesel Standard for Vehicles [81]. In addition, microalgae-based biodiesel fuel produces less pollutant gases such as CO and SOx than petroleum-based fuel.

Microalgae-based bio-oil has a high heating value, low density and low viscosity compared with fossil-based oil produced by fast pyrolysis of wood [82]. It is also preferable to lignocellulose-based oil due to its better quality. Figure 4 presents a schematic diagram of third generation biofuel production. Table 1 comparing the results of bio-oil produced by algal pyrolysis technique that reported by different researchers. Microalgae have advantages such as the ability to eliminate inorganic nutrients from wastewater and to generate higher quantities of green biomass due to their tendency to uptake nitrogen and phosphorous [10]. Therefore, a promising strategy to enhance the economic and production efficiency of microalgal-based biofuels is by coupling microalgal cultivation with wastewater treatment [83,84]. This strategy has several advantages over other feedstocks such as (a) lower cost due to simple solar energy requirements, (b) the ability to effectively reduce CO_2 concentrations, (c) the absence of required extra organic carbon sources unlike for biological nitrification and denitrification, (d) fewer sludge handling issues, and (e) a tendency to increase the dissolved oxygen level (i.e. O_2 concentration) in water bodies [85]. On the other hand, this kind of biomass has some limitations such as its high cost and the fact that biofuel produced from algae is less stable than that produced from other sources. This is because the oil generated by algae is highly unsaturated, which means it is more volatile, especially at high temperatures, and therefore more likely to degrade [10].

In addition, microalgae have great potential to achieve high lipid content due to their high photosynthetic ability. Specifically, the lipid production capacity per unit dry is between 15 to 300 times that of conventional crops [10]. Anaerobic digestion of organic biomass, which is known as methanogenesis, is used to produce biogas fuel. The main requirements for this process are cellulosic and hemicellulosic sources. Thus, microalgae are promising source of biofuels.

Production of biofuel from biomass using microorganisms can be done through biochemical or thermochemical processes.

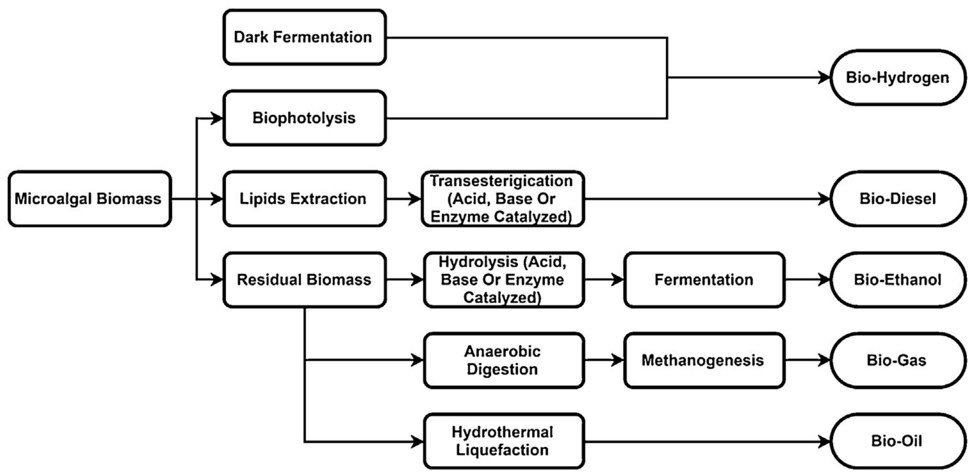

FIGURE 4
A schematic diagram of microalga-based biofuels production.

Biochemical processes can be classified into alcoholic fermentation, anaerobic digestion, transesterification and photobiological hydrogen production. Thermochemical processes include heating and decomposition of biomass in the absence of oxygen. Currently, thermochemical processes are more favorable due to their better conversion efficiency, required production time, and lower production costs compared to biochemical processes. In addition, it provides a simpler production route but with using high temperatures. Specifically, the biochemical method relies on heat, chemicals, and biocatalysts, such as enzymes and microbial cells, and might need several days to complete. In contrast, thermochemical methods rely on heat and/or physical catalysts only and require shorter time to complete [86].

Third generation bioethanol

Algae have attracted wide attention as an alternative renewable source for bioethanol production to overcome the problems accompanying first and second generation biofuels [94]. The investigation of algae as biofuel feedstock started in the late 1950s and then got wide attention after the oil crisis in the

TABLE 1

Comparison of the algal pyrolysis results reported by different researchers.

