Biorefinery of Lignocellulosic Biopolymers

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Abstract - Lignocellulosic biomass has been widely investigated as a natural renewable source of feedstock to produce high value added products which can replace energy and materials obtained from non-renewable sources. Polymers are products largely employed in industry in many different applications, which nowadays are mostly produced from petrochemical derivatives, generating huge amounts of waste of difficult treatment prior to disposal. In order to replace these polymers derived from petroleum, efforts have been made in the development of biopolymers, in the biorefinery context, derived from biomass possessing physicochemical properties similar to those derived from petroleum so that they can successfully replace these materials. A review on the different types of biopolymers obtained from biomass, as polysaccharides, lipids, proteins, polyesters produced by plants and microorganisms, and other assorted biopolymers is accomplished. An evaluation of physicochemical properties and applications of different types of biopolymers is approached. It is also discussed about the degradability of biopolymers differentiating oxo-degradability and biodegradability. A brief historic background about biopolymers is also exposed.

Keywords - Biopolymers; Lignocellulosic biomass; Biorefinery; Degradability; High value added.

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1 INTRODUCTION

Energy improves the life condition and its consumption is directly related to the growth of any nation. A high rate of increasing human population and the consequent growing demand for food, energy and water are the most serious problems faced by the World, consequently, the increasing of residues amount. Current total global waste is around 6.5 billion tons, which 30% of it remain uncollected, the others 70% is led to landfills and dumpsites (CHANDRAPPA & DAS, 2012). Also, it is estimated that 10% of total global waste is plastic, which is relevant regarding the world plastics production that has grown from 1.9 tons to approximately 330 million tons between 1950-2013 (SELTENRICH, 2015). So, the use of oil derived products has generated a large concern about greenhouse gas emissions (GHG), as well as the high dependence on these products, which are not degradable.

The world reserves of oil, natural gas and coal by the end of 2014 were around 1700 thousand million barrels, 187 trillion cubic meters and 891 million tons, respectively. In addition, their production were close to 4220 million tons, 3460 billion cubic meters and 3933 million tons, respectively. Also, their consumption have increased from 1989 to 2014, correspondingly around, 30%, 80% and 65% (BRITISH PETROLEUM, 2015). The expectative for oil reserves, natural gas and coal to be eliminated is 41, 64 and 155 years, considering that even with new technologies these resources are not infinite so their replacement need alternative sources to reduce their consumption. Between all alternative sources, biomass presents high potential for liquid fuels, which consume a massive fraction of oil reserves from all over the world (SANTOS *et al.,* 2013).

All kinds of biomass (forestry, agriculture, aquaculture including algae and seaweeds, residues from industry and households as well as wood, agriculture crops, organic residues) can be used by biorefineries. For instance, paper industry can be (partly) expressed as a biorefinery (DE JONG & JUNGMEIER, 2015). Industry Experts (2012) states that "bioplastics constitute a class of plastics that are obtained from renewable biomass sources, such as vegetable fats and oils, corn starch, pea starch, sugarcane, potato starch, cellulose from trees, straw, cotton or microbiota, as opposed to fossil-fuel plastics, which are petroleum-based derivatives". Reaching the conditions for conventional plastics replacement by degradable polymers is the major interest to the society, particularly for short-term applications such as packaging, agriculture, etc (GAJANAND *et al.*, 2014). Therefore, the potential of biodegradable polymers has been predictable for a long time since they could be an remarkable way to overcome the limitation of the petrochemical resources in the future (AVÉROUS & POLLET, 2012).

The worldwide attentiveness in bio-based polymers has enhanced in the last years due to the desire and need to find non-fossil fuel-based polymers due to high variability in prices (fossil oil, biomass raw materials) and fluctuating demand request for robust systems to be competitive in the long term (DE JONG & JUNGMEIER, 2015). Furthermore, the elevated consumption of plastic materials has generated a high amount of residues, which are generally dropped in landfill sites, where still are constantly damaging the environment (KUMAR *et al.*, 2010).

However, even though the majority of synthetics polymers used are produced from petrochemicals, they are not biodegradable. Biopolymers have been the topic of many researches (BABU et al., 2013)**.** Moreover, these environmentally friendly products have increased 10-20% per year. Nevertheless, as reported by BBC RESEARCH (2014), the worldwide usage of bioplastics is expected to grow at a 41.4% compound annual growth rate (CAGR) from 2010 through 2015, reaching 3.2 million metric tons. In addition, in Europe it is expected to increase at a 33.9% compound annual growth rate (CAGR), reaching around 753 thousand metric tons through 2015. While in North America, the usage is expected to reach over 1.4 million metric tons and in South America the expectation is to reach less than 400 thousand metric tons till 2015 (AVÉROUS & POLLET, 2012).

The growing interest about a green and sustainable chemistry has also contributed to demand attention to biomass, and precisely on lignocellulosic feedstock. Biomass is a promise for renewable and infinite resource for chemicals, generally without competition with food industries compared to starch or vegetable oils (LAURICHESSE & AVÉROUS, 2014). By this perspective, biorefineries appear to be a solution, considering that they can be a facility, a plant, a cluster of facilities, or a process which can convert biomass into a range of products (DE JONG & JUNGMEIER, 2015).

In this paper, it will be presented an overview of biopolymers made from renewable resources. The review will focus on biomass and biorefineries sources, properties and trend applications for bio-based polymers using renewable resources that can replace petroleum-based polymers, such as polyester, polylactic acids, and other natural bio-based polymers.

2 BIOMASS AND BIOREFINERY

Growing concerns over climate change are stimulating a new economy of bioenergy. IEA (2013) reported over a medium-term, global bioenergy generation and capacity may scale up significantly reaching 560 TWh in 2018, the growth rate can reach over 65% from 2012, as well as the world biofuel production is projected to reach almost 140 billion liters in 2018. Therefore, there is a large expectative on biomass growth for the next years, and consequently more development of biorefineries.

2.1 Biomass definition

Biomass is any organic, which means it is a decomposable substance derived from plants (wood and agricultural crops, herbaceous and woody energy crops), municipal organic wastes as well as manure (IEA BIOENERGY, 2013). In accord with (VASSILEV et al., 2010), who says that biomass is a complex contemporaneous (non-fossil) product produced by natural resources (originated from growing land- and water-based vegetation via photosynthesis or generated via animal and human food digestion).

From a chemical perspective, biomass is a very complex combination of organic compounds and minor quantities of inorganic mixtures. Combined with abundant organic carbon, it is consistently rich in oxygen, while relatively poor in hydrogen. In addition, it counts with large quantities of water, small amounts of nitrogen, sulfur and other elements. Biomass can be basically allocated into four classes of compounds, which make up the bulk of the organic components: carbohydrates, lipids, proteins and lignin (FNR, 2012).

2.2 Biorefinery definition

As stated by (NREL, 2015), a biorefinery is a facility that incorporates conversion processes and equipment to produce fuels, power, and chemicals from biomass. A biorefinery can take advantage of the differences in biomass components and intermediates and maximize the value derived from the biomass feedstock, which have been identified as the most promising route to the creation of biobased products (Figure 1). Likewise, all designated efforts to scale up the economy potential of biomass is resulting in the idea of using renewable resources to employ and develop a sustainable chemistry, as well as its applications on biorefineries (SANTOS et al., 2013; CGEE, 2010). Still, an integrated biorefinery is a processing facility that integrates multiple chemical reaction pathways to convert biomass into value-added products along with heat and power (NG et al., 2015).

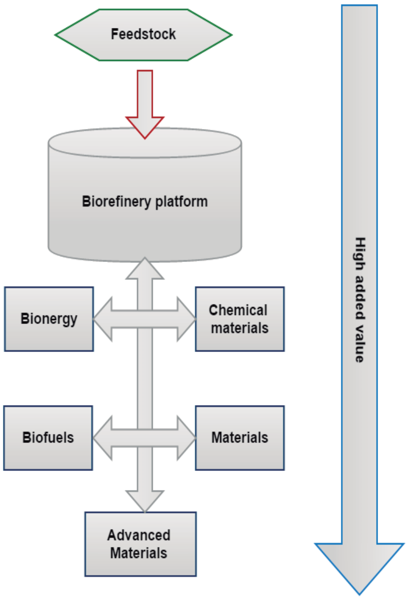


Figure 1. Biomass utilization in line with the concept of biorefinery.
Adapted from Santos *et al.*, 2013

Biorefinery can be divided into different platforms. According to FNR (2012) these platforms are biochemical, thermochemical, micro-organism and combined heat and power platform. All platforms can generate fuels, chemicals and materials. However, CGEE (2010) defends that biorefineries can be divided by the composition of biomass. For example, if a biorefinery is based on carbohydrates, biomass can be divided into groups of technology: biochemical (chemical and enzymatic hydrolysis, biochemical conversion and lignin utilization) and thermochemical platforms (pyrolysis, gasification and combustion). In addition, a biorefinery can be based on essentially lipids, such as seeds, which have a complex composition with high amounts of fatty acids with protein fractions and starch. In this case, the focus is on the food supply and biofuels industry.

