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REVIEW

The Influences of Promising Feedstock Variability on Advanced Biofuel Production: A Review

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Abstract

The contribution of biofuels is expected to continuously increase in the global fuel market, as they are environmentally-friendly and provide renewable energy. Four generations of biofuels are categorized and are primarily based on their feedstock sources and the production technologies that are used. The influence of promising feedstock types and the availability on the production technologies and the fuel properties of advanced-generation biofuels are not systematically examined in the literature. Hence, this research extensively reviews the potential impact of feedstock sources and their variability on the production and characteristics of biofuels. The approaches of theoretical analysis and inference referred to relevant works in the literature were applied. The findings suggest that the potency of the commercialized mass production of advanced-generation biofuels is facilitated by a much more flexible selection and the sufficient availability of promising feedstocks. Lignocellulose biomass is recognized as the most significant feedstock source for second-generation biofuels, while microalgae do the same for third-generation biofuels. Moreover, the microalgae of some strains are able to produce the highest amount of bio-alcohol of all available feedstock sources. The cell walls of lignocellulose biomass and microalgae mostly consist of lignin compounds and cellulose materials, respectively. Biological pretreatment is considered to be the most promising process, prior to biofuel production. The biofuel yields from lignocellulose biomass and microalgae, using biological pretreatments, could increase by 120% and 22–159%, respectively, in comparison with those of any other pretreatment process. Moreover, more double bonds and larger unsaturated fatty acids in raw lipids cause the inferior oxidative stability, but superior fluidity of biofuel. The possible impact of Genetically-Modified Crops (GMC) on the eco-environment and human genes remains a serious concern and requires further tracking and analysis. Genetically-modified technology is still immature to achieve the expected characteristics of biofuels from those modified crops. The unceasing exploitation of promising biomass feedstock sources is crucial for the rapid and steady development of advanced-generation biofuels.

Keywords: Lignocellulose material, Biofuel, Feedstock variability, Energy crop, Fuel characteristics

1. Introduction

Bioenergy, which accounts for 10% of the global renewable energy, has become one of the major options for the supply of energy [1–4]. The two most distinguished bioenergy examples are biodiesel and bioethanol. In particular, bioethanol has been used widely as an alternative fuel to petroleum-derived gasoline for on-road vehicles and marine vessels [5–7]. It is primarily made from sugarcane, provides about half of the global bioethanol demand and is

regarded as one of the most successful examples of biofuel development [8–12]. The contribution of biofuels to the total global renewable energy is expected to increase continuously [13–15], and thus, the dependence on fossil fuels as an energy source will be reduced accordingly. The USA has been a global leader in biofuel production and consumption, particularly bio-ethanol and biodiesel. The amount of biodiesel production and consumption between 2010 and 2017 [16] in the USA, is shown in units of millions of gallons (Mil. Gal.) in Fig. 1. The

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biodiesel industry appears to have developed vigorously in the USA and the rest of the world since 2010.

Biofuel belongs to the group of carbon-negative energy, which implies that the total quantity of CO₂ captured and consumed is more than the CO₂ emissions during the life-cycle of such bioenergy [17–19]. Hence, bioenergy is regarded as an environmentally-friendly energy resource. The global CO₂ release can be reduced by replacing more fossil fuels with bioenergy. In the European Union (EU), 20% of greenhouse gases (GHGs) are emitted from the transportation sector [20–22]. The widespread use of biofuels will thus help to diminish the threat of the greenhouse gas effect and the extent of global climate change.

The global production and usage of first-generation biofuels are steadily growing, with the development of more mature production techniques [23,24]. However, the feedstocks used for the first-generation biofuels are mostly from agricultural crops, which have been a major source of human food for thousands of years. Crop prices have thus soared with the global development of biofuels. In addition, the eco-environment and habitats of the original creatures have been destroyed by the unrestricted expansion of arable land for the cultivation of crops for biofuels [25–27]. First-generation biofuels are thus considered to be the biofuel option that has the least effect on sustainable development [28,29]. The shortcomings of first-generation biofuels have actively facilitated the rapid development of second- and third-generation biofuels, which are also referred to as advanced-generation biofuels in

Nomenclature

CAPEX	Capital expenditure
CSE	Conventional solvent extraction
EU	European Union
GHG	Greenhouse gas
GMC	Genetically modified crop
LCB	Lignocellulose biomass
MSW	Municipal solid waste
OPEX	Operating expenditure
PBR	Photobioreactor
PSSE	Physical-supported solvent extraction
SFE	Supercritical fluid extraction
SRC	Short-rotation coppice
WRF	White-rot fungi

this article. The major difference between first-generation and advanced-generation biofuels lies in their feedstock source [30–32]. In contrast to crop-derived feedstock for the first generation biofuels, non-foods, particularly lignocellulose-based materials, are generally used for the production of the second-generation biofuels [33–35]. These raw lignocellulose materials include agro-industrial residue or architectural waste, such as wood chips, grass, stalks or the boughs of plants, wheat straws, rice husks, etc. [36,37]. Microbial organisms, such as algae, cyanobacteria, and bacteria are recognized as the major feedstock used for third-generation biofuels [38,39]. Biohydrogen and bioelectricity, which are produced from a photosynthetic mechanism, are considered as fourth-generation biofuels; however, this category has not yet been widely recognized. The developing trends of the general feedstocks used and the typical biofuel characteristics of the

