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# Prospective Biodegradable Plastics from Biomass Conversion Processes

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Additional information is available at the end of the chapter

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## Abstract

The biomass energy source has been a promising renewable alternative for fossil fuels and their inevitable environmental impacts on Earth's life, from which the greenhouse gas (GHG) emissions and the environment pollution followed by consequent ecosystem imbalance are major concerns. Biofuels and bioplastics are well-known examples of renewable products obtained from biomass that has shown increasing potential to succeed the conventional fuels and plastics. However, biofuels and especially bioplastics have faced their main hindrance in their uncompetitive costs. Furthermore, the "drop-in" plastics are the market leaders, which reduce the carbon footprint but continue to state the biodegradability concern attributed to most of plastic products, the packaging sector. This chapter outlines the common features and feedstocks of biofuels and bioplastics aiming to support their associated production set toward the bio-based and biodegradable poly(lactic acid) (PLA) and polyhydroxyalkanoates (PHAs) as promising models with fast-growing production capacity forecasted for the next years and biodegradable solution for short-lived and disposable plastic materials.

**Keywords:** biofuel, bioplastic, biodegradable, PHA, PLA

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## 1. Introduction

Nowadays, the world has faced the side effects from fossil fuel dependence such as environmental pollution, greenhouse gas (GHG) emissions, and ocean acidification. Besides the large utilization of oil, coal, and natural gas to generate energy, a variety of petrochemical derivatives have also accounted to the ecological imbalance worldwide. The petrochemical plastics

are perfect examples of petroleum-based compounds, which imply a problematic ecological issue due to the high demand of their use for several applications, inappropriate discard, and environmental persistence [1, 2]. Conventional plastics take many decades to be decomposed in nature and produce toxins [3], particularly plastic additives (e.g., phthalates as plasticizers) and toxic monomer residues (e.g., vinyl chloride). Microplastics (particles less than 5 mm) in the oceans are seriously harmful to many aquatic organisms, and some of which inevitably end up in the human nutrition, the last consumer of this food chain [4].

As a result of the twentieth century development based on petroleum, coal, and natural gas exploitation, which were cheaply available, fossil fuels and their derivatives (e.g., fine chemicals, pharmaceuticals, detergents, plastics, fertilizers, lubricants, solvent, asphalt, and waxes) have become a major global threat directly linked to increasing levels of CO<sub>2</sub> in the atmosphere and consequent global warming. Since these fossil resources are not considered as sustainable and they are prejudicial from the ecological point of view [5], there have been rising concerns over their global impact, which has led to the development of technologies focused on the production of fuels and materials from renewable carbon sources, such as plant biomass [6]. Biomass has the potential to reduce GHG emissions by replacing fossil fuels. The combustion of biomass feedstock has been considered as carbon neutral or low-carbon fuel, since the plant crops assimilate carbon dioxide from the atmosphere during the growth. Accordingly, the so-called biofuels are a promising alternative to replace nonrenewable fuels [7, 8].

The main advantages of biofuels include their biodegradable and renewable properties; the generation of employment and technical development in rural areas; decentralized production from locally available domestic biomass; besides the combustion based on carbon dioxide cycle as mentioned above [8–10]. A global volume of more than 100 Bln L per year of conventional biofuels has been obtained, which is referred to as the first-generation biofuels including ethanol from sugar or starch crops and biodiesel from oils and fats. In addition, there have been many efforts focused on the second- and third-generation biofuels produced from a broad range of nonedible biomass feedstock [11].

Likewise, other chemicals and industrial products from fossil energy sources have been replaced by renewable ones. “Green” chemistry is a broad term referring to these compounds that support the sustainable development, from which the bioplastics can illustrate how the chemical industry is able to integrate sustainable innovation into a business model. On the other hand, the “green” chemistry companies must take into account efficient and less costly processes in order to make feasible their products commercialization [12]. Therefore, the economic viability of biofuel industry depends on facilities that integrate biomass conversion processes and equipment to produce value-added compounds, such as fuels, power, and chemicals. The larger the ability to derive value from biofuel, including byproducts and residues, the higher will be the feasibility of a bio-based industry from economic and environmental points of view [13].

A “green” biorefinery is a multifunctional and full-integrated system for biomass utilization. Besides the fuels obtained from “green” biomass, several products can be obtained from the “green” juice to the lignocellulosic materials, such as dyes, pigments, crude drugs, free amino acids, organic acids, enzymes, hormones, and minerals [5, 14]. Moreover, the biofuel byproducts have been a source of chemicals. Crude glycerol from transesterification of fats and oils,

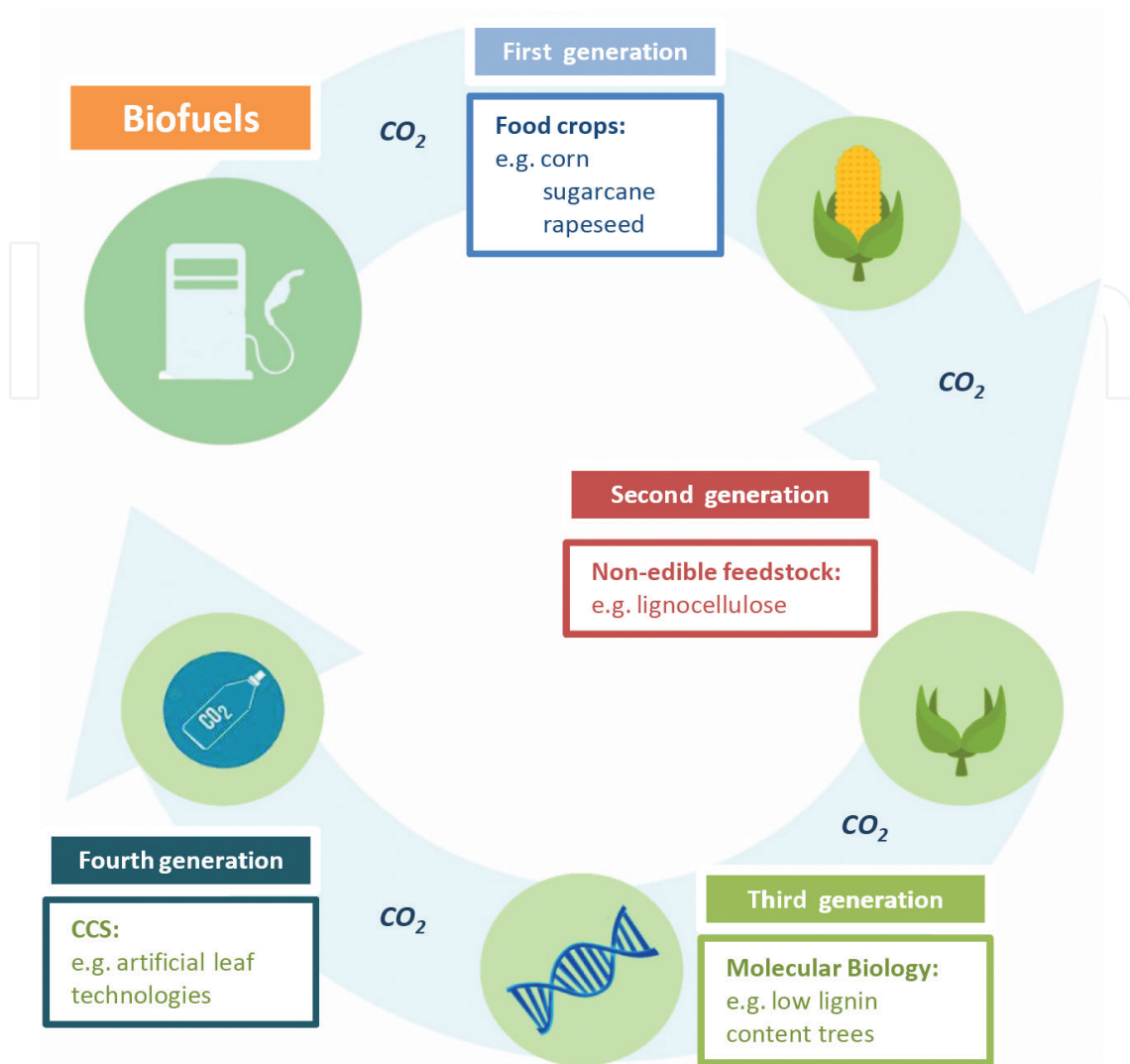
a byproduct of biodiesel industry, has been a promising feedstock to obtain a high diversity of products from microbial cultivation, which may be mentioned as 1,3-propanediol, dihydroxyacetone, succinic acid, propionic acid, ethanol, citric acid, biosurfactants, and bioplastics [15–24]. Lignocellulose hydrolysates are not only a source of the second-generation ethanol but also a feedstock of a multitude of chemicals such as xylose, mannose, galactose, acetic acid, ethylene, propylene, butadiene, xylitol, phenols, glucaric acid, glutamic acid, aspartic acid, syringols, eugenol, toluene, xylene, styrene, and others [14, 25–33].