2.3 Biorefinery Importance

According to (BALAT, 2006), the earth's natural biomass replacement represents an energy supply of around 3,000 EJ (3×10^{21} J) a year. It is not possible, however, to use all of the annual production of biomass in a sustainable manner. An analysis carried out by the United Nations Conference on Environment and Development (UNCED) presented a balance that biomass could potentially supply about half of the present world primary energy consumption by the year 2050.

In contradiction to the background of increasing globalization of industry, its services and flexibility necessity, it is crucial that special consideration is paid to interdisciplinary and high innovation in the area of research funding of biorefineries (FNR, 2012). As presented in Figure 2, the application of biorefinery concept has a massive importance due all the materials which could be provided from natural resources, not only biofuels but a large variety of chemicals. Another reason that can clarify the importance of biorefineries is that large companies such as Petrobras, Braskem-Quattor, Oxiteno, Shell and BP have invested technologies showing their perspectives about the future, where the biomass will become the base for renewable products, even with high expectative such as electrical car and possibility of reduction of biofuels consumption, which projection presents a growth rate of 10% per year for long-term (CGEE, 2010).

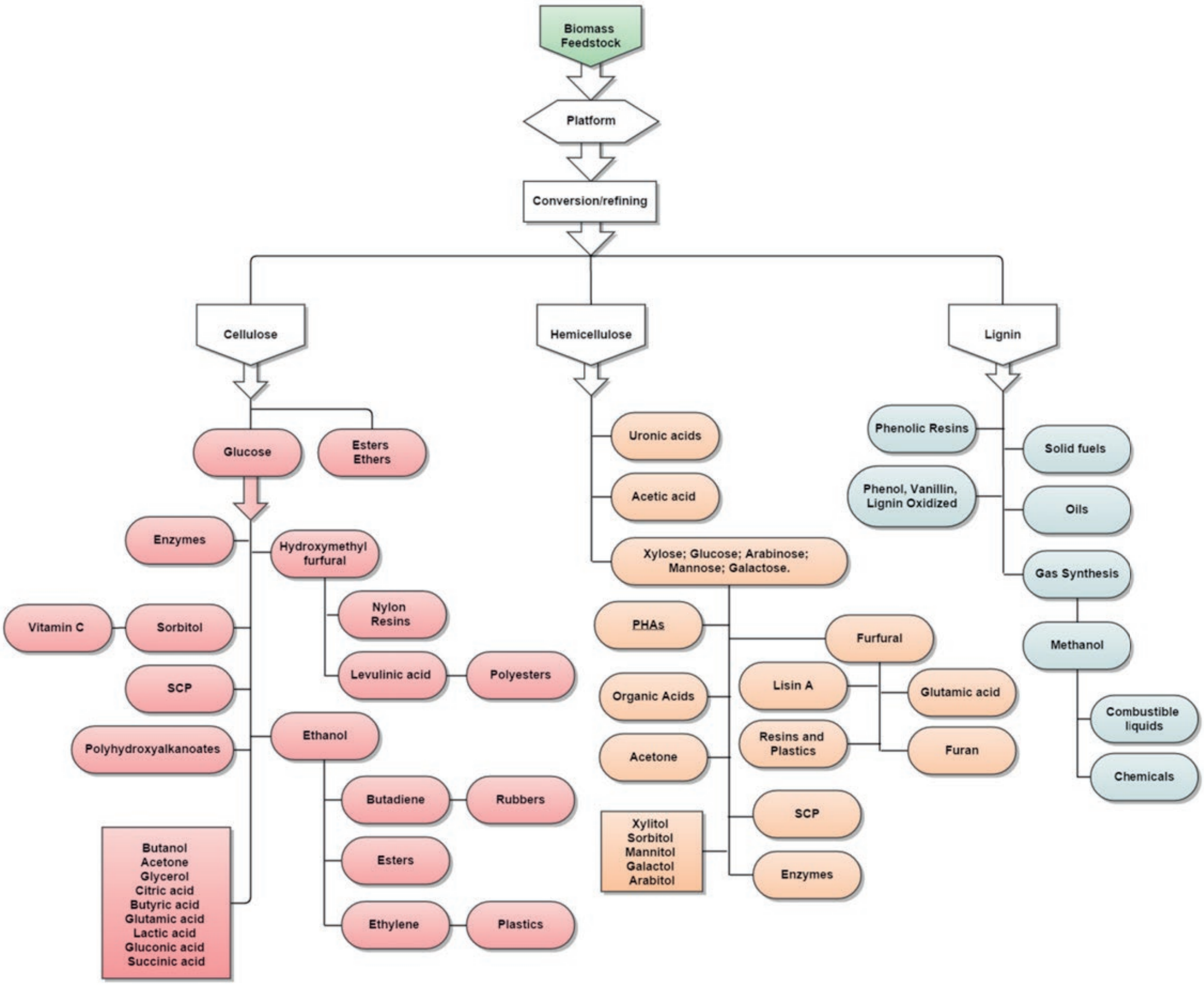


Figure 2. Some high value products from biorefineries.
Adapted from Santos et al., 2013.

2.4 Biorefinery feedstock

There are three main types of biomass materials from which bioenergy feedstock are derived: lipids, sugars/ starches, and cellulose/lignocellulose. Lipids are a feedstock source (energy-rich, water-insoluble molecules such as fats, oils, and waxes) resultant from nonwoody plants and algae. Some examples of lipid rich feedstock are soybean, oil palm and various seed crops.

In contradiction to the background of increasing industry globalization, its services and flexibility necessity, it is crucial that special consideration is paid to interdisciplinary and high innovation in the area of research funding of biorefineries (FNR, 2012). As presented in Figure 2, application of the biorefinery concept has a which are common agricultural sources of oils. Sugars and starches are the carbohydrates naturally found in food crops, such as corn grain, potatoes and sugarcane. Nonetheless, cellulosic/lignocellulosic biomass is compound of complex carbohydrates and non-carbohydrate molecules characteristically found in the leaves and stems of vegetation (WILLIAMS et al., 2015). Alternatively, a variety of biomass feedstock can be used to produce energy and bio-based products, as shown at Table 1.

The most important source in the future will be lignocellulosic biomass since this type of feedstock is widely available at moderate costs presenting less competition with food and feed production (DE JONG & JUNGMEIER, 2015). Moreover, carbohydrates (cellulose, hemicelluloses and starch) represent the main component in a biomass plant, serving predominantly as structure, storage, transport carbohydrates and in glycoconjugates (FNR, 2012).

Table 1. Some of the most common biomass feedstock. Source: Environmental and Energy Study Institute, 2015.

Types	**Resource Examples**
Grains and starch crops	Sugarcane, corn, wheat, sugar beets, industrial sweet potatoes, etc.
Agriculture residues	Corn stover, wheat straw, rice straw, orchard prunings, etc.
Food waste	Waste produce, food processing waste, etc.
Forestry materials	Logging residues, forest thinnings, etc.
Animal byproducts	Tallow, fish oil, manure, etc.
Energy crops	Switchgrass, Miscanthus, hybrid poplar, willow, algae, etc.
Urban and suburban wastes	Municipal solid wastes (MSW), lawn wastes, wastewater treatment sludge, urban wood wastes, disaster debris, trap grease, yellow grease, waste cooking oil, etc.

Table 2. Chemical composition of some lignocellulosic biomass which can be used aiming bioproducts production.

	% Cellulose	**% Hemicellulose**	**% Lignin**	**References**
Sugarcane straw	40-44	30-32	22-25	Adapted from: (GÓMEZ *et al.* 2010) (SANTOS *et al.* 2013) (SANTOS *et al.* 2012)
Sugarcane bagasse	32-48	19-24	23-32	
Hardwood	43-47	25-35	16-24	
Soft wood	40-44	25-29	25-31	
Corn stover	35	25	35	
Corncob	45	35	15	
Cotton	95	2	0.3	
Wheat Straw	30	50	15	
Sisal hemp	73.1	14.2	11	
Rice straw	43.3	26.4	16.3	
Coir	36-43	0.15-0.25	41-45	
Banana fiber	60-65	6-8	5-10	
Barley straw	31-45	27-38	14-19	
Lignocellulosic Biomass	30-50/ 35-50	20-40/ 20-35	10-30/ 10-25	(PANDEY *et al.* 2015) (SANTOS *et al.* 2012)

2.5 Lignocellulosic Biomass

As mentioned before, lignocellulosic biomass is a promising feedstock for future renewable fuels and bioproducts due its chemical and morphological characteristics (SANTOS et al., 2012). Lignocellulosic materials predominantly contain a mixture of chemical components (PANDEY *et al.*, 2015), being the main polymers cellulose, hemicelluloses, and lignin; also there are small amounts of other compounds such as ash, extractives, proteins, starch, etc. (SANTOS *et al.*, 2013).