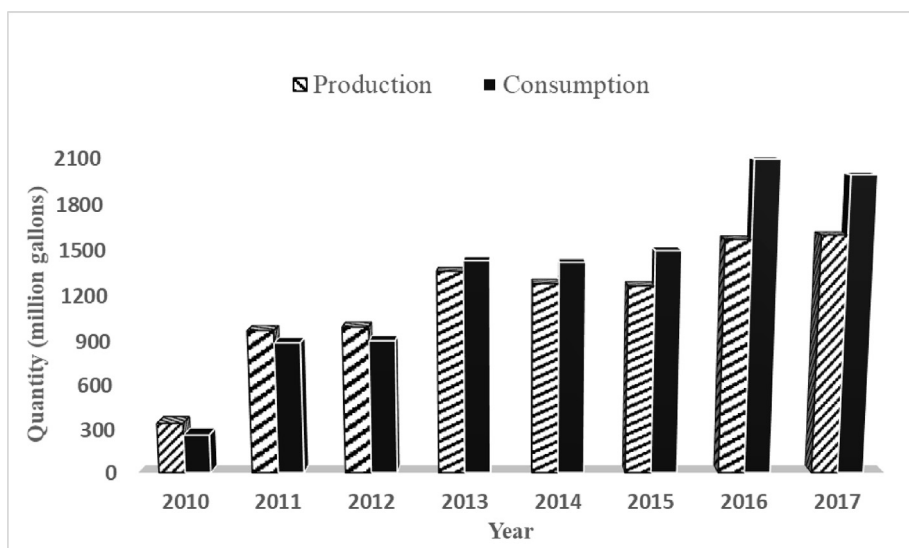


Fig. 1. Production and Consumption of biodiesel between 2010 and 2017 in the USA [16].

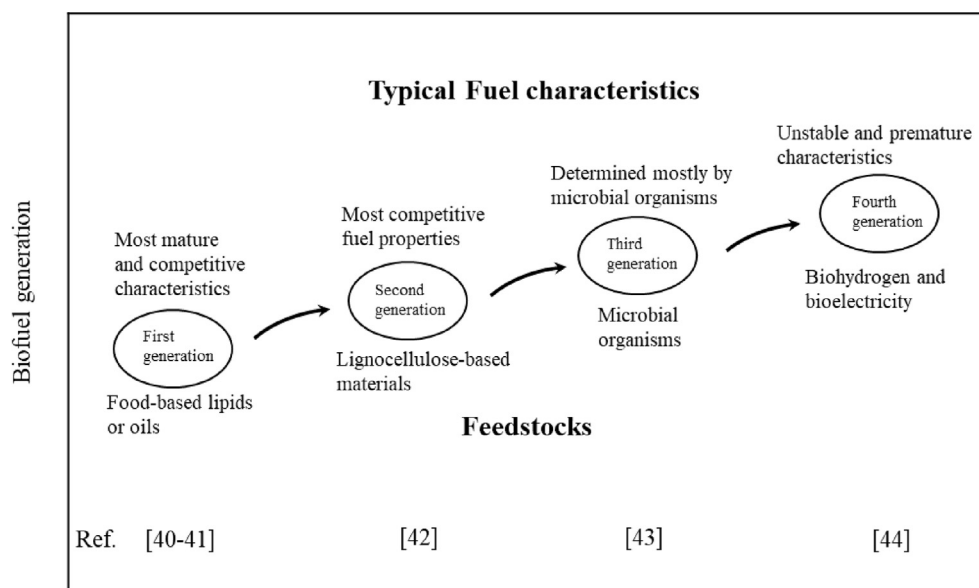


Fig. 2. Feedstock resource and typical fuel characteristics of corresponding generation biofuels.

first-to the fourth-generation biofuels are illustrated in Fig. 2. Non-edible feedstocks, including agro-architectural waste and lignocellulose materials and microbial organisms, are generally used to produce advanced-generation biofuels. The biofuels of the various generations and their corresponding feedstock sources, fuel characteristics and representative types are shown in Table 1 [40–44]. The more abundant feedstock resources, together with a variety of advanced manufacturing technologies, have facilitated the fast development of advanced-generation biofuels.

The chemical composition, fatty acid profile, characteristics, and availability of the potential feedstocks directly determine the fuel characteristics and the development trends of specific biofuels. However, the influence of promising feedstocks, particularly lignocellulose materials, on biofuel development has not been reviewed in the literature. The major works reviewed in the literature are summarized in Table 2. Dulrue et al. [45] used four evaluation criteria to compare various technologies from cultivation to the oil-upgrading stage. Chen et al. [46] reviewed the economic and technological difficulties in the production of biodiesel from microalgae. Lin and Lu [47] critically reviewed the sustainability criteria, as well as the certification and production technologies of biofuels. Tercero et al. [48] conducted a technical evaluation of the biodiesel that was cultured from microalgae in a closed-pond photobioreactor, while Li et al. [49] reviewed various lipid extraction methods for biofuel production. Lee et al. [50] reviewed the lipid

extraction technologies and cell lysis methods from microalgae. Kumari and Singh [51] considered the different pretreatment methods of lignocellulosic waste, while Suparmaniam et al. [52] reviewed the configuration and design of a modern photobioreactor (PBR) for culturing microalgae. However, the various promising feedstocks for the production of various-generation biofuels have not been properly evaluated in the literature as yet. Hence, the recent development of potential feedstock sources and production technologies for advanced biofuels are systematically reviewed in this study. Moreover, the types, chemical profiles, and characteristics of diverse lignocellulose and micro-organism feedstocks are examined. The potential impact of the biomass feedstock variability on the fuel properties of advanced biofuels are finally discussed and reviewed in the manuscript.