Aside the environmental concern on fossil fuels being burnt into atmosphere, its plastic derivative is another critical issue, whose 60% of the total solid waste is discarded in landfills for 100 years of environmental persistence [1, 2]. Bioplastics from renewable energy sources that exhibit biodegradable characteristics are good candidates to replace short-lived and disposable plastic products, which accounts 50% of the total plastic production and so contributing for a significant diminishing of their long-term ecosystem intake and consequent harmful effects [4, 34, 35]. A biorefinery concept comprising biofuel and bioplastic production is an alternative solution to aggregate value to both industries and to improve the feasibility of a production set partially or totally disassociated from petrochemical compounds [23]. This chapter outlines a brief review on biofuels and bioplastics, and some of their interchangeable features in order to support a biorefinery model for bio-based and either biodegradable plastics belonging to biofuel production sets. Further, a special focus is dedicated to the production of poly(lactic acid) (PLA) and polyhydroxyalkanoates (PHAs) from biofuel feedstocks and byproducts as promising bio-based and biodegradable plastics with fast-growing development foreseen for the next years.

## 2. Biofuels: an overview

Biofuel refers to solid, liquid, or gaseous fuel obtained from renewable feedstocks, from which bioethanol and biodiesel are the most produced transportation fuel as potential substitutes for gasoline and diesel fuel [9, 36, 37]. According to their production technology, biofuels are classified into the first-, second-, third-, and fourth-generation biofuels (**Figure 1**). The first-generation biofuels are produced from edible sources, such as grains, oil seeds, sugar and starch crops, and animal fats. Well-established examples of the first-generation biofuels are ethanol from sugarcane in Brazil, corn ethanol in the USA, biodiesel from rapeseed oil in Germany, and palm oil-based biodiesel in Malaysia. The second-generation biofuels are obtained from nonedible feedstock, such as lignocellulosic materials including cereal straw, forest and wood residues, sugarcane bagasse, short-rotation crops, and vegetative grasses [37].

The second-generation biofuels are an alternative to mitigate the main concern about the first-generation biofuels: food versus fuel. An additional advantage is the utilization of agricultural byproducts and municipal solid wastes and thus lowering costs and improving the urban waste management [37]. The former Directorate-General for Energy and Transport has proposed the third- and fourth-generation biofuels, which are classified as advanced biofuels. The third-generation biofuels are obtained using molecular biology techniques, such as low-lignin content trees and genetically modified microalgae. The fourth-generation biofuels are those that should provide carbon capture and storage (CCS) processes with improved

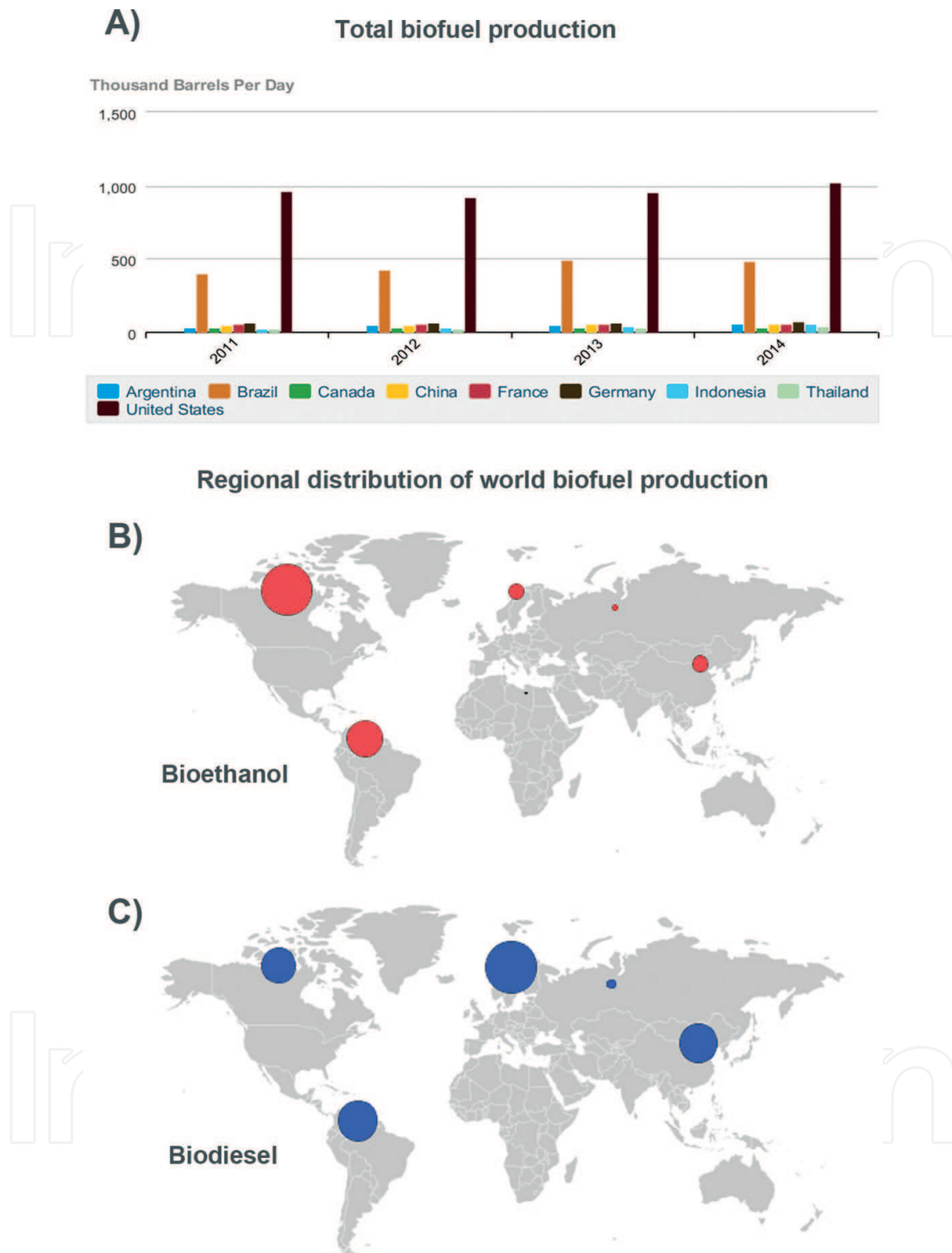


**Figure 1.** The first-, second-, third-, and fourth-generation biofuels.

CO<sub>2</sub> assimilation by genetically modified plants and CO<sub>2</sub> storage as geological formations by carbonation, crude oil, and gas headings [38].

The relative low increase in global oil production and rising prices of barrel between 2004 and 2009 were a boost to biofuel production [39]. Despite some previous experiences with biofuels such as in the 1970s with Brazilian National Alcohol Program [40] and in the 1990s with European biodiesel [41], only after 2003 major policy measures were legislated for promoting biofuel production in the EU and the USA followed by advancements in oil extraction technologies, which induced a global awareness about the requirement of alternative and ecological solutions regarding the depletion of petrochemical reserves and the environmental side effects from a century of its utilization. The International Energy Agency forecasts a percent global increase of transportation biofuels from 2% to up to 20% from 2012 to 2040, respectively [39, 42].

Nowadays, the USA, Brazil, and the EU have been the largest biofuel-producing countries whose the first-generation biofuels, bioethanol and biodiesel, are still the most well-established and current produced biofuels, which attend most of the commercial demand (**Figure 2**).