The percentage of each one of these components depends on type of biomass, type of tissues, plant age and local climate conditions (SANTOS *et al.*, 2013). In addition, Vassilev *et al.* (2010) highlight that biomass composition depends on a variety of another factors, such as growth processes and conditions (sunlight, water, soil, air, pH, season, nutrients, etc.), fertilizer and pesticide doses used, plant distance from pollution sources (highways, cities, factories or mines), location (near sea or edge forest), harvesting time and collection techniques, transportation and storage conditions, variation of ash fraction, blending of different biomass types. Furthermore, the presence of lignin, hemicelluloses, ash, etc., and their spatial interlaces have created physical obstacles to defend cellulose from degradation (ZHAO *et al.*, 2012). In Table 2 chemical composition of different lignocellulosic biomass is exposed.

Cellulose ($C_6H_{10}O_5$) is a biopolymer (Figure 3) with major incidence in the world. Iit is one of the most important polysaccharides containing 6 carbons (C6) in the plant cell wall and has been broadly considered as feedstock in many industrial activities, e.g. for the pulp production. Cellulose is an unbranched linear polymer of glucose (PANDEY *et al.*, 2015). It is a polydispersed linear homopolysaccharide polymer consisting of anhydro-D-glucose units with a β-(1β4)-linkage (SANTOS *et al.*, 2013; PASANGULAPATI *et al.*, 2012). The degree of polymerization (DP) of natural cellulose is on the order of 10,000 (MAITY, 2015). There are four types of cellulose, native or natural cellulose which has a polymorph structure of cellulose I; however, cellulose I can be converted to other polymorphs, such as II, III, and IV through a variety of treatments (ZHAO *et al.*, 2012).

Hemicelluloses (Figure 4) are carbohydrates which present differences in their chemical composition and structure. In general, hemicelluloses may be described as heteropolysacharides from plant cell wall, which are formed by different kinds of C6 and C5 sugars: D-glucose, D-xylose, D-mannose, D-galactose and L-arabinose, D-mannose, D-glucuronic acid and L-fucose. In addition to various sugars, other compounds which are important in many industrial applications are also found, e.g. acetyl groups, uronic acids. Hemicelluloses are

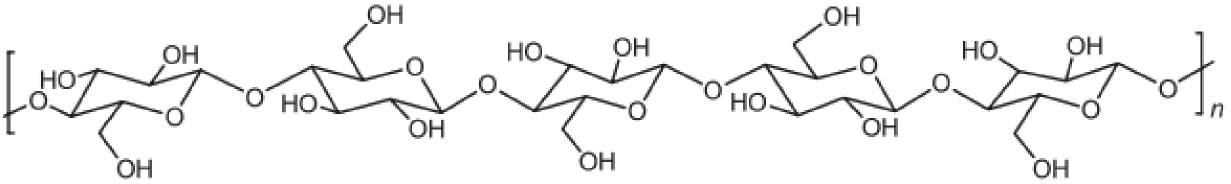


Figure 3. Chemical structure of cellulose molecule.
Source: (SANTOS *et al.* 2012)

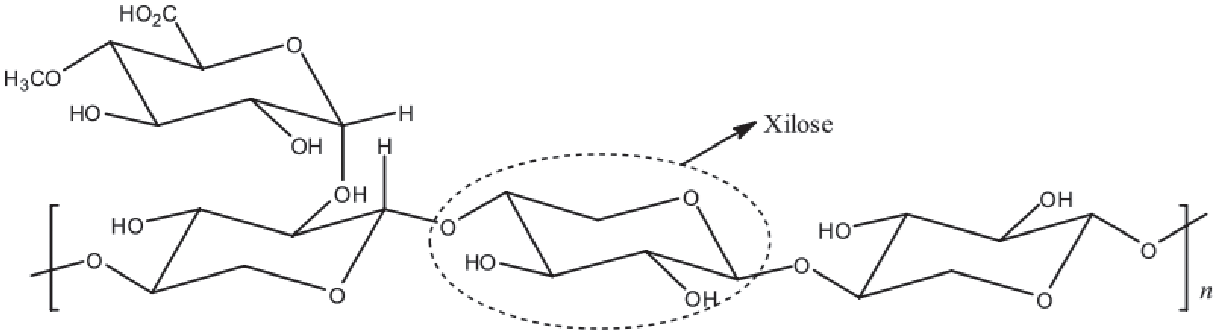


Figure 4. Chemical structure of hemicelluloses.
Source: Santos *et al.* (2012).

amorphous (RODRIGUES, 2011) and a large, complex carbohydrate molecule that helps to cross-link cellulose fibers in plant cell walls (WILLIAMS *et al.*, 2015). Moreover, hemicelluloses can form hydrogen bonds with cellulose and lignin, therefore they are entitled as “cross linking glucans” (PASANGULAPATI *et al.*, 2012). For instance, the principal hemicelluloses of hardwoods are O-acetyl-4-O-methylglucuronoxylans, in softwoods the main hemicelluloses are O-acetylgalactoglucomannans, and in Gramineae such as cereal straws, arabinoxylans are the most abundant, which are similar to harwood xylans but the amount of L-arabinose is higher (ZHAO *et al.*, 2012).

Lignin is an amorphous biopolymer which presents a chemical structure that distinctly differs from the other macromolecular constituents of lignocellulosic biomass. The chemical structure of lignin ($C_9H_{10}O_2(OCH_3)_n$) is irregular, where n is the rate of CH_3O for groups of C9: n = 1.4 for hardwoods and 0.94 in softwoods (RODRIGUES 2011). It is the second most important macromolecule (Figure 5) with large occurrence among biomass types (SANTOS *et al.*, 2013). It is a noncarbohydrate polymer that fills the spaces between cellulose and hemicelluloses (WILLIAMS *et al.*, 2015). Lignin is a very complex molecule generated of phenylpropane units linked in a three-dimensional structure (PANDEY *et al.*, 2015). The precursors of the phenylpropane units which form lignin are p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol alcohol (PANDEY et al, 2015; SANTOS *et al.*, 2012). The three basic monomeric units that constitute lignin, which vary between species and cell tissue type, are p-hydroxyphenyls (H), guaicyls (G), and syringyls (S) (ZHAO *et al.*, 2012; SANTOS *et al.*, 2013).

In lignocellulosic biomass, elements other than carbon, hydrogen, oxygen, and nitrogen are found. These compounds are called inorganic constituents; the total amounts of inorganic compounds are measured as ash. For each ton of burned bagasse, 25 kg of ash are produced, which represents the last residue generated by the sugarcane chain (SALES & LIMA, 2010). The ash from plants, such as trees (with long life cycle) have a mineral composition very different from plants that are harvested several times a year, for example cereals, because of the dynamic flow of nutrients within the soil. In their composition there a predominance of SiO_2 and CaO, and they present lesser amounts of Mg, Al, K and P oxides (NUNES *et al.*, 2016).

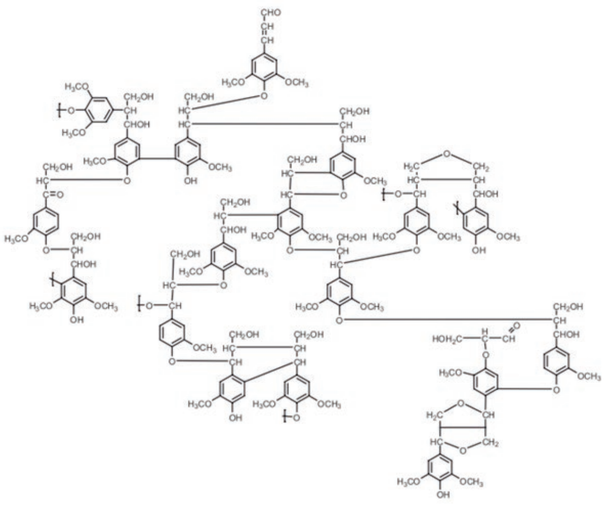


Figure 5. Chemical structure of eucalypt lignin molecule.
Source: Santos *et al.*, 2012.

3 BACKGROUND TO BIOPOLYMERS

Technology evolution is directly connected to the capacity of creating alternatives to improve life quality. In this last century, great part of technologic advances are linked to the use of polymers as an alternative material. Literature shows initial recording of formal use of polymers from the discovery of an extracted veneer of tree sap “Rhusvernicflua” by the Chinese, dated for about 3,000 years. Following the evolutionary chain, amber use with compression moldable properties was recorded in the first century B.C.. This thermoplastic resin was coming from fossilized trees. In the subsequent century, techniques for forming and shaping cipher animals for production tools are designed like combs and buttons and other items (WIEBECK & HARADA, 2005).