2. Methodology used in this study

This review work used the approaches of theoretical analysis and the inference referred to previous relevant works published in the literature. The research findings obtained in this study are then summarized. The research experience and results derived from the experiments carried out in the laboratory of the author are also considered, while preparing the manuscript. The primary aim of this study is to construct a relationship between the availability of various feedstock resources, their production technologies, as well as the fuel characteristics of advanced-generation biofuels.

Table 1. Category of biofuel generations and corresponding feedstock sources.

Category	Biofuel generation			
	First	Second	Third	Fourth
Feedstock sources	Food-based lipids or oils such as animal fats and vegetable oils	Lignocellulose-based materials including agro-industrial residue and architectural waste	Microbial organisms such as algae, cyanobacteria, and bacteria	Biohydrogen and bioelectricity produced from a photosynthetic mechanism
Fuel characteristics	Most mature and competitive alternative biofuel to petro-derived fuel	Owning most developing potential and abundant feedstock resources	Mostly determined by compounds of microbial organisms	Unstable and premature characteristics
Typical biofuel	Biodiesel, bioethanol, etc.	Lignocellulose bioalcohol, green diesel	Biogasoline, biohydrogen, biomethane	Bioelectricity, biohydrogen
References	[40,41]	[42]	[43]	[44]

This study originates from the necessity to develop renewable biofuels as an alternative for petroleum-derived diesel or gasoline, to mitigate for their greenhouse gas effects and enhance eco-friendly environment protection, and to search for promising feedstocks, which is considered to be the most crucial step in the promotion of biofuel growth. The literature regarding the available potential feedstocks, including food-based lipids and oils, lignocellulose-based materials, microbial organisms, etc. for biofuel production, are extensively collected and evaluated. The fatty acid profiles of biofuels made from various representative types of feedstock are carefully assessed, by comparing different fatty acids compounds. After a thorough review and evaluation of the promising feedstocks for manufacturing advanced-generation biofuels, this study ends by providing adequate suggestions for promoting biofuel competition.

3. Lignocellulose-based materials for the production of advanced-generation biofuels

The major feedstocks used for manufacturing first-generation bio-alcohol are sugar- or starch-rich crops, such as sugarcane, beet, corn, wheat, sorghum, etc. Bio-alcohol, particularly bioethanol and biobutanol, can be directly produced through processes of fermentation and distillation, followed by water removal, for those feedstocks that are sugar-rich [53–55]. Enzymatic saccharification is carried out prior to fermentation for converting starch into sugar, when starch-abundant feedstocks are used [56,57]. Much more abundant feedstocks, rather than those that are crop-based, can be used for bio-alcohol production, and these include lignocelluloses, perennial plants, such as miscanthus and switchgrass, wood chip, rice straw, and bagasse [58–60]. These abundant feedstocks can be used to produce second-generation bio-alcohols, as their growth does not compete with fertile land, and they are not edible food sources. In addition, feedstocks that contain rich carbohydrates can also be used to produce bio-alcohol, with the help of adequate microorganisms, for example, enzymes [61,62]. Various types of feedstock, from the conventional sugar- and starch-based types to those that are cellulose-, lignin- and microalgae-based, are all available for bio-alcohol production. The production quantity of bio-alcohol per growing area of microalgae could reach about 5000–15000 gallons/acre, which is 13 times greater than that of switchgrass, 23 times greater than that of sugarcane, and even 46 times greater than that of sweet sorghum [63–65].

Table 2. Previous review work of relevant studies.

References	Major review works
Delrue et al., 2012 [45]	Four evaluation criteria, including greenhouse gases (GHG), the emission rate, the water footprint, and the Net Energy Ratio (NER) were used to compare various technologies for each stage from cultivation to oil upgrading. It was concluded that low-carbon energy sources are necessary for reducing GHG emissions.
Chen et al., 2017 [46]	An economic evaluation of and the technological difficulties in the production of biodiesel from microalgae are reviewed. The production costs of microalgae biodiesel are mainly from microalgae cultivation, followed by the harvesting and lipid extraction. The industrialization of the biodiesel production process from microalgae is also proposed.
Lin and Lu, 2021 [47]	The sustainability criteria, certification and production technologies for biofuel products are critically reviewed. The perspectives and trends of advanced biofuels are evaluated for their future development according to a policy and techno-economic analysis. This study suggests the application of advanced purification and conversion processes to enhance the competitiveness of advanced biofuels. The government policies for advocating biofuel development are discussed.
Tercero et al., 2014 [48]	A production plant for biodiesel from microalgae that have been cultured in a closed pond photobioreactor (PBR) is technically evaluated. Aspen Plus® was applied to simulate the whole production process. Both the operating expenditure (OPEX) and capital expenditure (CAPEX) were considered in order to carry out an economic analysis. The results showed that the current technology for the manufacture of biodiesel from microalgae is not economically competitive with that of petroleum-derived diesel.
Li et al., 2019 [49]	The major extraction methods in biofuel production, including Conventional Solvent Extraction (CSE), Supercritical Fluid Extraction (SFE), Physical-supported Solvent Extraction (PSSE), etc., are reviewed. Their extraction principles, limitations and application are also discussed in this study.
Lee et al., 2021 [50]	The lipid extraction technologies and cell lysis methods for microalgae are reviewed. Deep eutectic solvents, switchable solvents, ionic liquids, and organic solvents are considered for extracting lipids from microalgae. Single-step processes, together with cell disruption, are found to be more effective for lipid extraction.
Kumari and Singh, 2018 [51]	Lignocellulosic waste is considered as a feedstock for biofuel production. A suitable pretreatment process, such as physical, chemical, biological, as well as a combination of these, would be used prior to primary production approach. The different pretreatment methods, biomass resources and chemical compositions are compared and discussed.
Suparmaniam et al., 2019 [52]	Microalgae are cultured in a modern photobioreactor (PBR) system, from a tubular to a flat panel. The PBR configuration and design improvement for the microalgae cultivation system are reviewed in order to enhance the economic benefits during the cultivation and harvest processes. This article also attempts to produce microalgae biofuel by using a more cost-effective and sustainable approach.