Feedstock	Conditions	Main results	Ref.
Spirulina sp.	Stainless steel fixed-bed reactor made of steel, 125 g microalgae, [a]450–600 °C, [b]8 °C/min, nitrogen, [c]30 ml/min, [d]60 min	The best yield of bio-oil was 46% and achieved at 550 °C, While bio-char was secondary product with maximum yield of 33% at 500 °C	[87]
Lipid-extracted residue of *T. minus*	Stainless steel fixed-bed reactor, 5 g microalgae, [a]300–500 °C, [b]10 °C/min, nitrogen, [c]50 ml/ min, [d]60 min	The highest bio-oil yield was 29.82% at 450 °C. The produced bio-oil was riches with alkane/alkene and nitrogenous compounds.	[88]
S. dimorphus	Quartz glass fixed-bed reactor made of, 10 g microalgae, [a]300–600 °C, [b]40 °C/min, nitrogen, [c]100 ml/min.	The products include bio-oil (best yield 39.6%), bio-char (best yield 36%) and bio-gas (best yield 25%) were obtained at 500, 300, and 600 °C respectively.	[89]
Four algal and lignocellulosic biomass samples	Fixed-bed tubular quartz reactor, 3 g microalgae, [a]300–900 °C, nitrogen, [c]50 ml/min, [d]60 min	Microalgae yielded more bio-oil than lignocellulosic, and the best yield was 32.69% obtained for C. vulgaris microalgae at 500 °C.	[90]
Isochrysis and defatted *Isochrysis*	Tubular-quartz fixed-bed reactor, 2.5 g microalgae, [a]475 °C, nitrogen, [c]400 ml/min.	bio-oil yielded from lipid extracted residue of microalgae (36.86%) was lower than that yielded from regular microalgae (41.32%) at 475 °C	[91]
Blue-green algae blooms	Fixed bed reactor, 5 g microalgae with different particle size, [a]300–700 °C, [b]40 °C/min, nitrogen, [c]0–400 ml/min, [d]15 min	The best bio-oil yield was 54.97%. and was achieved at 500 °C.	[92]
C. vulgaris and *D. salina*	Quartz-glass fixed-bed reactor, 1 g microalgae, [a]300–700 °C, nitrogen, [c]400 ml/min, [d]20 min	The best bio-oil yields of *C. vulgaris* and *D. salina* were 49.2% and 55.4% at 500 °C, respectively. Temperature increasing from 300 to 700 °C, increased and decreased the gas and char yields, respectively.	[93]

[a] Temperature of process.
[b] Heating rate.
[c] Volumetric flow of carrier gas.
[d] Duration of process.

1970s [95]. Bioethanol can be produced by any of the three algal processes that have been discussed (mixotrophic, heterotrophic, and autotrophic). After hydrolysis, algal starch, cellulose or other accumulating carbohydrates can be converted to ethanol. [96].

The high photon conversion efficiency of algae makes them promising candidates for renewable bioethanol applications. The algae-bioethanol production process is simpler than that of lignocellulosic biomass because it does not require the chemical and enzymatic pre-treatment steps that are necessary to breakdown lignocellulosic biopolymers into fermentable sugars [97]. An example of algae-bioethanol production technologies is that developed by Algenol Biofuels Inc. which utilizes sunlight trapping microalgal cells as a tiny biorefinary using a specialized bioreactor. The production rate is 6000 gallons of ethanol per acre per year. This production rate is much higher than that produced from corn which is reported to be 400 gallons of ethanol per acre per year [95]. Table 2 summarizes the advantages and limitations of bioethanol alcohol. Figure 5 represents a schematic diagram of the bioethanol produced by different generations of biofuels.

TABLE 2

Advantages and disadvantages of bioethanol fuel [98–100].

Advantages	Disadvantages
• It has a high-octane number (108), high flame speeds, broader flammability limits, and higher heats of vaporization which lead to better efficiency	• It has a lower energy density than gasoline (66% of the gasoline energy) • Its corrosiveness • It has low flame luminosity • It has lower vapor pressure which making cold starts difficult • miscibility with water • toxicity to ecosystems • It has high emission of acetaldehyde

Third generation biodiesel

Microalgae are considered a very promising choice for biodiesel production and a variety of microorganisms can be used for this purpose. Both microalgae autotrophs and heterotrophs can be used for biodiesel production but vary in their biodiesel yield [101]. Table 3 shows the oil yield of different microalgae species [10].