In the middle ages, mutually the development and the use of polymeric materials not claimed to be a significant impact in history until 1550, when it was developed natural rubber latex originated from a rubber tree in Central America. In 1839, Charles Goodyear developed a rough and resilient rubber, based on natural rubber study. Also, he added sulfur in the molecular structure of the rubber in the vulcanization process, marketing the polymer use as an engineering material. In 1845, Robert William Thompson developed the tire with natural rubber from improvements of its properties. The high demand of tires in the 21th century was responsible for marking of synthetic rubber development. (WIEBECK & HARADA, 2005)

At the end of 21th century, polymeric materials development was not instituted on systematic process of scientific and technological research, because the study of organic chemistry was nonexistent until then. Considering that Alchemists were focused on improvement process mining and processing of metals. This contributed expressively to the aim of development of metallurgy and inorganic chemistry (SHUMMER, 2003).

The studies of polymers were significantly driven by the need and demand for organic chemistry. In 1828, Friedrich Wöhler (German chemist) synthesized urea from ammonium cyanate, marking this period as the time for knowledge of new substances. During the period of 1844 until 1870, the discover of new molecular structures of organic substances increased expressively from 720 to 10,700 and inorganic from 3,250 to 5,300 (SHUMMER, 2003).

The mentioned period was noticeable form both quantitative and qualitative advancement of synthetic polymeric materials, which were fundamental to replace natural products like leather, wood, fibers, etc. In agreement, Christian Frederick Schönbein established (1846) the first synthetic polymer of cellulose nitrate, industrialized years after to manufacture billiard balls. Subsequent, Leo Baekeland developed bakelite in 1907, a product used until today (BOWER, 2002).

The 1920´s decade, has a significant importance due to a consolidated modus operandi of polymeric materials, focus on machines such as extrusion, injection, blow, etc. On the other side, the ascension petrochemical and stability of inputs of oil derivatives marked the timeline. In this period, the economics and the science increased outstanding with a concept presentation of macromolecules presented by Hermann Stauginger in 1922. (BOWER, 2002). In Brazil (1920’s), the first alcohol industry was implemented, 30 years before installation of the first petrochemical in the country. It is possible to produce a range of materials (such as acetic acid, ethyl chloride, diethyl, etc.) from ethanol (BASTOS, 2007). At the same time, U.S. started to manufacture isopropanol and glycol due the large demands from the Second World War. Over all, Brazil and Japan are petrochemical pioneers and these facilities were installed in 1952 and 1955, respectively (TORRES, 1997).

In 1928, Wallace Hume Carothers developed two polymer classes (polyester and polyamide) used in manufacture of fibers for synthetic tissues, applying their studies of condensation polymerization. In 1939, Dupont produced and sold nylon stockings. In 1941, polyester (ethyleneterephthalate) was applied in the manufacture of plastic packaging, registering the market PET. In the same time, Germany was the pioneer in polyurethane production and foam derived this material by polycondensation (BOWER, 2002).

In the late 2000s, the pressure for products with high environmental sustainability and the high oil prices, made possible the return of alcohol chemistry in the economic environment world-wide. As a result of these variables, "green plastic" was born based on three important factors which are "political correctness", "environmentally sustainable" and finally "economically viable" (SANTOS & HATAKEYAMA, 2012).

4 BIOPOLYMERS

The fundamental raw materials for polymers are petroleum, coal, natural gas and biomass, which contain the main constituents such as carbon, hydrogen, oxygen and nitrogen, and a few polymers may possibly contain other components as well as silicone, phosphorous, sulfur, metals and metalloids. Nowadays, the main source of these chemicals is petroleum, but because of declining crude oil reserves, global warming, socioeconomical and environmental concerns, any renewable resource has received attention. (KARAK, 2012). In addition, regarding the growth of oil prices and the need for biodegradable products, an alternative is the use of the biorefinery concept to produce biopolymers. For instance, from lignocellulosic biomass, e.g. sugarcane, it is possible to obtain methyl-cellulose, carboxymethyl-cellulose, cellulose, cellulose acetate, polylatic acid, acrylic acid, polyhydroxybutyrate (PHB), polyethylene (PE), xanthan gum, furfural resins, phenolic resins (SANTOS *et al.*, 2013).

4.1 Definitions

There is a different manner to describe biodegradable polymers. As defined by ASTM D883 (2000),"a degradable plastic in which the degradation results from the action of naturally occurring microorganisms such as bacteria, fungi, and algae." Also, compostable polymers when submitted to degradation by natural processes during the composting procedure, subdivide into CO_2, H_2O and inorganic compounds at a rate consistent with other compostable materials and leave no distinguishable toxic residue in the environment.

There are two categories of biodegradable: biodegradable plastics (as defined by ASTM) and oxo-degradable plastics, which contain inorganic additives that should cause the plastic to degrade by a process initiated by oxygen (DECONINCK & DE WILDE, 2013). However, a polymer may be degradable but not biodegradable as showed in Figure 6. The reason why it happens is because the term degradable is widely used to polymers or plastics that disintegrate by a number of processes such as physical disintegration, chemical degradation, and biodegradation by biological mechanisms (NIAOUNAKIS, 2015). Also, there are bio-based plastics which are not biodegradable, such as polyethylene, acetyl cellulose and nylon (TOKIWA *et al.*, 2009).

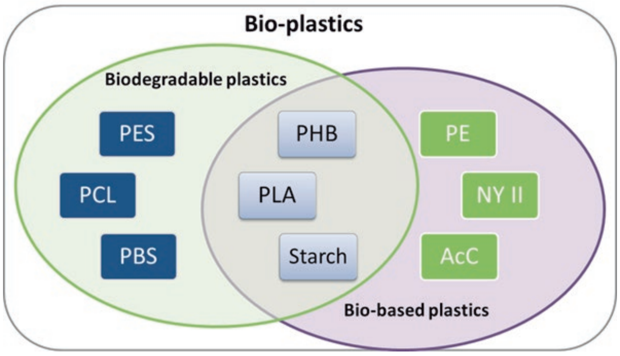


Figure 6. Bio-Plastics including bio-based and biodegradable plastics. Adapted from Tokiwa *et al.* (2009).

According to standards, mainly EN13342, compostable polymers should fulfill four principles: regarding chemical characteristics, material must contain at least 50% of organic material; regarding biodegradation, the product must achieve 90% of biodegradation within 6 months; concerning disintegration, after 12 weeks the product should disintegrate to less than 2mm; about ecotoxicity, the end compost should not generate negative effects to germination and growth of plants (DECONINCK & DE WILDE, 2013).

4.2 Polymer Oxo-degradation

Oxo-degradable polymers are currently used in Europe, Gulf States, China, Mexico and others. They are based on conventional plastics (such as PE-polyethylene, PS - polystyrene, PP- polypropylene and PET – polyterephthalate), which should degrade through a process initiated by oxygen and enhanced when light or heat are added to the process. The most common additives are metal salts of carboxylic acids or dithiocarbamates (based on Fe, Co, Mn, Ni). Moreover, the only guide for testing oxo-degradable plastics is ASTM D 6954 (2013). However, they are designated for degradation in landfill, because they only disintegrate if oxygen is present, if not it will remain inert (DECONINCK & DE WILDE, 2013).

4.3 Polymers Biodegradation

Biodegradation of polymers is a process merging activities such as biological, chemical and mechanical, which lead to change the chemical structure of a naturally occurring metabolic product as illustrated in Figure 7. Environmental circumstances for polymers biodegradation depend mostly on the growth rate of microorganisms that is faster under favorable growth conditions (such as for majorities of microbes growth at pH = 7.4 and a temperature of 37ºC) and a combination of microbes (*Aspergillus, Psedomonous, Actinomycetes*, etc.), which is enhanced than compared to only one specific microbe. Generally, higher the hydrophilicity, higher will be the rate of biodegradation (KARAK, 2012).

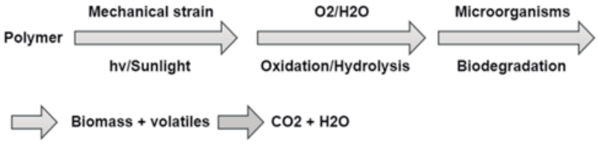


Figure 7. Biodegradation of vegetable oil-based polymers by physical, chemical and biological action.
Adapted from Karak (2012).

There are several biological waste treatment alternatives for biopolymers, as shown in Table 3. These options afford different conditions in terms of temperature, oxygen, and microorganisms for the rupture of biopolymers. Also, it can be an aerobic or anaerobic process (NIAOUNAKIS, 2013).