Due to the limited available arable land for growing food-based feedstocks, the quantity of first-generation biofuels that are produced is by far not enough to effectively replace fossil fuels [66]. In addition, the production technology of first-generation biofuels must be improved, particularly from the perspective of both the stability of its fuel properties and its mass production rate [67–69]. Therefore, the development of competitive production technology for advanced biofuels has been regarded as a crucial trend for the growth of bioenergy. The feedstocks of second-generation biofuels are primarily provided by non-foods, particularly lignocellulose-based raw materials and Municipal Solid Waste (MSW) [70,71]. In addition, advanced production technology of second- and third-generation biofuels is generally not at a mature stage, and thus their production costs and selling prices are still significantly higher than those of first-generation biofuels [72–74]. Hence, the abundance of feedstock resources and the extent of

the maturity of the manufacturing technologies show that there is an adverse trend in the sequential generation of biofuels, and this is shown in Fig. 3. This means that the feedstock resources of the first-generation biofuels, which are produced by the highest mature technology, are the most limited and are primarily sourced from edible oils or animal fats. In contrast, the manufacturing technologies of advanced-generation biofuels are still developing. However, the feedstock resources for producing those biofuels are much more abundant than those used for first-generation biofuels. This implies that much more effort should be made to improve the production processes and reduce the manufacturing expenditure, particularly in the feedstock pretreatment [75–77] of advanced-generation biofuels.

Adequate pretreatment is generally required in the whole production process of advanced second- or third-generation biofuels. For example, hydrolysis is a typical pretreatment method for cellulose bio-alcohol production [78,79]. Either a physical

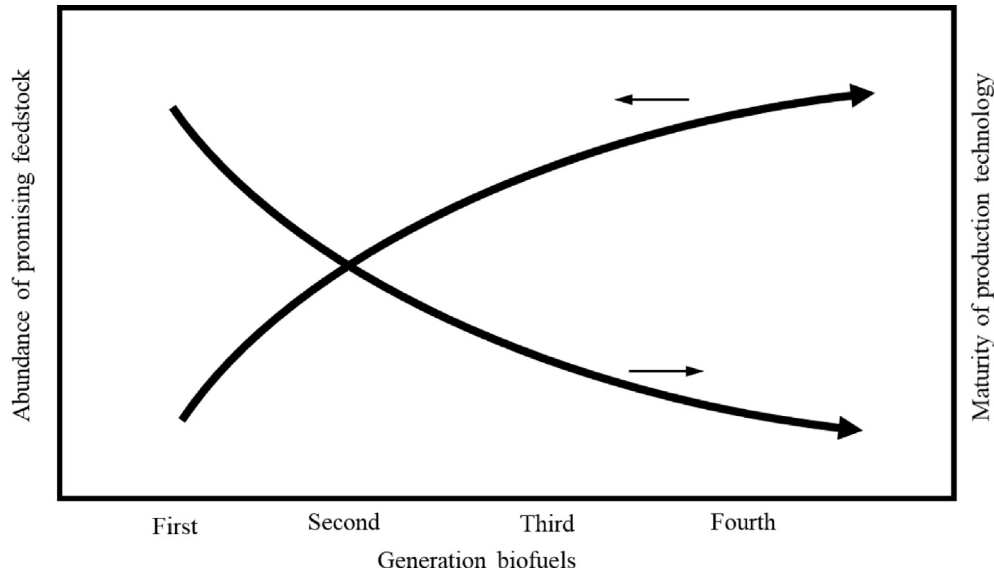


Fig. 3. Developing trends of abundance of promising feedstocks and maturity of production technology for various generation biofuels.

method, using high-temperature steam, a chemical method using acid or alkali hydrolysis catalyst [80,81], or a cellulose digesting enzyme method [82,83], may be adopted in the pretreatment process, based on a comprehensive consideration of the processing cost, the feedstock material used, and the processing time required in the whole lignocellulose-based bio-alcohol production process [84–86].