**Figure 2.** (A) Total biofuel production of main producing countries from 2011 to 2014. Regional distribution of world biofuel production in 2014: (B) bioethanol and (C) biodiesel [43].

However, there is still a big difference between the world ethanol and biodiesel production, while the first is predominant in the USA and Brazil accounting most of the biofuel production, the latter is mainly produced in the EU, which retains the largest biodiesel production [43, 44]. Bioethanol comprises more than 80% of liquid biofuels in the USA,

Brazil, Canada, Australia, and China, while the European biodiesel accounts for more than 60% of total biofuel produced in these countries [39].

A sustainable alternative to petrochemical fuels and the environmental concern with such fuels have also drawn the attention of the international scientific community, which is reflected in the increasing number of biofuel-related publications. Approximately 50 additional papers were published every year regarding biofuels from 1990 to 2005. After 2005, this expanding rate increased to 550 biofuel-related papers. Most of published papers on biofuels are still related to first-generation biofuels based on edible feedstocks, constituting 46% of biofuel publications from 1990 to 2014, while papers related to lignocellulosic biofuels total 40% of biofuel literature, from which remains 14% of published studies concerning algae third-generation biofuels [39].

Whereas bioethanol is the largest produced biofuel of the world, research studies on biodiesel production from vegetable oils constitute 60% of the literature on liquid biofuels. *Jatropha* and palm oil were the most widely studied feedstocks for biodiesel production followed by soybean and rapeseed oils. Among the most important lignocellulosic materials for the second-generation biofuel production are crop residues such as straw and bagasse; forest, municipal, and livestock wastes; and energy grasses. Finally, the algal feedstocks have received significant attention and have become one of the main biofuel categories. Therefore, the fast increase of biofuel-related publications can be considered as a direct result of research and development expenditure on biofuel science in the last years [39].

In 2015, several policies were finalized in favor of the biofuel market. In Brazil, the mandatory anhydrous ethanol blending ratio was increased from 25 to 27%. In the EU, the Renewable Energy Directive and the Fuel Quality Directive were reviewed in the transport sector by 2020, and the US Environmental Protection Agency proposed new mandates to increase the production levels of biofuels. Most of these political changes are driven by blending mandates and sustained fuel use to attend the demand of transportation sector. Future prospects report a modest expansion of the global ethanol production from 116 Bln L in 2015 to 128.4 Bln L by 2025, with half of this growth originating from Brazil, while a more prominent biodiesel production is expected for this period from 31 Bln L in 2015 to 41.4 Bln L by 2025 as a result of political incentives of the USA, Argentina, Brazil, Indonesia, and the EU [44].

Coarse grains and sugarcane are expected to remain the dominant feedstock for bioethanol production and vegetable oils to continue as the main biodiesel feedstock. Whereas the biodiesel production processes aiming at the utilization of nonagricultural biomass, waste oils, and animal fats are expected to develop in the EU and the USA, the second-generation ethanol from lignocellulosic materials is projected to share less than 1% of total ethanol production by 2025. According to these projections, biofuel production will consume 10.4% of coarse grains and 12% of vegetable oils. The ethanol industry will utilize 22% of global sugarcane crops to supply its production [44]. This prospect shows a continuous establishment of current technologies and evidences the need of developing competitive ones in order to make feasible the second-, third-, and fourth-generation biofuels, not only to spare petroleum reserves but also should replace this fossil fuel and, consequently, to diminish the environmental impacts attributed to its utilization with additional preservation of agricultural land intended for food crops.

Besides bioethanol and biodiesel fuels obtained from sugar fermentation and transesterification reaction of oils and fats, respectively, there are some alternatives consisting of liquid and gaseous biofuels, which are facing technological challenges of cost effectiveness and supporting structure for their economical viability. Pyrolysis is a high-temperature heating (300–900°C) of vegetative biomass in the absence of air resulting in three products: biochar, bio-oil, and syngas. Although this technique is relative old and was utilized in ancient China and by the indigenous Amazonians to generate biochar 100 years ago, the bio-oil is unstable, corrosive, and immiscible with hydrocarbon fuels and difficult to ignite, which needs a significant upgrading to be used as a petrol fuel alternative [41, 45, 46].

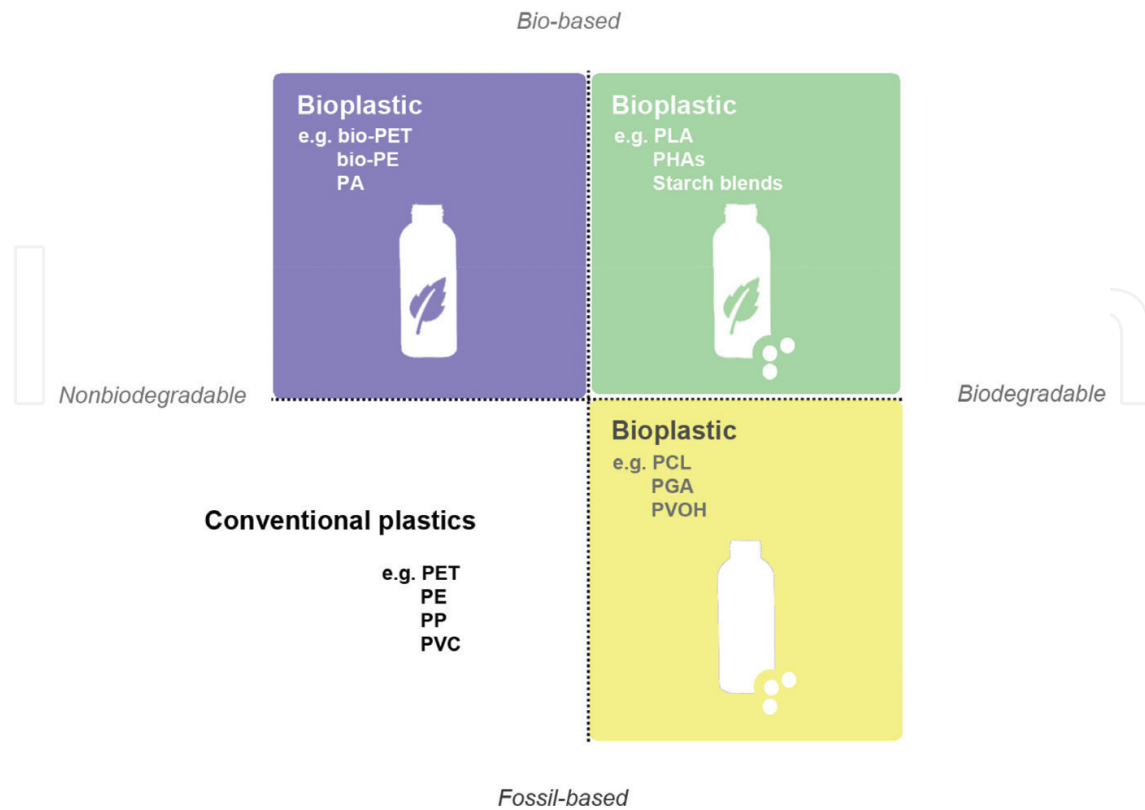
Some liquid biofuels such as butanol, liquefied biomass, syngas complexes, and sugar hydrocarbons have been developed to meet the existing fossil fuel specifications and hence to minimize the infrastructure and engine compatibility issues. They are the “drop-in” biofuels. Nevertheless, many efforts must continue to be made for the economical viability and the establishment of the “drop-in” biofuels as a renewable alternative in the future [41, 47]. Biogas is a gaseous alternative to natural gas from anaerobic digestion of organic wastes, which is constituted of methane, carbon dioxide, and a small percentage of sulfur hydroxide, water vapor, and hydrogen [41, 48]. Despite the minor biogas utilization in the energy sector, there is an impressive global potential for anaerobic digestion from agricultural and domestic wastes that could supply one quarter of the current natural gas and cover 6% of the global primary energy demand [41, 49].