According to ASTM D883 (2000) "biodegradation of polymers is determined by the visual and/or measurement of changes in mass and physical properties." Considering biodegradation as a general term, which a polymer must present a specific performance, Table 4 summarizes all standards related to it, as well as test methods for industrial composting, marine and anaerobic digestion and active environmental landfill.

Table 3. Types of biological waste treatment for biopolymers.
Adapted from Niaounakis (2013).

Temperature	**Anaerobic (bacterias without fungi)**	**Aerobic (bacteria with fungi)**
50-60ºC	*Thermophilic digestion:* Chemical pulp, starch, PLA, starch/PCL, PHA	*Industrial composting* Chemical and mechanical pulp, PLA, starch/PCL, PHA, PBAT
< 35ºC	*Mesophilic digestion* Chemical pulp, starch, starch/PCL, PHA	*Home composting:* Chemical and mechanical pulp, starch, starch/PCL, PHA, PBAT

Table 4. Biodegradation Standard.
Source: Halley & Avérous (2014).

Industrial Composting Environmental			
Region	**Performance Specification**	**Test Method**	**Measurement Method**
Australia	ISO 17088	ISO 14855	CO_2 measurement
Europe	ISO 17088/ EN 12432	ISO 14855	CO_2 measurement
Japan	ISO 17088	ISO 14855	CO_2 measurement
The United States	ASTM D6400	ASTM D5338	CO_2 measurement
Marine Environmental			
Region	**Performance Specification**	**Test Method**	**Measurement Method**
Australia	None	ISO 14851/ ISO 14852	CO_2 measurement
Europe	None	ISO 14851/ ISO 14852	CO_2 measurement
Japan	None	ISO 14851/ ISO 14852	CO_2 measurement
The United States	ASTM D7081	ASTM D6691	CO_2 measurement
Anaerobic Digestion Environmental			
Region	**Performance Specification**	**Test Method**	**Measurement Method**
Australia	None	ISO 14853	CO_2 measurement
Europe	None	ISO 14853	CO_2 measurement
Japan	None	ISO 14853	None
The United States	ASTM D7081	ASTM D5511	CO_2 measurement
Active Landfill Environmental			
Region	**Performance Specification**	**Test Method**	**Measurement Method**
Australia	None	None	-
Europe	None	None	-
Japan	None	None	-
United States	None	D5526/ D7575	CO_2 measurement

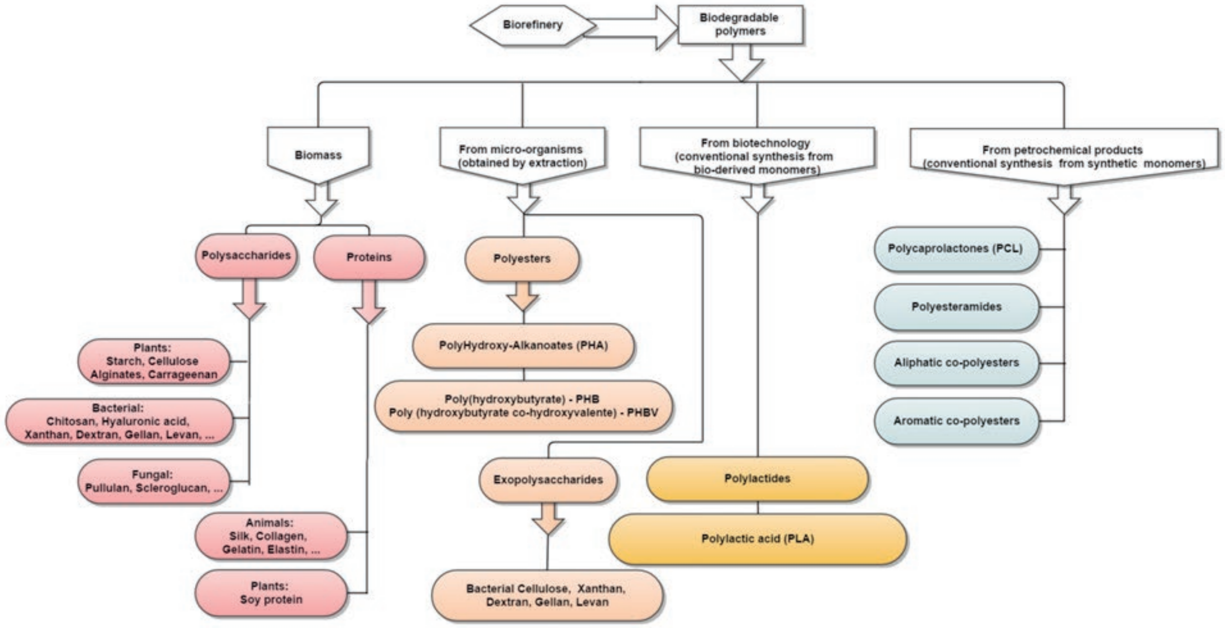


Figure 8. Categories of biodegradable polymers
Adapted from: Novak et al. (2014); Avérous (2013).

4.4 Types of Biopolymers

Biopolymers are made by the replication of many identical or similar small molecules covalent linked to form a long chain (KARAK, 2012). Furthermore, biodegradable polymers also called biopolymers, can be organized according to their chemical composition, synthesis method, processing method, economic importance, application, etc. Also they are divided in compostable polymers into derived from renewable and petrochemical (CLARINVAL & HALLEUX, 2005; RUDNIK, 2013) (Figure 8).

There is a variety of manners to classify biopolymers. According to Clarinval & Halleux (2005), biopolymers from natural resources can be sorted into six groups regarding to chemical point of view such as polysaccharides (starch, cellulose, chitosan, lignin), proteins (gelatin, wheat gluten), lipids (plants oils, animal fats), polyesters produced by micro-organisms or by plants (polyhydroxyalkanoates, poly-3-hydroxybutyrate), polyesterssynthesized from bio-derived monomers (polylactic acid), and assorted polymers (natural rubbers and composites). However, from Rudnik (2013) perspective, biopolymers that are produced from petroleum sources can be organized into five groups regarding their preparation method such as aliphatic polyesters and copolyesters (PBS - poly(butylene succinate), PBSA – poly(butylene succinate adipate)), aromatic copolyesters (PBAT - poly(butylene adipate terephthalate)), PCL - poly(ε-caprolactone), PEAs – polyesteramides and PVA – poly(vinyl alcohol). Another point of view is presented by Santos *et al.* (2013) that show some examples of biopolymers that can be acquired from sugarcane.

4.5 Polysacharides based

4.5.1 Starch Based

This polysaccharide polymer is generally the largest source of carbohydrates that has been intensively studied in order to produce thermoplastic polymers to replace some petrochemical polymers (JIANG & ZHANG 2013). The most important sources of starch are corn, wheat, potato, tapioca, rice (DECONINCK & DE WILDE, 2013) maize, cassava, bananas, sorghum and yeans (CARVALHO, 2013). In order to produce a thermoplastic material, the natural crystalline arrangement of starch must be fragmented. It is achieved by the application of heat, pressure, mechanical work or by addition of plasticizers, for example glycerine, polyols or water (CLARINVAL & HALLEUX, 2005). Besides, Jiang & Zhang (2013) state that starch occurs in the form of discrete granules and is compost by a mixture of linear amylose and amylopectin, which is a highly branched and high molecular weight macromolecule composed mostly of α-(1/4)-D-glucopyranose units, with α-(1/6)-linkages at intervals of approximately 20 units (Figure 9). Deconinck & de Wilde (2013) exposed that applications can be for packaging, films, catering, foam, plant pots, etc. Also, its end life application depends on the used copolymer, but biodegradability is a significant added value for organic collection bags, mulching film and body bags.

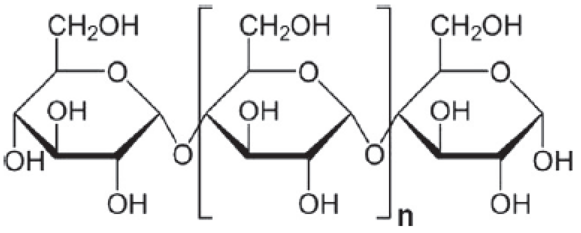


Figure 9. Starch chemical structure.
Adapted from: Jiang & Zhang (2013).

Deconinck & de Wilde (2013) provided benefits and challenges of starch based biopolymers. The positive points highlighted were that they are renewable sources, can be potentially biodegradable as industrial and home composting, heat resistance is up to 110°C, it is permeable and can be produced by the same conversion process that non-degradable plastics. However, the negatives aspects focus on possible competition with food crops and also, it has higher cost comparable with conventional polymers.