4. The biological pretreatment of lignocellulose biomass and microalgae

The cell wall of lignocellulose biomass is generally composed of 10–35% lignin, 30–50% cellulose and 25–30% hemicellulose. These three components are jointly linked to form a complex structure, namely, a lignocellulosic matrix [87,88]. In addition, microalgae might consist of 2–40% lipids, 4–57% carbohydrates and 8–71% protein. The actual composition of microalgae depends on the species and the cultivation conditions [89]. Biological pretreatment is regarded as a promising approach for pretreating lignocellulose biomass (LCB) prior to the primary manufacturing process for advanced-generation biofuels [90]. The pretreatment process is a requisite for the biochemical conversion from lignocellulose, microalgae and bacteria feedstock, because of the rigid and complex matrix of those cell walls. Many pretreatment approaches are available, such as mechanical grinding, milling or chipping, gamma or microwave irradiation, immersion in acid or an alkali solution, or steam explosion, etc. [91]. Biological pretreatment has the dominant advantage of using simple operating equipment, having low energy consumption during processing, having safe

and green operating procedures, and having low downstream operating costs [92]. Hence, biological pretreatment is recommended for the production of advanced-generation biofuels. The major difficulty of breaking through the cell wall components of lignocellulose biomass (LCB) lies in the cellulose crystallinity, the accessible surface area and the fact that it is mostly a lignin compound [93]. The cell wall structure of microalgae is different from that of lignocellulose biomass (LCB), due to the absence of persistent lignin content. However, the cell wall component of microalgae is composed of cellulose and pectin, which provides a firm structure, so that hydrolytic enzymes are inhibited from accessing the micro-algal biomass.

The downstream biofuel yield of microalgae cells after biological pretreatment is 22–159% higher than those without prior biological pretreatment [94]. The biofuel yield from lignocellulose biomass (LCB) might

Table 3. Representative types of the feedstocks used for biofuel production.

Type	Feedstocks
I	Vegetable oils such as cottonseed oil, rapeseed oil, and corn oil, etc.
II	Agro-industrial residues and architectural waste including bagasse, spent mushroom substrates, and wood chips, etc.
III	Plants through genetic modification such as willow, and eucalyptus, etc.
IV	Energy crops such as Amaranth, poplar, and purple alfalfa.
V	Organic waste like waste cooking oil, olive pulp, and waste paper stock, etc.
VI	Microalgae like cyanobacteria, red algae, etc.
VII	Bacteria like <i>Clostridium acetobutylicum</i> , <i>Caldicellulosiruptor</i> , etc.

increase by 120%, while the delignification of LCB by White-Rot Fungi (WRF) is increased between 3% and 72% [95]. The biological pretreatment approach has been more widely applied to the pretreatment process of biofuels made from LCB, rather than microalgae. However, the application of the biological pretreatment to microalgae biofuels seems much more promising. This is primarily due to the fact that microalgae are generally composed of lipids, proteins and carbohydrates, which are without recalcitrant lignin compounds [96]. The major purpose of the biological pretreatment of biofuels made from microalgae is to prevent cell-wall breakage and the hydrolysis of the macromolecules [97]. In contrast, lignin removal and the enhancement of the digestibility of cellulose material are the primary objectives of biofuel production from LCB [98]. Biogas production, using anaerobic digestion from microalgae, requires the pretreatment of the hydrolysis of macromolecules, instead of the delignification effect of LCB [99].

Fungi are frequently used to carry out biological pretreatment for the removal of lignin content and to break down the lignocellulosic matrix for LCB, while the hydrolysis of macromolecules and the destruction of the cell walls of microalgae are performed by hydrolytic or enzymatic bacterial pretreatments [100]. The time required for biological pretreatment by bacteria, enzymes and consortia is usually much less than that required by fungi and ensiling [101]. The actual time spent on pretreatment is determined by the biomass type, its composition and its chemical structure. However, much more time is used for the pretreatment process of LCB, especially at its delignification stage [102].

5. Exploiting diverse feedstock sources for advanced biofuels

5.1. Categorizing potential feedstock types

The continuous exploitation of promising and cost-effective feedstock sources is crucial for the steady development of advanced second- and third-generation biofuels. There are a few, but inconsistent, ways of categorizing feedstock types [103,104]. The promising feedstocks for the production of biofuels of various generations can be conveniently categorized into seven types, based on their sources: (I) vegetable oils, such as palm kernel oil, soybean oil, corn oil, castor oil, canola oil, cotton-seed oil, rice bran oil, rapeseed oil, and so on; (II) agro-industrial residues and agricultural waste, including spent mushroom substrates, hay, waste trees, stalks, bagasse, corn waste, straw, wood dust, chips, and so

on [105]; (III) plants, such as pasture, reed, willow, eucalyptus, etc. through genetic modification [106]; (IV) energy crops, such as Amaranth, poplar, *Brassica campestris*, sorghum, beetroot, corns, reed, and purple alfalfa [107]; (V) organic waste, such as waste animal fat, pulp, waste paper stock, waste cooking oil, olive pulp, etc. [108]; (VI) microalgae, such as cyanobacteria (blue-green algae), green algae, red algae, etc. [109]; and (VII) bacteria, such as *Clostridium acetobutylicum*, *Caldicellulosiruptor*, *Pyrococcus*, *Thermococcus*, etc. [110].

As mentioned above, Type I feedstocks are the major source of first-generation biofuels. The Types II to V feedstocks are primarily used to produce second-generation biofuels. The Type VI and VII feedstocks are classified as those used for the production of third-generation biofuels. Table 3 shows the seven feedstock types that are used for producing biofuels of the various generations.