Syngas is a gaseous fuel obtained from gasification or pyrolysis of vegetable sources and consists of carbon monoxide, hydrogen, carbon dioxide, and small percentages of methane, water vapor, sulfur hydroxide, carbon oxide sulfide, ammonia, and others. This product can be directly burned to generate electricity, or more commonly, it is purified for the synthesis of methanol, ethanol, methane, dimethyl ether, and other fuels. The hydrogen obtained from the syngas purification process can be used for electricity generation and as a vehicle fuel. The synthesis gas can also be processed to liquid hydrocarbons like diesel fuel via Fischer-Tropsch synthesis, which is an exothermal polymerization process converting  $H_2$  and CO into hydrocarbons and water. The product distribution depends on different process parameters like temperature, pressure, and the catalyst material resulting in short- or long-chain hydrocarbons. However, the purification process of syngas is still rather costly and energy consuming [10, 41, 50].

### 3. Bioplastics: bio-based and/or biodegradable plastics

Plastics are organic polymers with high molecular weight, which are synthetically produced. The expression bioplastics have commonly been used to make a distinction from petrochemical polymers, which is partially misleading, since a polymer derived from biomass is not necessarily biocompatible, biodegradable, and ecologically friendly [4]. Bioplastics fulfill at least one of these two characteristics: biomass derivative or biodegradability. Thus, a bioplastic must be bio-based, biodegradable, or both (**Figure 3**). Bioplastics exhibit the same or similar properties as conventional plastics with additional environmental benefits such as reduced carbon footprint, organic recycling, or both [51]. This is a broad and logical bioplastic definition adopted by European Bioplastic Association [4, 51, 52].





**Figure 3.** Bioplastics: bio-based and nonbiodegradable (blue); fossil-based and biodegradable (yellow); bio-based and biodegradable (green).

One of the bioplastic families is bio-based (or partially bio-based) and nonbiodegradable plastics, such as polyethylene (PE), polypropylene (PP), or polyethylene terephthalate (PET), also called as “drop-in” bioplastics, since they are the renewable alternative for petroleum-based plastics [53]. Polyvinyl chloride (PVC) is another commodity example of a nonbiodegradable, and in fact, one of the least environment-friendly synthetic plastics produced from renewable resources [4]. Bio-PE has been produced by Braskem (Brazil) on a large scale. A partially bio-based PET has been used for beverage bottles. Other examples of bio-based and nonbiodegradable plastics include polyamides (PA); polyesters such as polytrimethylene terephthalate (PTT), polybutylene terephthalate (PBT); polyurethanes (PUR); and polyepoxides. Important examples of bio-based and biodegradable plastics are thermoplastic starch blends (TPS), cellulose-acetate plastics (CA), poly(lactic acid) (PLA), and polyhydroxyalkanoates (PHAs). They are primarily used for short-lived applications, such as packaging and disposable products [53]. They are recognized as ecologically friendly, and some of them have been used for medical applications due to their lower or zero toxicity and high biocompatibility [54].

The third group constituted by non-bio-based and biodegradable polymers from fossil resources is a small group used in combination with other bioplastics, such as starch blends or applications, in which their biodegradable and mechanical properties [53] are desired. Examples of biodegradable petrochemical-based plastics are polycaprolactone (PCL), polyglycolide (PGA), and polyvinyl alcohol (PVOH) [4, 55]. Poly(butylene adipate-*co*-terephthalate) (PBAT) and polybutylene succinate (PBS) are bioplastics in class transition, since partially bio-based versions of these

compounds are current being developed. PBAT is produced from 1,4-butanediol (1,4-BDO), terephthalate, and adipic acid. The bio-based adipic acid is not available yet for commercialization, and thus, PBAT can theoretically be up to 50% bio-based. Likewise, PBS is produced from 1,4-BDO and succinic acid, which can also theoretically be 100% bio-based [56]. Therefore, in a near future, PBAT and PBS are expected to be into the family of bio-based and biodegradable plastics.

#### **4. Biofuels and bioplastics in a circular economy**

Since most of conventional plastics and fuels are made from petrochemical compounds, in the opposite way, bioproducts derived from biomass such as biofuels and bioplastics share several favorable characteristics. All the advantages concerning the biofuel and bioplastic utilization can be addressed to a sustainable process, which has mainly driven by energy saving and reduction of GHG emissions [4]. According to the Intergovernmental Panel on Climate Change (IPCC), the CO<sub>2</sub> concentration of 450 ppm within the global atmosphere is the maximum limit to avoid a global warming increase of 2°C, which means a reduction of 50% of GHG emissions by 2050 [10, 57]. One alternative to reducing GHG emissions is the use of low carbon fuels [10] and bio-based plastics [4]. Since they are obtained from plant biomass, the released CO<sub>2</sub> can be at least minimized by plant CO<sub>2</sub> consumption during photosynthesis, reducing the carbon footprint in the global atmosphere [5].

The rural development with employment opportunities can be achieved from biomass utilization to produce bioproducts such as biofuels and biopolymers [4, 5, 10]. The job creation is a global priority, especially in developing countries with high unemployment levels [10]. Most of references regarding biofuels and bioplastics agree that these bioproducts reduce the oil dependence as a sustainable alternative from diversified feedstock [3–5, 9, 10]. Most of crude oil reserves are centralized and located within countries under political uncertainties [10]. Among the top 15 countries with the world's biggest crude oil reserves are Middle Eastern countries, Venezuela, Russia, Libya, Nigeria, Kazakhstan, China, and Brazil [58]. Therefore, biofuels and bioplastics exhibit an advantage regarding the security of energy supply supported by a local production from available domestic biomass [10].

The research reports and reviews have constantly warned about the depletion of fossil fuel reserves like petroleum, natural gas, and coal [9, 36]. On the other hand, 100 Bln tonnes of crude oil and natural gas have been discovered in the last 40 years; however, the consumption rate of these resources has also increased. The US alone consumes 25% of total oil supply, while having 1.6% of global oil reserves. According to some authors, at the current consumption rate of oil supplies, the fossil fuel reserves will be depleted within 40–70 years [1]. Regardless the period of time for oil reserves depletion, it is a true fact that they are finite, and despite the recent increase in their exploitation, the future of petrochemical sources remains uncertain [39].

The rising consumer consciousness and environmental awareness are the biggest drivers for biofuel and bioplastic production. The global society has become aware of environment concerns and has continuously improved its sustainability standards. Therefore, there is a global trend on using products from renewable sources even in the face of low oil prices [4, 10]. Several