Using biodiesel in diesel engines might have minor impacts on operating performance. The gross heat value of biodiesel is 126,200 BTU per gallon which is similar to that of diesel fuel (115,000–138,700 BTU per gallon) [64]. The production of biodiesel involves the formation of fatty acids (FA) as precursors which in turn involves the catalyzed conversion of acetyl CoA to malonyl CoA by acetyl CoA carboxylase (ACCase) [102]. This pathway generates between 16 to 20 types of carbon fatty acids which are used in the synthesis of triacylglycerols as well as cellular and organelle membranes. Triacylglycerols are accumulated in higher percentages (30–60% of dry cell weight) by some oligeanous microalgae than by first-generation crops [101]. The major triacylglycerol manufacturing pathway for lipid accumulation in algae occurs in the chloroplast. To promote the biodiesel yield, yeast, oligeanous algae and bacteria have been investigated for lipid content. Some microalgal species possess a high triacylglycerol content of up to 80% of their total dry biomass [103]. However, there are production difficulties which must be eliminated for the commercialization of these species. These difficulties include scaling up their culture and investing in stress control for lipid production [104].

To develop the microalgal ability for high lipid accumulation, stress control strategies are commonly used. These strategies involve manipulating the nutritional or cultivation circumstances (i.e., temperature, pH, nitrogen, phosphate concentrations, etc.) to make microalgal cells adapt to the changing environmental conditions. In addition, recombinant DNA technology has been

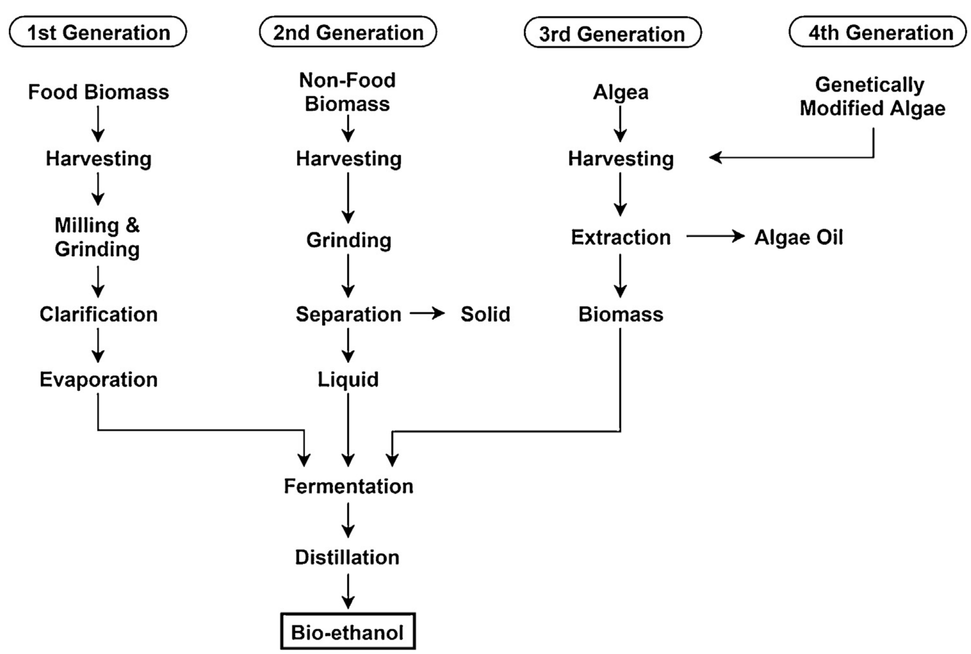

FIGURE 5

A schematic diagram of bioethanol production based on different generations.

TABLE 3

Oil contents of different microalgae strains [10].