5.2. Fatty acid profiles of biodiesel from various feedstocks

The chemical properties and fuel characteristics of biofuels were determined by the fatty acid composition of the feedstocks used for production [111]. Animal fats are generally composed of a larger weight fraction of saturated fatty acid, which would cause inferior fluidity properties, especially in cold regions or frigid climate, with a superior oxidative or thermal stability [112]. In addition, more double bonds in the chemical structure of fatty acids of biofuels frequently result in an intense reaction of the biofuel with the surrounding oxygen, which causes structural breakage and the deterioration of fuel properties [113]. Sardine oil-biodiesel, which contains more double bonds and much less saturated fatty acids, were found to have a higher iodine value and a lower kinematic viscosity, in comparison with those of biodiesel, which are made from animal fats, such as chicken fat and pork lard [114].

The Type I, V and VI feedstock types in Table 3 have been extensively used to manufacture biodiesel. The fatty acid profiles of biodiesel produced from the representative feedstocks of Types I, V and VI are compared and revealed in Table 4. The microalgae *Chaetoceros muelleri*, which is a Type VI feedstock, is cultured in deep-sea water and the extracted lipid is used to make biodiesel. The waste cooking oil belonging to Type V feedstocks in Table 3 has been widely used to produce biodiesel. The other biodiesel that is shown in Table 4 [115–129] was made from Type I feedstocks in Table 3. The feedstocks, other than Types I, V and VI in Table 3, are more apt to produce other biofuels, such as bio-

Table 4. Comparison of the fatty acid profiles of biodiesels from various feedstocks (wt. %).

Types of fatty acids	Chemical structure	Biodiesel from oils or fats										
		<i>Camellia oleifera</i> Abel oil	Waste cooking oil	Marine fish oil	Salmon oil	<i>Chaetoceros muelleri</i>	Canola oil	Palm oil	Rapeseed oil	Soybean oil	Sunflower oil	Tallow fat
Myristic acid	C14 : 0	0.06	0.54	3.16	5.08	47.26		1.10		0.10	0.10	2.60
Myristoleic acid	C14 : 1	0.02	–	–	–	1.16		–				0.30
Palmitic acid	C16 : 0	10.55	14.18	19.61	15.39	6.84	4.20	42.08	4.20	11.60	6.40	24.30
Palmitoleic acid	C16 : 1	0.36	0.74	5.16	7.55	27.59	0.30	0.15	0.10	0.20	0.10	2.60
Heptadecanoic acid	C17 : 0	–	0.17	1.82	0.46	–	0.20	3.87	0.10	0.10	0.20	2.00
Stearic acid	C18 : 0	2.43	3.77	5.24	4.00	0.15	2.00	42.95	1.60	3.90	3.60	18.20
Oleic acid	C18 : 1	69.07	47.51	20.94	20.76	3.32	60.40	7.03	59.50	23.70	21.70	42.20
Linoleic acid	C18 : 2	8.42	24.83	2.69	3.78	0.55	21.20	0.48	21.50	53.80	66.30	4.40
Linolenic acid	C18 : 3	0.29	4.97	0.90	0.99	0.06	9.60	–	8.40	5.90	1.50	1.30
Arachidic acid	C20 : 0	0.06	0.80	4.75	0.15	2.54	0.70	0.14	0.40	0.30	0.30	0.20
Gondoic acid	C20 : 1	0.51	–	–	–	0.87	1.50	–	2.10	0.30	0.20	0.60
Eicosadienoic acid	C20 : 2	0.12	0.17	0.81	0.30	0.62	0.10	–	0.10			
Eicosatetraenoic acid	C20 : 4	–	0.38	2.54	2.08	–		–				
Eicosapentaenoic acid	C20 : 5	–	0.03	3.70	9.49	0.16		–				
Behenic acid	C22 : 0	–	0.10	1.55	0.09	5.80	0.30	–	0.30	0.30	0.60	0.10
Docosaenoic acid	C22 : 1	7.97	0.18	0.98	–	0.98	0.50	–	0.50	0.10	0.10	0.10
Docostetraenoic acid	C22 : 4	–	0.14	3.86	0.30	–		–				
Docospentaenoic acid	C22 : 5	–	0.05	2.44	4.94	0.12		–				
Docoshexaenoic acid	C22 : 6	–	0.04	15.91	13.99	1.04	–	–				
Behenate	C24 : 0	0.08	–	–	–	–	–	0.10	0.10	0.10	0.20	–
Nervonate	C24 : 1	0.06	–	–	–	–	–	–	0.10	0.30	–	–
Saturated fatty acids	–	13.18	19.77	37.06	25.70	62.59	7.40	48.45	6.60	16.40	11.40	47.80
Mono-unsaturated fatty acids	–	78.00	48.37	26.35	33.35	33.92	62.50	43.10	62.30	24.70	22.10	46.50
Long carbon-chain fatty acid	C20 – C22	8.66	1.89	37.30	39.52	13.10	3.10	0.14	3.60	1.40	1.40	1.00
References		[115]	[116,117]	[118]	[117]	[129]	[121,122]	[119,120]	[123]	[124]	[126,127]	[125,128]

alcohols, bio-gasoline, or bio-natural gas. The biodiesel produced from palm oil, as shown in Table 4, has the largest saturated fatty acids and stearic acid (C18:0) content, which amounts to 48.45 wt. % and 42.95 wt. %, respectively. The biofuels made from animal fats, such as tallow fat and fish oil, like marine fish oil and salmon oil, appeared to have a significantly larger content of saturated fatty acids than those from vegetable oils, such as corn oil and sunflower oil. The rapeseed oil biofuel was observed to have the lowest saturated fatty acids and much higher mono-unsaturated fatty acids, which reached 6.6 wt. % and 62.5 wt. %, respectively. Moreover, the biodiesel from *Camellia oleifera* Abel oil consists mostly of mono-unsaturated fatty acids (78 wt. %). The oleic acid (C18:1) of the *C. oleifera* Abel oil-biodiesel even amounts to 69.07 wt. % [115]. This biodiesel is thus considered to have an inferior oxidative stability, but superior low-temperature fluidity, and it is adapted to usage conditions in cold weather.