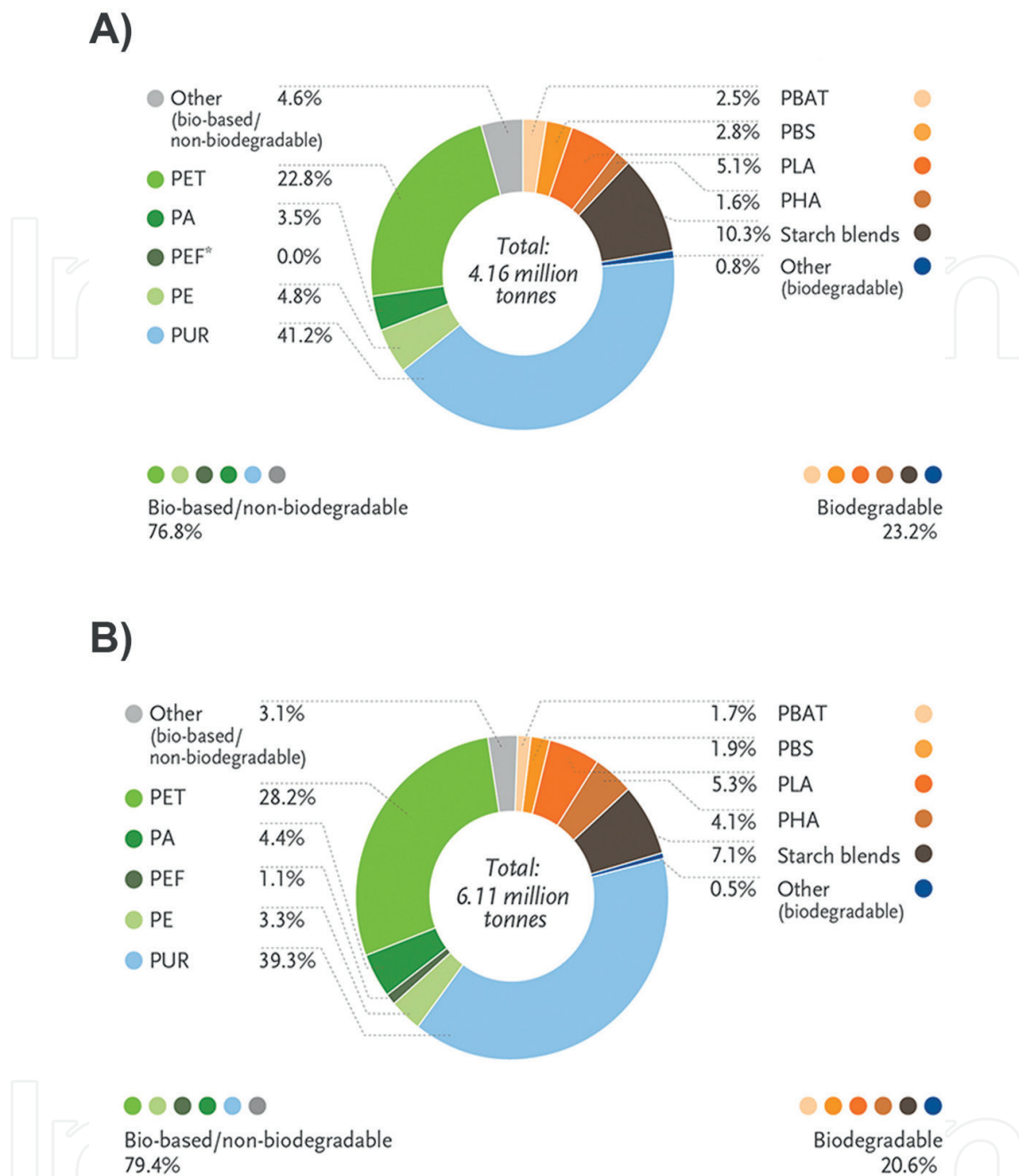
companies have followed this tendency and have associated their brand logos to renewable or biodegradable products as ecologically friendly companies with social and environment responsibility [4, 59]. Biodegradability and compostability are interesting properties of some products obtained from biomass, especially concerning short-lived or disposable plastic materials, which account 50% of the total plastic production [4, 34, 35]. In general, about 10% of municipal waste is consisted of plastics, primarily constituted of fossil-based PE, PET, PP, PS, and PVC [1]. Composting is other alternative solution for short-lived and disposable bioplastics, which can be disintegrated under microbial fermentation resulting in humus-rich soil. Therefore, composting is a good alternative for packaging materials, such as agricultural and horticulture films. Further, compostable plastics is an additional effort for waste stream management [51, 60].

## 5. Bioplastic market and future prospects

The bioplastic industry is a young and innovative sector [51]. The bio-based plastics share has increased from 1.4 to 2% of global polymer capacity, from 2011 to 2013 [56]. Thereafter, in recent years, this share has been stagnating, and the bioplastic growth rate has become the same of any plastic. While a prominent production capacity growth of 10% per year was observed from 2012 to 2014, this growth rate decelerated to 4% per year from 2015 onwards, which can be attributed to the lower oil prices, the unfavorable political support, a slower growth rate of the capacity utilization, and global debates about land and food crops use. However, the bio-based and biodegradable PHAs, the high-performance PA, and “drop-in” PET are exceptions that have shown fast increase rates of their production capacities [61].

In 2016, the bio-based plastic income was about \$ 15 billion worldwide [61] with more than 43% of total bioplastic produced in Asia. The USA, Latin America, and Asia have implemented measures to attract investment and promote market development to achieve their production goal. The European bioplastic market is still restricted by a lack of economical and political incentives for scaling-up its production capacity. As one can see in **Figure 4**, the worldwide production capacity is forecasted to increase from 4.2 million tonnes in 2016 to 6.1 million tonnes by 2021 [51]. If the bio-based thermosets such as epoxies, ethylene propylene diene monomer rubber (EPDM) and CA were included in this forecast, the increase values of bioplastic production capacities can be extrapolated to 6.6–8.5 million tonnes for the same period [61].

Currently, the bioplastic market is dominated by bio-based and nonbiodegradable plastics with highlights of bio-based PUR and “drop-in” PET. “Drop-in” plastics exhibit the same properties and are identical to their petrochemical counterparts and thus do not demand further adaptation for processing. Some bioplastics have lower material performance and end up being utilized for blending with petrochemical polymers. Therefore, creating high-performance biopolymers at a competitive cost is still a key concern [12]. PUR market share is expected to remain stable, whereas PET share is forecasted to grow from 22.8% in 2016 to 28.2% by 2021 [61]. One of the big investors of bio-based PET has been The Coca-Cola Company with its Plant Bottle technology [59]. Bio-based PE is another “drop-in” bioplastic, which has been obtained from sugarcane-derived ethylene by Braskem Company in Brazil [4]. Among the bio-based and biodegradable polymers, Starch blends and CA markets are



**Figure 4.** Global production capacities of bioplastics by material type in 2016 (A) and expected for 2021 (B) [51, 61].

expected to continue steady, and PLA and PHA production capacities are expected to considerably grow in the next years [61].

There are infinite possible applications for bioplastics including textiles, construction and building, electrics and electronics, consumer goods, agriculture and horticultures, and automotive, although their largest application field is still the packaging, which shared almost 40% of the total bioplastic market in 2016. This percentage is expected to increase to 42% by 2021 (Figure 5). In the automotive industry, bioplastics make cars lighter to save fuel and, consecutively, make them to reduce their carbon exhaustion [51].