Microalgal species	Oil composition (%)
Ankistrodesmus TR-87	28–40
Botryococcusbraunii	34–75
Chlorella sp.	50
Chlorella protothecoides (autotrophic/ heterotrophic)	40–55
Dunaliellatertiolecta	33
Hantzschia DI-160	66
Nannochloris	25
Nannochloropsis	35–47
Cenedesmus	34
Stichococcus	32–40
Tetraselmissuecica	20–35
Phaeodactylumtricornutum	20–28

utilized to improve biodiesel production. For example, a photosynthetic organism, C. cryptica, was used to isolate and characterize an acetyl-CoA carboxylase (ACCase) gene in 1993. This gene was also transformed into the diatoms C. cryptica and Navicula saprophila. However, only a small increase in the lipid concentration of the microalgae was observed [105]. Biodiesel advantages and limitations are summarized in Table 4.

Fourth generation

In fourth-generation biofuels, genetically modified microorganisms such as microalgae, yeast, fungi and cyanobacteria are utilized as sources. The ability of microorganisms to convert CO_2 to fuel through photosynthesis is utilized [106]. The multiple advantages of microalgae such as their high growth rate and oil content and low structural complexity enhance their numerous commercial applications [86]. In addition to genetic modification, some fourth-generation technologies involve pyrolysis (in a temperature range between 400 to 600 °C) [86], gasification, upgrading, and solar-to-fuel, pathways [107]. The general purpose of these modifications is to improve the HC yield and create an artificial carbon sink to eliminate or minimize carbon emission [108]. These technologies are still in early developmental stages [108].

Cyanobacteria

Cyanobacteria have attracted a lot of attention in bioenergy and biofuel industries. Recently, the genomic revolution has greatly developed metabolic engineering for several photosynthetic organisms. *Synechocystis* was the first photosynthetic organism for which the genome was completely sequenced [109]. *Synechocystis*, which has the ability for both photoautotrophic and heterotrophic growth, is a freshwater, non-filamentous, non-nitrogen fixing organism. The most valuable characteristic of this strain of cyanobacteria as a genetic and physiological case study of photosynthesis are the available genomic, biochemistry, and physiological information. It is also well known as a model system for the investigation of oxygenic photosynthesis in higher plants due to its small genome size compared to higher plant systems [110].

Eukaryotic microalgae

Eukaryotic microalgae-based technology has attracted a lot of attention recently due to the availability of eukaryotic genomic information. Interest in this technology began in the 1980s [105]. Generally, eukaryotic cells are formed in the random integration of exogenous genes into the nuclear genome. Several kinds of microalgae have been successfully generated by gene transformation into the cellular nucleus, chloroplasts and mitochondria [111]. The most investigated eukaryotic microalgae is *Chlamydomonas reinhardtii*. It is a very common model organism used to investigate the essential mechanisms of biological processes, such as oxygenic photosynthesis, circadian rhythms, and flagella biogenesis [112].

The first investigation of the chloroplast DNA map of *Chlamydomonas reinhardtii* was in 1978 and led to successful genetic transformation in the *Chlamydomonas reinhardtii* chromosome, chloroplast, and mitochondrial genome by 1993 [113–115]. *Chlamydomonas* has shown great ability to produce recombinant proteins. It enables the generation of various types of proteins including complex mammalian therapeutic enzymes and monoclonal antibodies at commercial levels with presenting production platforms [116].

Chlorella which is another kind of unicellular green algae organism with a transformation system [117] which has attracted the attention of researchers lately. Several steps have been taken since its transient expression system was first described by Jarvis et al. in 1991 [118]. In recent years, marine diatoms have attracted a lot of attention due to their wide prevalence, ability to adapt to varying environments, and substantial biomass production in water [119].

Techno-economic and environmental analysis

A lot of effort has been made to determine the techno-economic characteristics of biofuel production and to integrate them with its environmental impact [120–122]. However, the results of these studies vary due to the difference in the basis of the production process such as the availability of the feedstock and the production technique adapted as well as the assumptions made in these studies [123]. The U.S. National Renewable Energy Laboratory (NREL) conducted a valuable economic and environmental study of biodiesel production from algae. Their study estimated the cost of biodiesel production is in the range between \$0.53 to 0.85/L, which is close to what was estimated by Nagarajan et al. after a careful consideration of the cost of land and transesterification that found a range between \$0.42 to 0.97/L [124]. These estimated costs are close to the commercial value of diesel fuel which indicates the high promise of biodiesel choice.

On the other hand, Kern et al. investigated the possibility of enhancing the cost-competitiveness of algal biofuel production by adding an up-front investment in anaerobic digestion to increase the flexibility in using lipid-extracted algae as feed or to recover nutrients and energy. Their investigation showed that there is no additional economic value due to discourage feed meal prices [120].