5.3. Selection of promising feedstocks for competitive biofuel production

5.3.1. Potential resource of vegetable oils for biofuel production

Vegetable oils are extracted from nuts, seeds, and even the leaves of plants. In addition, oilseeds of some bushes also provide a source of vegetable oils. Nowadays, the seeds of *Jatropha curcas*, *Pogamia Pinnata*, *Calophyllum inophyllum*, and castor beans have become common biofuel feedstocks. Some species of wild bushes cannot absorb enough nutrients and water because they grow on unfertile hillsides. Hence, such bush species generally contain neither a high amount of seed oil nor do they have a sufficient economic value [130]. Therefore, in order to increase the quality and quantity of oil sources for biofuel production, these oil crops are required to be properly selected, cultivated, proliferated, and even genetically modified.

The disadvantages of seed oil from *Jatropha curcas* and castor beans include the fact that its content is a toxic substance, manual collection is required, and the seed-oil is very expensive [131,132]. These disadvantages may be effectively resolved by the genetic modification of the plants and the design of automatic collection machinery for such plant seeds. The *Jatropha curcas* seed is considered to be a significantly important raw material source for biodiesel production in South-east Asia and India [133],

because it is adaptable and can be grown in barren areas, and its growth has almost no negative impact on tropical rain forests [134]. A few international petroleum companies have devoted many efforts into investigating the biological characteristics of *Jatropha curcas* crops and the efficiency of their conversion to biodiesel [135].

5.3.2. Lignocellulose materials for the production of second-generation biofuels

In comparison with the feedstocks of advanced-generation biofuels, the costs of vegetable oil feedstocks are generally higher [136]. The feedstock costs include growing the nutrients, the breeding, the manual collection of oilseeds, seed transportation, oil extraction, the refining process, and process management [137,138]. Although edible plant oil crops present a high quality of oil and the superior stability of the fuel properties, they are not encouraged to be used as raw materials for advanced-generation biofuels [139]. Instead, agricultural and architectural biomass wastes and lignocellulose materials are the primary feedstock sources of second-generation biofuels. The cost of these materials is relatively lower compared to the plant oil sources described above. In addition, the conversion of such waste into bioenergy complies well with both environmental protection and the development of a circular economy. Agricultural waste, such as the stalks, stems, leaves, etc. of barley, rice, wheat, maize, rye, and other grains, are promising feedstocks for second-generation biofuel production [140,141].

Ligneous plants often contain a higher calorific value than herb plants. In particular, trees are much more adaptable to growth on barren land, so as to avoid competition with food crops grown in arable lands. The lignocellulose materials of trees generally have a higher bioenergy conversion efficiency than herb plants, such as soybean, corn, sugar beet, sugarcane, etc. [142,143]. Sawdust, wood chips, and wood waste from the timber industry are also suitable feedstocks for the production of second-generation biofuels [144,145]. Moreover, the large-scale proper planning of afforestation can provide an important source of feedstock for biofuel production. Afforestation has additional advantages, including the absorption of carbon dioxide and other greenhouse gases, water and soil conservation, the prevention of landslides in forest areas, ecological protection, and the maintenance of a variety of biological species [146,147].

5.3.3. Feedstocks from genetically-modified crops (GMCs) and energy crops for the production of advanced-generation biofuels

Genetically Modified Crop (GMC) technology has been widely applied for increasing crop yields, improving specific crop characteristics, adapting to harsh environments, such as barren or contaminated soil, decreasing pests and diseases, reducing fertilizer and labor management, resisting climates that are too hot or cold, etc. [148–151]. After being carefully selected, some species of wild crops are also able to be genetically modified for domestication, and they can be adjusted to become more suitable feedstocks of biofuels. However, serious doubt continues as to whether GMC technology will destroy the eco-environmental and human gene factors [152,153]. Moreover, GMC technology is still not mature enough to meet all the targets of modifying crop characteristics, as described above [154,155].

Energy crops can be divided into two types of herbal and Short-Rotation Coppice (SRC). Herbal crops include grass, high famine grass, rye, and other herbaceous species. SRC includes poplar, eucalyptus, willow, bamboo, and other crops, which can be used as paper, building materials, or biofuel feedstock [156–158]. Boehmel et al. [159] found that the highest energy conversion efficiency of energy crops is willow in south-west Germany. Although corn has a higher output energy, it also requires a higher input energy for growing [160]. Miscanthus, which is also an excellent energy crop species, has the dominant advantage of having a high crop yield and low input energy that is required for growth, due to the large amount of fiber contained in its stem structure [161–163]. Suitable herbaceous energy crops include *Medicago sativa*, alfalfa, *Panicum virgatum*, reed canary grass, *Miscanthus sinensis* [164], and so on. Compared to ligneous plants, herbaceous energy crops have the dominant advantage of high management flexibility and a short rotation, and they can easily be changed for the type of crop cultivated [165,166]. Energy crops do not compete with human food and thus have become important feedstock sources for advanced-generation biofuels [167,168].