4.5.2 Cellulose Based

This polysaccharide polymer (as mentioned before and illustrated in Figure 3) has a composition similar to starch (JIANG & ZHANG, 2013). Some examples of industrial applications include the production of pulp, paper, membranes, dietary fibers, explosives and textiles (CLARINVAL & HALLEUX, 2005). Deconinck & de Wilde (2013) informed that applications designated for cellulose based polymers could be for instance, packing (films and twist wraps), tape, and envelope windows. Moreover, its life options are industrial and home composting, by anaerobic digestion. Cellophane still is biodegradable in soil, water and marine conditions. It is possible to recycle cellulose acetate with paper and cardboard.

Deconinck & de Wilde (2013) say that for cellulose based biopolymers, benefits are similar to starch. Some challenges reported are the use of carbon disulfide for cellophane production which has a negative contribution to LCA due to high energy and water consumption for this purpose. Also, biodegradable plastics from chemicals, under thermophilic conditions, can produce industrial composting by anaerobic digestion. But, negative aspects are low heat resistance, gas barrier properties and only a few types can be degraded at low temperature. Figure 10 shows some of organic acids that can be produced from cellulose.

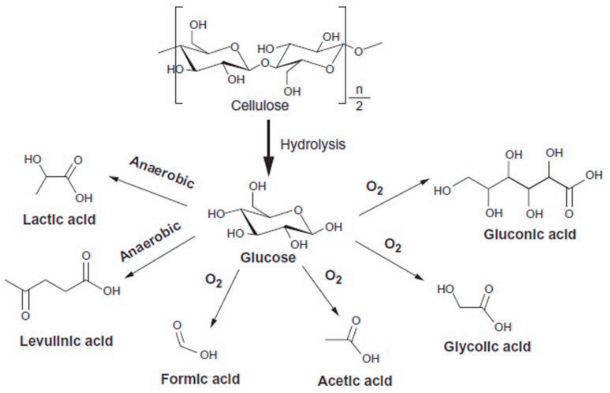
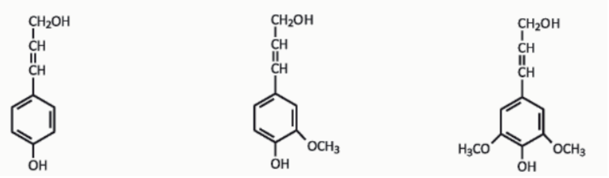


Figure 10. Organic acids produced from cellulose.
Adapted from: Chen (2015).

4.5.3 Lignin Based

Lignin (one of the main components of wood) is a very stable and complex product, water insoluble and resistant to an amount of physical and chemical treatments. Typically, the rejected liquor from pulp mills is the source of commercial lignin, which involves sodium ligninates or lignin sulfonates. The chief components of lignin are p-hydroxyphenyl, guaiacyl and syringyl (Figure 11). Also, some applications can be car dashboard panels, computer or television frames; fasal that look slightly like wood and can be pulverized, decorated, or varnished in the same way as wood; lignopol is in the form of pellets, which look like wood and can be milled; ecoplast is composed of wood powder, starch and a binder. It can be injected or thermoformed; napac is produced to resist exposure to UV light and its applications are flower pots, CD boxes, interior car parts and non-food packaging (CLARINVAL & HALLEUX, 2005).



p-Hydroxyfenyl Guaiacyl Syringyl

Figure 11. Structure of the main subunits of lignin precursors.
Adapted from: Clarinval & Halleux (2005).

4.5.4 Obtained via chemical synthesis

These biopolyesteres have many characteristics in common with conventional non-degradable polyesters (DECONINCK & DE WILDE, 2013). Bacterial fermentation of carbohydrates

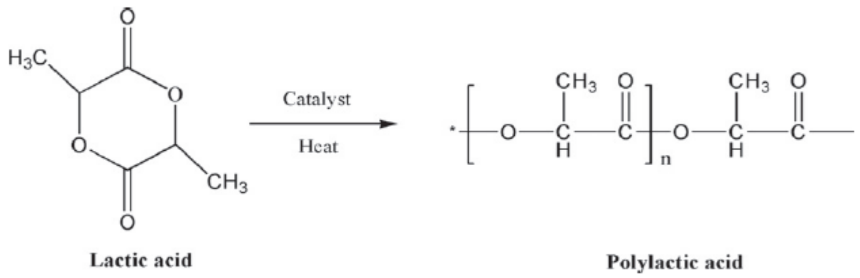
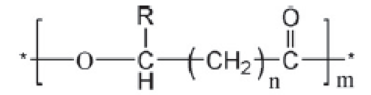


Figure 12. Synthesis of PLA.
Adapted from: Jiang & Zhang (2013).

(e.g. corn, sugarcane, potatoes) can produce lactic acid (JIANG & ZHANG, 2013). Depending on the microbial strain used during the fermentation process, L-lactic acid or D-lactic acid will be obtained. PLA can be synthesized from lactic acid by direct polycondensation reaction or ring-opening polymerization of lactide monomer. It is a thermoplastic polymer that can replace traditional polymers such as PET, PS, and PC for packaging to electronic and automotive applications (BABU *et al.*, 2013) (Figure 12). According to Avérous (2013), PLA-based constituents are mostly used on different markets such as biomedical, textile, and packaging. Moreover, Deconinck & de Wilde (2013) indicated that packing applications include trays, bottles, films, shrink films; medicine applications include implants, screws, sewing equipment; also electronics applications (cell phone, computer) and catering application (cups for cold drink). After the end of life, options presented are industrial composting and anaerobic digestion at temperature up to 50-55°C, chemical and mechanical recycling.

4.5.5 Produced by bacteria

PHAs are biodegradable polyesters directly produced by bacterial metabolism (Figure 13). Babu et al, (2013) highlight that feedstock include cellulosics, vegetable oils, organic waste, municipal solid waste, and fatty acids, which depends on the specific PHA prerequisite. Usually, a large fermentation container is filled with mineral medium and inoculated with a seed culture, which contains bacteria. Also, the carbon source is fed until PHA accumulation is complete, which in general requires a minimum of 48h for fermentation time (JIANG & ZHANG, 2013).



n = 1	R =	hydrogen	poly(-3-hydroxypropionate)
		methyl	poly(-3-hydroxybutyrate)
		ethyl	poly(-3-horoxyvalerate)
		propyl	poly(-3-hydroxyhexanoate)
		pentyl	poly(-3-hydroxyoctanoate)
		nonyl	poly(-3-hydroxydodecanoate)
n = 2	R =	hydrogen	poly(-4-hydroxybutyrate)
n = 3	R =	hydrogen	poly(-5-hydroxyvalerate)

Figure 13. General structure of PHAs.
Source: Jiang & Zhang (2013).

4.5.6 Petrochemical origin

Biodegradable polyester derived from petroleum are produced by polycondensation reaction among aliphatic diacids and aliphatic diols or by ring-opening polymerization of lactones. Also, classic synthetic aliphatic polyesters include PCL, PBS and their copolymers (JIANG & ZHANG, 2013).

As showed by Jiang & Zhang (2013), PCL is synthesized by ring-opening polymerization of caprolactone, which consists in a semicrystalline aliphatic polyester. In addition, PBS is synthesized by polycondensation between succinic acid and butanediol. Another important aliphatic aromatic copolyester is PBAT that shows higher chain stiffness than fully aliphatic polyesters due to the insertion of terephthalic groups in the molecules, which is an aliphatic-aromatic copolyester (JIANG & ZHANG, 2013).

5 CHEMICAL PROPERTIES

Nowadays, there are many polymers derived from natural renewable resources, which are available for many applications. Once lignocellulosic biomass is majorly composed of three polymers - cellulose, hemicelluloses and lignin - it is possible to obtain several different polymeric materials from this type of biomass. Some of the possible biopolymers which can be obtained from lignocellulosic biomass are methyl cellulose, carboxymethyl cellulose, cellulose acetate, polylactic acid (PLA), acrylic acid, polyhydroxybutyrate (PHB), polyethylene (PE), xanthan gum, furfural resins and phenolic resins (SANTOS *et al.*, 2013).

Methyl cellulose (MC): when compared to cellulose presents higher thermal stability and higher solubility in water associated with an increase on the degree of substitution, which are characteristics that expand the biopolymer commercial applicability (SANTOS *et al.*, 2013). At low temperatures, methyl cellulose can dissolve in water to form a solution, but as the temperature increases, hydrogen bonds between the polymer and the surrounding solvent break, and hydrophobic junctions are formed to produce a gel. The gelation temperature depends on the salt concentration in the solution, as the salt concentration increases, water molecules tend to surround the salt and consequently the gelation temperature decreases (ZHANG *et al.*, 2014).