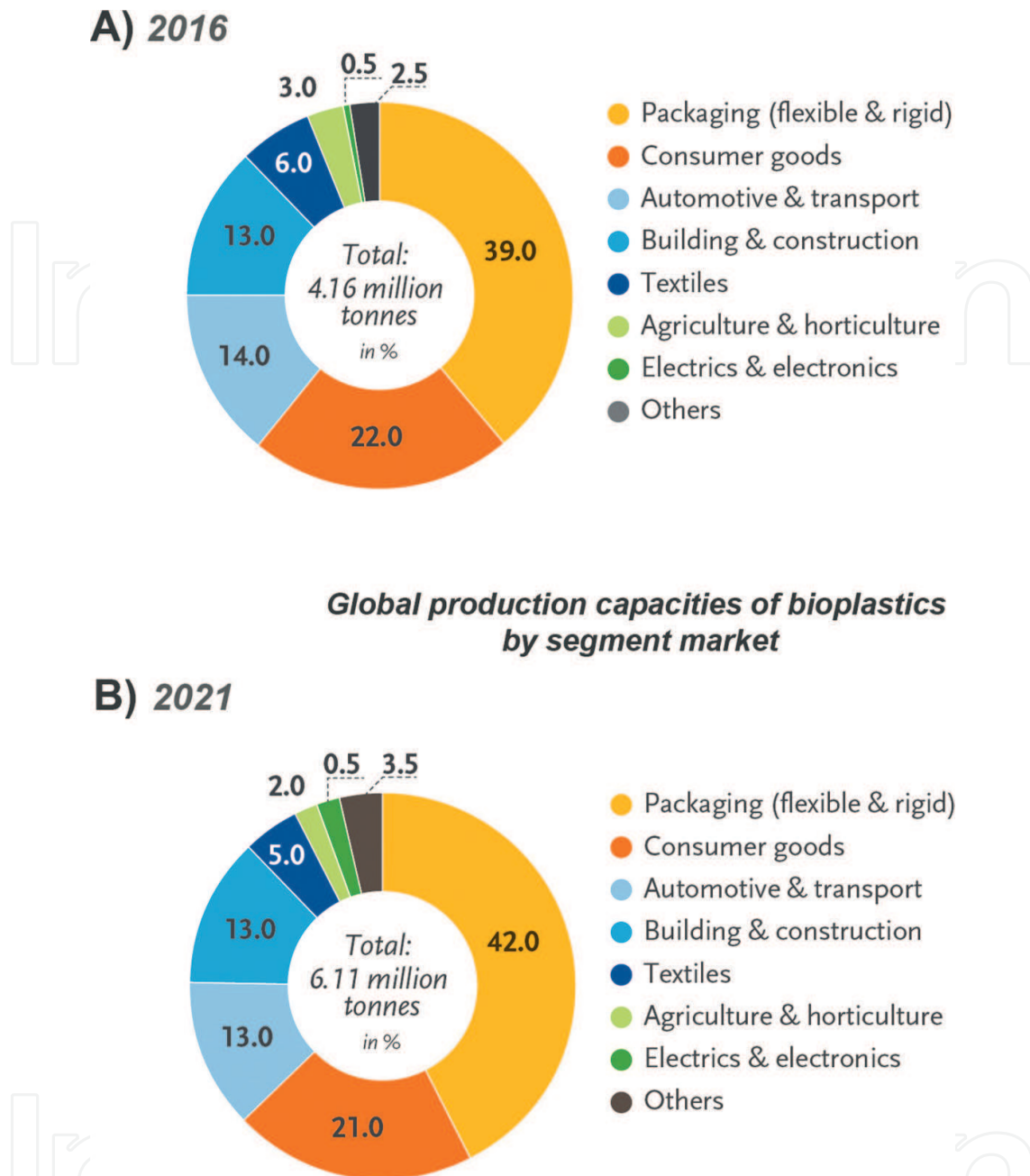


Figure 5. Global production capacities of bioplastics by market segment in 2016 (A) and expected for 2021 (B) [51, 61].

## 6. PLA and PHAs: promising bio-based and biodegradable plastics

Several companies have introduced starch and polyethylene blends as degradable materials for a number of short-lived applications, such as mulch films, beverage bottles, food containers, and plastic bags. Whereas starch component can be degraded, the polyethylene residues remain in the ecosystems. Therefore, many companies have failed associating plant-based blends with misleading biodegradable properties. Thenceforth, in order to restore the credibility of the bioplastic industry, the standard organizations have been concerned with distinguishing degradable, biodegradable, and compostable plastics [12]. Further, some countries

such as Italy and France have started to devote strong political support for biodegradable plastics, especially for the packaging sector, which is the biggest in the plastic market. The packaging industry has been interested in biodegradable plastics for short-lived and disposable applications. In agriculture, most of applications are limited to biodegradable plastics. Although the biodegradable polymers are not market leaders, they are expected to grow strongly supported by environmental concerns [61].

Among the aliphatic biodegradable polymers, the main population of degrading microorganisms in different ecosystems has followed the order: PHAs = PCL > PBS > PLA [55]. PCL is fossil-based [4], and currently, PBS and PBAT are not fully bio-based. PBS is constituted of 1,4-BDO and succinic acid that are primarily fossil-based, although they could theoretically be obtained from microbial cultivation. Bio-based 1,4-BDO entered the market only in 2016. BioPBS is produced exclusively in Asia by Public Company Limited and Mitsubishi Chemical Corporation (PTT MCC Biochem) in Thailand [62]. Additional projects are not expected for the next years due to low oil prices. PLA has attracted a growing interest and nowadays accounts 20% of biodegradable plastic market [4]. The most dynamic development is forecasted for PHAs, whose production capacity is still small. However, the PHA market is foreseen to grow almost three fold by 2021 [61].

### 6.1. Poly(lactic acid) (PLA)

Poly(lactic acid) (PLA), also called polylactide, refers to polymers based on lactic acid molecules, which is abbreviated as PLA. Therefore, the starting compound of PLA is lactic acid, a monomer that can be L(+) lactic acid or D(-) lactic acid due to the presence of a chiral carbon atom. The cyclization of two lactic acid molecules results in a dimer called lactide. Accordingly, there are two homochiral lactide L,L and D,D and a heterochiral meso-lactide L,D. *Lactococcus lactis* LL0018 and *Lactobacillus casei* produce L-lactic acid, while *Lactobacillus delbrueckii* LD0025 and *Sporolactobacillus inulinus* SI0073 produce D-lactic acid, with up to 99% purity. *Lactobacillus helveticus* LH0030 is able to produce a racemic lactic acid, containing almost an equal mixture of L-lactic acid and D-lactic acid. Thus, the final lactic acid content is directly dependent of the fermentation process. Thereafter, a major concern is the purification of culture broth in order to obtain pure lactic acid. The lactic acid polymerization methods provide high molar mass polymers with high chiral purity, which are primarily based on catalysts with Sn and Zn metal, resulting in polymers with molar masses up to  $10^6$  [63]. The most common route to obtain PLA is ring-opening polymerization of the intermediate dilactide. Direct condensation of lactic acid generally results in lower molecular mass [64].

The PLA currently available is based on linear macromolecules and presents low melting temperature. Consequently, more research must be developed aiming to improve the physical properties of such PLA [63]. PLA is a thermoplastic and is converted to a variety of products by injection molding, blow molding, foaming film extrusion, and fiber extrusion. The PLA applications include geotextile, agricultural film, packaging, 3D printing, absorbable sutures, and prosthetic devices [64]. The PLA is 100% bio-based and biodegradable under certain conditions. Nature Works is a leader company of PLA production. Among new bio-based polymers, PLA is the most well-established, and its market is expected to grow annually at a rate of 10% until 2021, with comparable prices to fossil-based plastics [61].

## 6.2. Polyhydroxyalkanoates (PHAs)

Polyhydroxyalkanoates (PHAs) are microbial aliphatic polyesters synthesized as intracellular granules under nutrient imbalance and excess carbon source by several bacteria [65]. PHAs are a family of polymers constituted of monomers ranging from 3 to over 14 carbon atoms with more than 150 different monomer composition [3, 52]. PHAs have been classified into short-, medium-, and long-chain length PHAs ( $\text{PHA}_{\text{SCL}}$ ,  $\text{PHA}_{\text{MCL}}$ , and  $\text{PHA}_{\text{LCL}}$ , respectively).  $\text{PHA}_{\text{SCL}}$  with monomers consisting of 3–5 carbon atoms exhibit thermoplastic properties, whereas  $\text{PHA}_{\text{MCL}}$  are constituted of monomers ranging from 5 to 14 carbon atoms, which are elastomeric materials. Poly(3-hydroxybutyrate) (PHB) is the most common and studied PHA. The PHA constituents are directly related to the carbon sources utilized for bacterial cultivations and the metabolic role of PHA synthases [3]. Such variety permits utilize PHAs in a large number of applications, such as packaging materials, biocompatible implants, and controlled drug delivery system [66].

PHAs are fully biodegradable and biocompatible and so are attractive for medical uses. They also meet the standard specification for marine degradability, which can be a biodegradable alternative for plastic wastes that end up within the ocean and are fragmented as microplastics. Furthermore, PHAs are compostable and at the same time exhibit good resistance to grease and oils besides boiling water [4]. Several companies are involved in the PHA market, although it is still small, mainly attributed to their relative high cost of production. However, PHA producers are optimistic, and several sugar companies are investing in PHAs, which are expected to triple their production capacity by 2021 [61].

## 7. Biofuel feedstocks for PLA and PHA production

The fermentation routes represent the most active areas of biopolymer production, which are generally performed at biorefineries based on particular agricultural feedstocks. A future trend is the utilization of multiple feedstocks according to the available resources and economic conditions, in order to increase the feasibility of bioplastic production [12]. This is also applicable to biofuels that are dependent on specific biomass sources, which are mostly terrestrial plants [9]. As aforementioned, PLA and PHAs are typically obtained from microbial cultivation and so can be adapted to multiple feedstocks. Particularly, PHA-producing bacteria are naturally very versatile and produce these biopolymers from many carbon sources. Next, it is shown some examples of PLA and PHA production from biofuel feedstocks and related byproducts, which may support a biorefinery model comprising biofuels and these bio-based and biodegradable plastics. Further, **Figure 6** presents a flow chart describing possible routes involving biofuels, PLA, and PHA bioplastics.