Recently, Olcay et al. evaluated the conversion of red maple wood, cellulosic feedstock, using aqueous-phase processing (APP) techniques with different parameters such as pretreatment methods, product slates, and gas sources [121]. Their lifecycle analysis results for GHG varied, due to the different refinery configurations, from 31.6 to 104.5 gCO_2 per MJ which is 64% lower and 19%

TABLE 4

Bio-diesel's advantages and disadvantages [98–100].

Advantages	Disadvantages
• Generates fewer pollutant emissions such as COx, SO_2, PM and HC compared to diesel • Its production is easier and faster than diesel • It has shown better performance in vehicles due to its higher-octane number • It helps to prolong engine life and minimizes the engine maintenance required • Unlike diesel engine, it does not need additional lubricant to be used • It has a magnificent potential for stimulating sustainable rural development and as a solution for energy security issues • It has a higher cost efficiency than diesel • Unlike diesel, it does not require any drilling, transportation or refinement • Compared with diesel fuel, it has better sulfur content, flash point, aromatic content, and biodegradability • It is safer to handle and less toxic than diesel fuel • It is non-flammable, non-toxic, and it reduces tailpipe emissions, visible smoke and noxious fumes and odors • It does not require any engine modification • It has high combustion efficiency, portability, availability, and renewability	• Its combustion generates higher NO2 and NO than diesel • It has a higher pour point and cloud point which may cause fuel freezing and difficulty starting in cold weather

higher than that reported for petroleum fuel, respectively. Their estimated cost of production was in the range between \$0.26 to 1.67/L, which is 61% lower and 146% higher than that reported for petroleum-based jet fuel price, respectively.

Policies and future needs

The future for biofuel production should focus on lowering the production cost and utilizing technological advance to increase the production of biofuel from marine biomass. Specifically, efforts should focus on developing new high active and stable catalysts, higher efficiency reactors, continuous operation bioreactor, and minimizing the required energy and GHG emissions as well as waste. In addition, government support will be the key for shifting communities towards green energy.

For example, the current estimated production price of biodiesel does not encourage its adoption over petro-diesel fuel. The absence of clear government policies is a main cause of the poor biodiesel industry. Thus, governments should create and expand policies to help marketing of biodiesel by direct or indirect financial support such as tax credits and subsidies. On the other hand, there is still some room for possible reduction in the cost of biodiesel production. Specifically, most investigations have focused on algal growth, but more attention should be paid to increasing lipid content due to its potential to increase production yields of biofuels. Also, utilizing algal residue for biogas production may improve the economic benefits of this process.

Conclusions

Biofuel will play an important role in meeting the world's energy need in the future. In this paper, the four generations of liquid biofuels are reviewed in terms of their feedstocks, production technologies, environmental influences and economic evaluations. Each generation has advantages and limitations. To reduce the growing use of petroleum fuels, a renewable supply of raw material is needed. Several parameters affect the availability and production of biofuel feedstock such as geographical location, the economic condition of the population, and food-fuel demands. First generation biofuels cannot replace fossil fuels due to competition with food needs. In contrast, third and fourth generation biofuels are more promising choices because they do not involve such food-fuel competition. Another valuable parameter to secure the sustainability of liquid biofuels is advances in technology. Improvements in cost effectiveness and yield conversion systems are required for widespread commercial production of biofuel. This goal will probably be achieved by utilizing metabolic engineering tools which improve biofuel both quantitatively and qualitatively by modifying existing biological pathways. This has the potential to alter feedstock or identify more useful microbes to get better conversion rates. More investigations are needed to achieve higher yields and more cost-effective production processes. For greenhouse gas reduction, second and third generations biofuels have shown much better performance compared to first generation biofuels. More reduction in greenhouse gas emissions is expected from fourth generation biofuels. Currently first-generation liquid biofuels are considered the most cost-effective. However, production is limited to certain countries due to high land and water demand. The second and third generation liquid biofuels still have production cost limitations due to high investment costs and low efficiencies of feedstock conversion to biofuel. Further development and perfection of production technologies of both second and third generation bioethanol and biodiesels may enhance their cost-effectiveness. Overall, the future of liquid biofuel may be an integration of some or all of the four generations.

Conflict of interest statement

The authors declare no financial or commercial competing interest.

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