Carboxymethyl cellulose (CMC): is an ether prepared out of a substitution of a hydroxyl group from glucose by a carboxymethyl group from sodium monochloracetate, with prior cellulose swelling using alkali. Sodium carboxymethyl cellulose is an anionic polyelectrolyte, water soluble, whose properties allow its use as thickener, emulsifier, adhesive, agglutinative, moist and dispersant agent. Its properties are dependent on the degree of substitution (DS- average number of carboxymethyl for glucose-anhydride unit) of carboxyl groups through the chain (SANTOS *et al.*, 2013). In other words, carboxymethyl celluloses are heterogeneous biopolymers due to molar mass distribution of parental celluloses and the statistical nature inherent in the substitution reaction leading to products heterogeneous in terms of chemical composition on different structural levels and in molar mass (SHAKUN *et al.*, 2015). Cellulose derivatives are generally compared by their degree of substitution, whose maximum value that can be achieved is 3. The selection of the carboxymethylation condition is essential to prepare a high substituted CMC. Most of the commercial CMCs have a degree of substitution from 0.4 to 1.4. Yeasmin & Mondal (2015) studied the influence of carboxymethylation reaction conditions and feedstock properties on the chemical properties of CMC produced. They found carboxymethylation mainly depends upon the accessibility of reactants and the availability of the activated hydroxyl groups. When particle size decreases, surface area, as well as available free OH groups for substitution reaction increases. Thus, the degree of substitution increases because the substitution is more favorable to happen, since the chance of collision between reactants and cellulose is greater.

Cellulose acetate (CA): is produced by the substitution of hydroxyl groups from cellulose by acetyl groups, using a mixture of acetic acid and acetic anhydride in the presence of sulfuric acid or perchloric acid (SANTOS *et al.*, 2013). Amongst the different types of cellulose acetate, the most exploited is the diacetate or secondary acetate with a degree of substitution (DS) of 2.4–2.5, which is acetone soluble and presents low toxicity. Because of the heterogeneous nature of the reaction, it is impossible to synthesize partially substituted cellulose acetates directly. Therefore, the hydrolysis step is required to produce cellulose acetate with the desired DS. Daud *et al.* (2015) developed a method to produce cellulose acetate in a one-step heterogeneous acetylation from oil palm empty fruit bunch. NMR analysis showed that the distribution of the acetyl moiety among the three OH groups of cellulose indicates a preference at the C6 position, followed by C3 and C2. It was also found that the cellulose acetate produced is highly amorphous with a low degree of crystallinity. Wu (2014) studied mechanical properties, biocompatibility and biodegradation of cross-linked cellulose acetate-reinforced polyester composites. It was found that the composites prepared from cross-linked cellulose acetate presented better mechanical properties than normal cellulose acetate due to greater compatibility between the components. It was also shown that the composites were both biodegradable especially when higher levels of cellulose acetate were achieved, showing a strong connection between cellulose acetate content and biodegradability.

Polylactic acid (PLA): is a rigid thermoplastic bio-based polymer formed by polymerization, via esterification, of lactic acid units, which are obtained from fermentation of sugars (SANTOS *et al.*, 2013). It is a linear, aliphatic polyester used in production of clothing, carpet tiles, bags, filtration systems, surgical and biomedical applications (NANDA *et al.*, 2011).

PLA is one of the main biodegradable polymers in current bioplastics markets, however it is not yet suitable to replace conventional synthetic polymers because of its high cost of production and several undesirable attributes including brittleness, poor thermal resistance, limited gas barrier properties, and poor UV light barrier properties (CHUNG *et al.*, 2013). It has been studied the use of lignin in blends with other biopolymers, such as polylactic acid to reduce the cost, improve antioxidizing stability and improve thermal stability (LAURICHESSE & AVÉROUS, 2014).

Acrylic acid (AA): polymers produced from acrylic acid and its esters are characterized by their transparence, easy adhesion, elasticity, heat stability and luminosity. This acid has in its structure terminal carboxylic groups which grant a polyanionic character to the molecule, providing ability for ionic exchanges and complexation with positively charged ions (SANTOS *et al.*, 2013).

Polyhydroxybutyrate (PHB): is a polymer of polyhydroxyalkanoates (PHA) family, which has granulated aspect and can be produced through fermentation (SANTOS *et al.*, 2013). Polyhydroxyalkanoates can be produced from renewable and sustainable sources and are biodegradable. PHBs may be indefinitely stable in air and have some mechanical properties similar to conventional thermoplastics like polypropylene or polyethylene, although PHB exhibits a higher rate of crystallization and higher degree of crystallinity, leading to brittleness and low elongation to break. Domínguez-Díaz *et al.* (2015) studied thermo-chemical properties of PHBs and observed that melting, crystallization and degradation temperatures of the PHBs initially increased with increasing the molecular weight. However, the highest molecular weight PHBs exhibited cold crystallization and reduction in melting temperature and melting enthalpy, suggesting difficulty to crystallize.

Polyethylene (PE): can be produced from methanol obtained from syn gas after biomass gasification (SANTOS *et al.*, 2013). It is a polymer partially crystalline, flexible, whose properties are dependent on the relative amount of crystalline and amorphous regions. The smallest crystalline units, lamellas, are planar and consist of chains perpendicular to the main plan and zig-zag folded. PEs are inert to most common chemicals due to its paraffinic nature, high molecular weight and partially crystalline structure. Under 60°C, PEs are soluble in most solvents. However, two phenomena can be observed: (1) interaction with solvents, causing swelling, partial dissolution, color appearing and material degradation with time; and (2) interaction with surfactant agents, resulting in the reduction of material mechanical resistance by effect of surface-cracking (COUTINHO *et al.*, 2003).

Xanthan Gum: is a polymer classified as a branched heteropolysaccharide which has the capacity of forming gels and viscous solutions in aqueous medium. Xanthan gum is an alternative to traditional gums because of its rheological properties, and because of that it is largely used as thickener, gelling agent, suspension agent, protective colloid and stabilizer in the industry (SANTOS *et al.*, 2013). This polysaccharide is stable in a broad pH and temperature range, as well as, its viscosity is not much affected by the addition of salts to the solution (LUVIELMO & SCAMPARINI, 2009).

Furfural resins: furfuryl alcohol is produced in a two-step process: (1) pentoses from hemicelluloses go through an acid hydrolysis, producing furfural; and then (2) aldehyde group is reduced to an alcohol by catalyzed hydrogenation. In acid conditions, furfuryl alcohol undergoes a very exothermic auto-condensation reaction, leading to the formation of a linear or branched polymer and water as products of the reaction. The resin, after the curing of the cross-linking between the polymeric chains, presents a structure which grants to the material excellent resistance to chemicals and fire (SANTOS *et al.*, 2013).

Phenolic resins: are prepared from lignin extracted by organosolv process as a replacement to phenol and they exhibit dimensional stability, thermal stability, chemical resistance and high temperature resistance (SANTOS *et al.*, 2013). Thermo-mechanical properties of phenolic resins are related to high density of bonds after the curing, which contributes to low resistance to impact (OLIVEIRA *et al.*, 2015).

6 APPLICATIONS

In Table 5, the main plastics of European consumption are presented. Also, some applications are displayed in Table 6.

Table 5. Demand of European plastics in 2013.
Source: Plastics Europe and EPRO (2015).

Plastics	**% Demand**	**Examples**
PET	9.9	Bottles
PE-HD	12.1	Toys, milk bottles
PVC	10.4	Window frames and boots
PE-LD/PELLD	17.5	Wire cables, reusable bags and film for packing
PP	18.9	Flowerpot, folder and car bumper
PS/PS-E	7.1	Glasses frames and plastic cups and most yoghurt pots
PUR	7.4	Sponges and insulation panels
Others	19.7	ABS bricks and PTFE (Teflon coated) pans

Table 6. Some applications of biopolymers.