### 7.1. Starch

Starch is a mixture of glucans, and consequently, a source of glucose obtained from various plants [67]. Starch has widely been utilized for bioethanol production, especially in US, where it is mainly extracted from corn crops [11], and it is also a raw material for starch blends, an established sector of bioplastic market [61]. Only few lactic acid bacteria possess starch-degrading

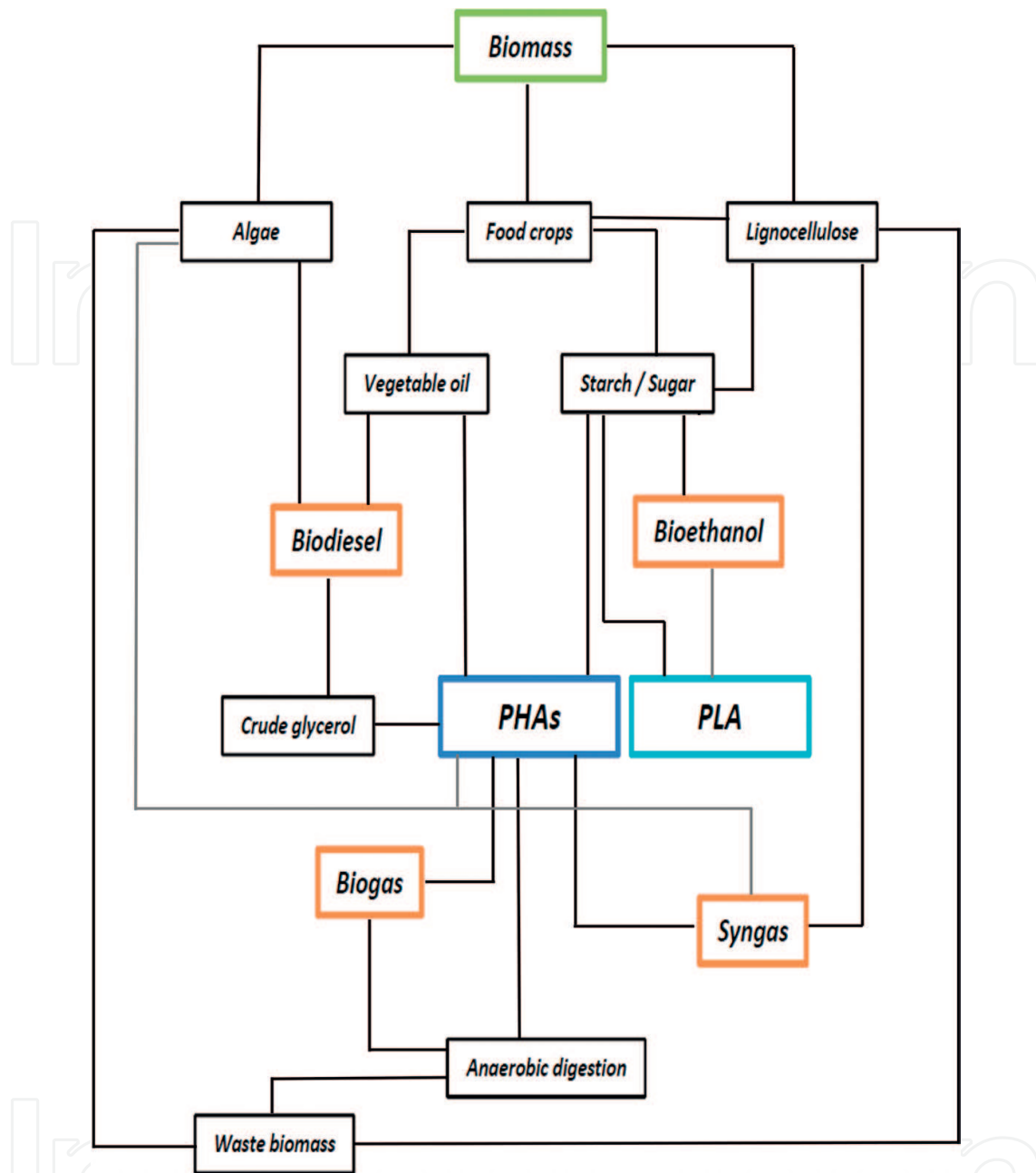


Figure 6. Common pathways for biofuels, PLA, and PHA production.

properties, and most of them exhibit low lactic acid production. However, many groups explore the acid or enzyme hydrolysis of starch compounds, such as wheat, corn, cassava, rice, potato, barley, rye, and sorghum, with subsequent use of sugars for lactic acid fermentation [67]. In the same way, starch has been a suitable carbon source for PHA production, including corn [68], potato [69], and cassava starch [70]. PHAs and PLAs have also been blended with starch materials, resulting in different physicochemical properties [4, 71].

## 7.2. Molasses

Molasses is a high sugar co-product generated from sugar manufacturing industries [72]. Sugarcane molasses have been utilized for ethanol production in Brazil, while beet molasses



is more common in Southeastern Europe, North America, and Asia, where it is primarily used for sugar production [40]. *L. delbrueckii* has been generally a lactic acid-producing bacteria using this carbon source, whose most abundant sugar is sucrose [73]. PHB is the most common product from molasses, since the sucrose content can be converted to acetyl-CoA and after to 3-hydroxybutyryl-CoA, the building block utilized by PHA synthase for PHB polymerization [3]. *Azotobacter vinelandii* and *Bacillus megaterium* are examples of PHB-producing bacteria utilizing sugarcane molasses [74, 75]. PHA<sub>MCL</sub> production has also been reported from *Pseudomonas corrugata* from soybean molasses [76].

### 7.3. Vegetable oil

Vegetable oils are feedstock for biofuels with biodiesel representing a well-known example, which is mostly obtained from soybean oil in US and Brazil and from rapeseed oil in Germany [37]. Intermediates from  $\beta$ -oxidation of alkanolic or fatty acids can provide hydroxyalkanoyl-CoA molecules for PHA<sub>MCL</sub> production by several bacteria such as *Pseudomonas* strains [3].

Some authors have reported PHA<sub>MCL</sub> production from waste cooking oil by *P. aeruginosa* [22]. *Aeromonas caviae* is also an additional example of bacterial strain that is able to synthesize the co-polymer poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) [P(3HB-co-3HHx)] from vegetable oil [77]. For the second-generation biofuel, nonedible oilseeds have been considered to avoid the debate food versus fuel, e.g., green seeds canola, high erucic mustard, Indian beech, etc., of which the most reported has been *Jatropha* [5]. Biosynthesis of co-polymers poly(3-hydroxybutyrate-co-3-hydroxyvalerate) [P(3HB-co-3HV)] and P(3HB-co-3HHx) from *Jatropha* oil has also been observed [78].

### 7.4. Lignocellulosic materials

The postharvest processing of food crops, forest, and wood residues generates large amounts of lignocellulosic materials, which consist of cellulose, hemicellulose, and lignin. Cellulose is a crystalline glucose polymer, while hemicellulose is amorphous and exhibits xylose and arabinose sugars. Lignin is a large complex of aromatic compounds. Lignocellulose materials can be converted to sugars by acid or enzymatic hydrolysis, which can further be used for ethanol production [5]. The bioethanol production from sugarcane bagasse in Brazil is a well-known example of the second-generation biofuel from lignocellulosic materials [40]. The bioconversion of lignocellulosic biomass by lactic acid bacteria is still limited, and a pretreatment including hydrolysis is necessary to convert these materials to sugars for lactic acid fermentation. Recombinant strategies involving heterologous expression can be a solution for this problem. Some authors have reported that a simple consortium of recombinant *L. plantarum* strains was able to produce cellulase and xylanase and thus showing potential for biomass conversion [67, 79].

*Saccharophagus degradans* is a natural PHA-producing bacteria from tequila bagasse [80]. However, the main focus on PHA production from lignocellulosic materials has been based on this substrate conversion into monomer sugars, which are used for microbial cultivation [72]. Sugarcane bagasse was submitted to acid hydrolysis, and then, it was utilized for PHB and P(3HB-co-3HV) production by *Burkholderia* sp. The co-polymer was obtained after addition of levunic acid to the medium, a 3HV precursor that can also be obtained from the hydrolysis of lignocellulosic compounds [81]. On the other hand, *Halomonas boliviensis* was able to

assimilate the sugars from enzymatic hydrolysis of wheat bran, in which it was utilized a crude enzyme preparation from *Aspergillus oryzae* [82].