5.3.4. The most promising feedstocks from algae and organic waste for the production of advanced-generation biofuels

Used cooking oil and animal fat, Municipal Solid Waste (MSW), and paper mill waste are categorized as organic waste. The use of organic waste for biofuel production not only reduces the waste quantities and removal costs, but it can also lessen their

impact on pollution in the environment [169–171]. Potato peels, which can be recycled to produce bioethanol in the same potato chip factory, are also a representative example of converting organic waste into bioenergy [172].

Algae, including macro- and micro-algae, are the feedstocks with the most potential for manufacturing advanced-generation biofuels, due to their dominant advantage of having a rich lipid content, having a fast proliferation rate, their ability to be cultivated on infertile land and their ability to absorb carbon dioxide (CO₂) for the photosynthesis of plants [173]. Algae are regarded as the most efficient organisms among all terrestrial plants for converting CO₂ to form chlorophyll by means of a photosynthetic reaction [174]. They contain various quantities of triglycerides, lipids, protein and carbohydrates, and the production of diverse biofuels depends on the exact strain of the algae [175]. The five major microalgae groups are green algae, brown algae, red algae, blue-green algae (also termed as Cyanobacteria) and diatoms, which are frequently used to produce advanced-generation biofuels, particularly Cyanobacteria. Genetic engineering technology has been widely used to modify the chemical compounds and fuel properties of algae and to meet the required characteristics of feedstocks for advanced-generation biofuels [176].

The optimum fatty acid profiles, chemical composition and cost-effectiveness of biofuels are considered to be produced from the appropriate mixing of various feedstocks fractions [173]. The cost of biofuels is therefore competitive, due to an adequate compromise between the selling price and fuel properties on the global fuel market.

6. Conclusions

Diverse biomass materials, particularly lignocellulose materials, are continuously being exploited for the production of advanced biofuels with superior fuel characteristics. While other review studies only focus on one or two issues of biofuel feedstocks, the potential impact of biomass feedstock variability on the production technology and fuel characteristics of advanced biofuels is systematically reviewed in this article. The potential feedstock resources that are used for the production of advanced generation biofuels for the various fatty acids profiles of biofuels from different raw materials, and for the promising pretreatment procedures of feedstocks, particularly the biological pretreatment method, are also discussed and reviewed in depth in this study. This article will provide helpful information for researchers and industrial professionals

in the relevant biofuel fields. The major conclusions of this study are summarized below:

- (1) Advanced biofuels have much less of a negative impact on the ecological environment than fossil fuels. The contribution from advanced-generation biofuels in the global renewable energy market is expected to increase continuously.
- (2) The discrimination of various generations of biofuels is primarily based on the feedstock types that are used for biofuel production. A wider and more flexible selection, at much greater quantities, of promising feedstocks could facilitate the mass production and commercialization of advanced-generation biofuels.
- (3) A wide variety of feedstocks is available for the production of advanced-generation biofuels. The potential feedstocks can be classified simply into seven types, based on their sources. Among these, lignocellulose biomass, such as agro-industrial residue and architectural waste, is the most important type of feedstock for the production of second-generation biofuels, while microalgae and bacteria are used for third-generation biofuels.
- (4) Bio-alcohol, ranging from conventional sugar- and starch-based materials, to cellulose- and lignin-based materials, to various strains of microalgae, can be produced from biomass feedstocks. Some species of microalgae are able to produce bio-alcohol at about 5000–15000 gallons/acre, or 13–46 times that of switchgrass or sweet sorghum.
- (5) Vegetable oils that are acquired from seeds, beans, nuts, the leaves of plants, and even the oilseeds of some bushes, are the major raw biomass materials, particularly for first-generation biofuels. Some indigenous oil crops of wild bushes may need to be modified adequately, in order to increase the amount and quality of their seed oils for advanced biofuel production. Energy crops have become a significant biomass source for advanced-generation biofuels, primarily due to the fact they do not compete with human food, as well as their high management flexibility, and their short rotation.
- (6) The complex cell wall component of lignocellulose biomass is composed mostly of lignin compounds and is obviously different from the cellulose and pectin walls of microalgae. Biological pretreatment is considered to be most promising for advanced-generation biofuels, due to its dominant advantage of being a green procedure and having low downstream operating costs. The biofuel yield from microalgae

cells and lignocellulose biomass increased by 22–159% and 120%, respectively, after biological pretreatment, in comparison with those without any pretreatment.

- (7) The fatty acid profiles of feedstocks primarily determine the fuel characteristics and chemical composition of the biofuels produced. More double bonds and higher unsaturated fatty acids frequently cause property deterioration. The biofuels produced from animal fats and fish oil generally have a higher oxidative stability, but they have inferior low-temperature fluidity.
- (8) The unceasing exploitation of promising biomass feedstock sources is a crucial issue for fast and steady development of advanced biofuels. Genetically-modified technology is still immature to achieve the expected characteristics of biofuels from those modified crops. Furthermore, the possible impact of genetically-modified crops on the eco-environment and human genes requires further evaluation and tracking.

Declaration of competing interest

The author declares no conflict of interest.

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