### 7.5. Crude glycerol

Nowadays, the crude glycerol is mainly obtained as a byproduct from the transesterification process of oils and fats for biodiesel production, which generates about 10% glycerol [83]. Since purified glycerol is a high-value chemical, alternative solutions are required to crude glycerol refining and one of the possible keys for this issue is the glycerol utilization in its crude form as carbon source in microbial cultivations, in order to obtain value-added chemicals such as bioplastics [84]. A glucose-affected mutant of *Cupriavidus necator*, former *Ralstonia eutropha* and a traditional PHA-producing strain, is able to accumulate PHB from crude glycerol [85]. Additionally, new wild bacterial strains have been isolated from the environment such as *Pandoraea* sp., which is able not only to produce PHAs from crude glycerol but also from sugarcane molasses and waste cooking oil, although the best polymer yields were obtained from crude glycerol [24].

### 7.6. Biogas and syngas

Biogas is a renewable gaseous fuel alternative to natural gas, which is generated from anaerobic digestion of organic wastes by numerous bacteria. The main component of biogas is methane [41]. Over 300 bacterial strains, including *Methylocystis paravovus*, *Methylosinus sporium*, and *Methylocella tundra*, have shown the ability to synthesize PHB from methane [86]. Furthermore, the integration of PHA-rich biomass production into a municipal waste water treatment plant with sludge digestion has been proposed to support the biogas and PHA production [87]. Synthesis gas or syngas is another gaseous biofuel obtained from gasification or pyrolysis of biomass feedstock. Carbon monoxide, hydrogen, and carbon dioxide are the most abundant constituents of syngas [41]. The purple nonsulfur bacterium *Rhodospirillum rubrum* is able to utilize carbon monoxide and carbon dioxide and has also been a model organism for the synthesis of PHA<sub>SCL</sub> and PHA<sub>MCL</sub> from syngas [88].

### 7.7. Microalgae

Microalgae, such as blue-green algae, dinoflagellates, and bacillariophyta, can have from 8 to 31% of their dry weight constituted of lipids. They have been revealed as the best potential source for oil extraction compared to common biofuel crops [9]. Cyanobacteria are a good candidate for bioplastic production, which present the ability to grow in a variety of environments. Genetically engineered cyanobacteria were transformed with the genes encoding PHB synthesis, and their metabolisms have been extremely investigated aiming to establish new routes for PHA synthesis. Additionally, PLA/algae blends can be prepared and employed in bone and cartilage tissue engineering due to their biodegradability and biocompatibility [89]. Therefore, microalgae are new and promising branch not only for biofuels but also for bioplastics.

### 7.8. Simultaneous production of PLA and PHAs and their polymer blends

PHB production has been described in lactic acid bacteria for the genera *Lactobacillus*, *Lactococcus*, *Pediococcus*, and *Streptococcus*. *Cupriavidus necator*, *L. delbrueckii*, and *Propionibacterium* have been cultivated in a bacterial consortia, which resulted in a co-production of lactic acid and

PHAs. The implementation of co-cultures brings the advantage of increasing the range of substrates that can possibly be converted into accessible sugars by at least one of the members of microbial consortia [67]. Since PLA and PHA<sub>SCL</sub> exhibit similar properties, PHA/PLA blend is one of the most studied blends. PHA<sub>SCL</sub> generally presents higher melting temperatures than PLA, and thus, their utilization results in polymer blends with different properties. The poor processability of PHB is a drawback for its industrial applications, and the PHB/PLA blends represent a good alternative, which also brings improved properties to PLA. Additionally, PLA is cheaper than PHAs [90]. Therefore, the production of PHA/PLA blends is very advantageous for PHAs reducing their production cost [3, 63, 71].

### 7.9. PLA and PHA as sources for fuels

Hydroxyalkanoate methyl ester, a product from PHA esterification reaction with methanol, produces combustion heats similar to ethanol. The esterified PHA could be used as fuel additive for gasoline and diesel, with good properties of viscosity, flash point, and oxygen content. The implementation of PHAs as biofuels does not require highly purified PHAs, which can be obtained from activated sludge or waste water [91]. Lactic acid bacteria have been considered good candidates for biofuel production, such as ethanol and butanol. Other interesting compound that could be obtained from lactic acid bacteria is formate, which is a precursor substrate for hydrogen production by fermentation processes [67].

## 8. Challenges to be overcome by biofuels and bioplastics

Despite numerous advantages regarding the production of biofuels and bioplastics such as renewability and /or biodegradability, there are many concerns about bioproducts derived from biomass. Nowadays, the biggest economical challenges are still fossil fuel dependence and cost effectiveness. The oscillating oil prices and the current technology, the existing fuel supply, and infrastructure make conventional fossil sources and “drop-in” solutions the best economical choice for fuel and plastic markets [4, 41]. The concept of bioplastics as a “green” alternative for petrochemical plastics is a complex matter, and their environmental impact must be better evaluated. Composting and recycling properties are key concerns that should be taken into account for a case-by-case life cycle assessment [4].

Other environmental and economical concern on biofuels is the debate fuel versus food, which can also be applied to bioplastics. Currently, most of biofuels and bioplastics are made from agro-based resources and lignocellulosic materials [5, 51]. The food crops such as corn and sugarcane with high carbohydrates content are up to now the most efficient and profitable option for biofuel and bioplastic industries. Further, these plants are adapted to produce high yields resisting to pests and weather conditions [51]. The renewable energy has also been recovered from lignocellulosic materials as residues of food crops or short rotation of nonedible plants, organic wastes by anaerobic digestion, animal manures, algae biomass, and an endless variety of alternative biomass sources. However, these technologies for biofuel and bioplastic production are still in their infant stage, which needs many upgrades to become economically feasible in face of the conventional fuels and plastics [4, 41].

In 2014, the land area required to grow the total biomass ascribed to the global production capacities of bioplastics was approximately 680,000 ha. About 0.01% of the global agricultural area of 5 Bln ha would be enough to supply the current world's bioplastic production [51]. If it is considered that the bioplastic industry is not yet well-established [4] summed to the land area demanded for biofuel production, the agricultural area utilized for a bio-industry can increase significantly, which necessarily leads to an over production of agricultural commodities [10]. Therefore, the increasing of the efficiency of feedstock and agricultural technology is mandatory to compensate the future increase of land use for biofuels and bioplastics [51]. On the other hand, only 1.25% of the entire land biomass is used for food crops, thus the expansion of agricultural lands is another possible solution to attend biofuel and bioplastic demands [5]. Accordingly, the sustainability initiatives should implement development schemes, which must be adapted to protect the land, communities and biodiversity [9]. Whereas bioenergy and biofuels have received political support during commercial production such as quotas, tax incentives, market introduction programs, the bio-based chemicals and plastics have suffered the effects of still weak policies and underinvestment by the private sector. Therefore, a strong political support from the whole society and government is imperative for the establishment of the bioplastic industry [61].

## 9. Conclusions

Biofuels and bioplastics are certainly a present and especially a future trend, whose promising perspectives have faced its main delay in the low crude oil prices and the lack of cost effective technologies. Bioethanol and biodiesel are expected to continue growing in the next year as well-established first-generation biofuels, according to the current political incentives for blending mandates. The lignocellulosic fuels are forecasted to still share a small percentage of bioethanol production, while biogas, syngas from biomass pyrolysis, algae-derived, and other advanced fuels are in their infant stage, which reflects the need of technological upgrades toward cost-effective processes. The bioplastic market has also found in the "drop-in" plastics an economically feasible alternative to associate the bio-based polymers with an ecologically friendly image, which is partially misleading, since bio-based plastics can help to reduce the carbon footprint, though the market leaders such as bio-PET, PE, and PUR are not biodegradable. Most of the plastic wastes are constituted of short term and disposable products; hence, the establishment of not only bio-based but also biodegradable plastic market is mandatory to minimize the strong persistence of conventional plastics in the environment and their inevitable damage to ecosystems. PLA is a bio-based and biodegradable plastic with a well-established and continuous growing market, while PHAs are the versatile alternative, which can be obtained from a variety of biomass sources and are expected to triple their production capacity for the next years. A biorefinery model comprising biofuels and bioplastics is one of the possible solutions to add value and support a bio-based industry, since both products have found common feedstocks into biomass. Despite the challenges faced by the bio-based industry, the environment concerns and the increasing global sense of social and environmental sustainability will continuously be the engine for biofuels and bioplastics.

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