Polymer	**Applications**	**References**
Cellulose Acetate Obs: biodegrability < 24 months	Cigarette filters, textiles, spectacle frames film media, Wound, dressings ADAPTIC_ Bioceta_: tootbrush	(Sin *et al.*, 2013)
Polycaprolactone (PCL) Obs: biodegrability>12 months	Ethicon: monocryl_dsuture, capronor_dcontraceptive, implant Agrotec: Agrothane_dpaint andmetal protection film	(Sin *et al.*, 2013)
Polyhydroxyvalerate (PHV) Obs: biodegrability 3-12 months	Compost bags, consumer packaging, agriculture/horticulture film, Rubbermaid, Calphalon,PaperMate, BioTuf, EcoGen	(SIN *et al.*, 2013)
Poly(Lactic) (PLA)	Fixed installations such as bone plates, bone screws, surgical sutures, spinning, molded plastic parts, fibers,films, foam, heat-stableapplications, electronics, camera components.	(NIAOUNAKIS, 2013) (INDUSTRY EXPERTS, 2012)
Polyhydroxybutyrate (PHB)	Films, disposables, medical, cups, lids, containers, cutlery applications, compost bags, consumer packaging, agriculture/horticulture film, Rubbermaid, Calphalon,PaperMate, BioTuf, EcoGen	(NIAOUNAKIS, 2013) (INDUSTRY EXPERTS, 2012) (SIN *et al.*, 2013)
Poly(alkylenealkanoate)s (PBS)	Injection molding, disposable goods (knives, spoons, forks), fibers, fishing gear, plant pot.	(NIAOUNAKIS, 2013)
Aliphatic-aromatic (co)polyester PBAT	Packaging, film, sheet, agriculture films, compost bags, plastic envelops, flower pots.	(NIAOUNAKIS, 2013)

Table 7. Overview of main characteristics of different biorefineries. Source: De Jong & Jungmeier (2015)

Concept	**Type of feedstock**	**Predominant technology**	**Products**
Conventional	Starch (corn, wheat, cassava) and sugar crops (sugarcane, sugar beet), wood	Pretreatment, chemical and enzymatic hydrolysis, catalysis, fermentation, fractionation, separation	Sugar, starch oil, dietary fibers, pulp and paper
Whole-crop	Whole crop (including straw) cereals such as rye, wheat and maize	Dry or wet milling, biochemical conversion	Starch, ethanol, distiller`s dried grains with solubles
Oleochemical	Oil crops	Pretreatment, chemical catalysis, fractionation, separation	Oil, glycerin, cattle feed
Lignocellulosic	Lignocellulosic biomass: e.g., straw, chaff, reed, miscanthus, wood	Pretreatment, chemical and enzymatic hydrolysis, catalysis, fermentation, separation	Cellulose, hemicelluloses, lignin
Green	Wet biomass: green crops and leaves, such as grass, lucerne and clover, sugar beet leaf	Pretreatment, pressing, fractionation, separation, digestion	Proteins, amino acids, lactic acid, fibers
Marine	Aquatic biomass: microalgae and macroalgae (seaweed)	Cell disruption, product extraction and separation	Oil, carbohydrates, vitamins

7 BIOREFINERY PROCESSES APPLIED TO BIOPOLYMERS PRODUCTION

According to FNR (2012), biorefineries are characterized by delivery of a wide range of semi-finished and finished products. Also, classification of biorefineries involves a range of aspects, such as: raw material, intermediates (e.g. synthesis gas biorefinery, lignocellulosic biorefinery, vegetable oil biorefinery, two-platform biorefinery), process (e.g. thermochemical biorefinery, biotechnology biorefinery), or product(s) (e.g. bio-ethanol biorefinery, fuel biorefinery). However, as specified by IEA Bioenergy Task 42 (2011), classification involves platforms (e.g. syngas, lignin, core intermediates such as C5-C6), products, feedstock and processes (e.g. thermochemical, chemical, biochemical, mechanical processes). As shown in Table 7, it depends on type of product (starch, sugar), feedstock and pretreatment.

Biopolymers can be natural (starch, cellulose) or produced (polylactic acid and polyhydroxyalkanoates) by some techniques for example fermentation. Thus, before defined the conversion techniques, it is important to highlight that there are a variety of pretreatments. Though, the planning steps depend on the physical and chemical properties of feedstock and the type of reactor used in the next step. Physical properties include size distribution, particle shape, moisture content, bulk and particle densities, compressibility and compaction ratio, contaminants, and flow ability. Also, chemical composition contains elemental analysis (C, H, O, Cl, N, S, F, K, Na, Mg, Ca, P, and heavy metals), which is critical to predict the decomposition comportment and product group (ZHANG *et al.*, 2010). Besides, Van Dyk & Pletschke (2012) said that substantial percentage of lignin has been confirmed to be the most important factor for limiting hydrolysis of biomass by cellulolytic and hemicellulolytic enzymes. In addition, they informed that removal of lignin may be achieved in several ways (physical (mechanical, thermal), chemical or enzymatic means).

As defined by Pandey *et al.* (2015), pretreatment is the key process to modify the recalcitrance in order to convert it into biofuel or other products. In addition, there is recalcitrance, a compact and rigid structure (ZHAO *et al.*, 2012), which is responsible for difficulty to microbial destruction (ZHU *et al.*, 2010). Recalcitrance can be attributable to crystallinity, degree of polymerization and low accessibility of cellulolytic enzymes into the substrate (SANTOS *et al.*, 2012). Consequently, pretreatment is crucial for reaching effective hydrolysis of substrates as enzymatic hydrolysis of native lignocellulose produces less than 20% glucose from the cellulose fraction (VAN DYK & PLETSCHKE, 2012). According to SANTOS *et al.* (2013) and Galbe & Zacchi (2010), when it is necessary to define the pretreatment effectiveness, there are these desirable characteristics, such as low investments and operational costs for the method; minimal residues amount; rapid reactions; chemical reagents which are not corrosive to avoid reactor costs; low load of adapted enzymes to achieve 90% of digestibility of cellulose pretreated and facilitate lignin and other elements recover to convert them into products with high value added. The most significant pretreatments can be verified in Table 8.

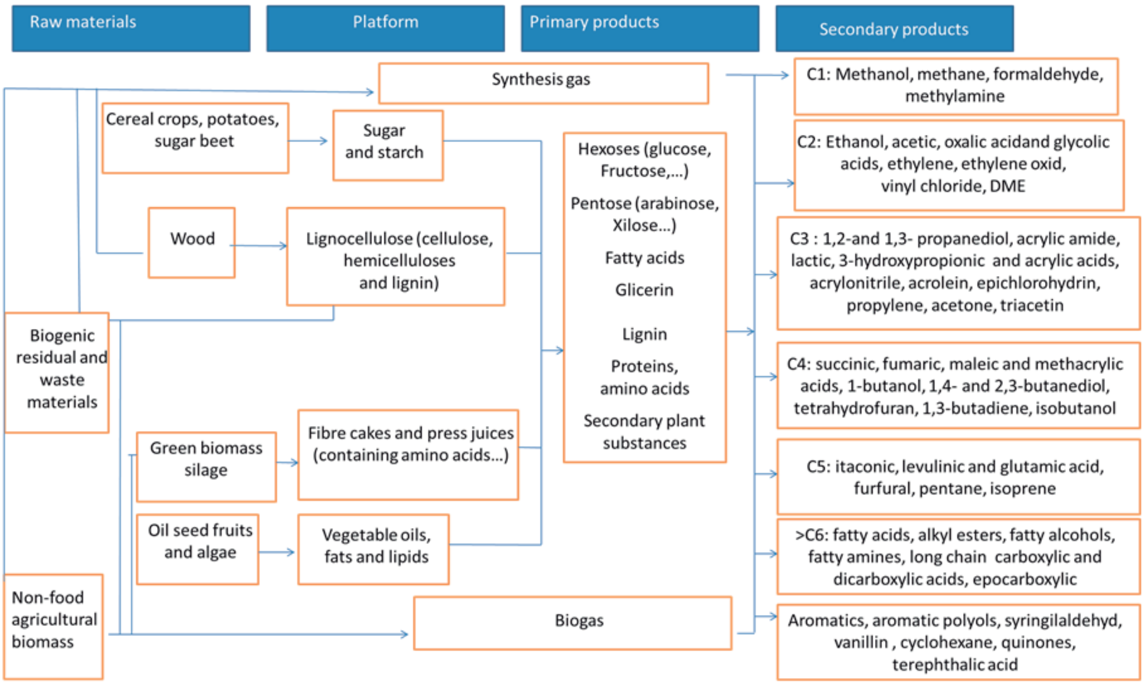
In order to compete with fossil energy sources efficient conversion technologies need to be utilized. For instance, biochemical conversions have been used for specific feedstock of high availability (ZHANG *et al.*, 2010) and generally they are used to process the sugars from cellulose and hemicelluloses into ethanol (RODRIGUES, 2011). This process can be divided into microorganism digestion (anaerobic and aerobic digestion) and fermentation, to provide ethanol and methanol (BALAT, 2006). Also, chemical conversion through acid hydrolysis can produce levulinic acid from C6 sugar and furfural from C5 sugars (RODRIGUES, 2011). Moreover, there are thermochemical conversions which have certain benefits over biochemical methods in terms of processing time of biomass and no pretreatment is required. The thermochemical method comprehends a method (pyrolysis, gasification, and torrefaction) that produces solid, liquid, or gaseous products, which consequently can be upgraded to fuels (synthetic biofuels). Some of the products that can be obtained from biorefineries of different platforms are shown on figure 14. These primary treatment methods create intermediates that should be first purified, frequently in several steps, and then further upgraded to fuels through catalytic treatments, for example, hydroprocessing, cracking, steam reforming, methanation, FTS, or other methods.

In principle, all types of biomass can be treated thermo-chemically (ZHANG *et al.*, 2010).

Table 8. Pretreatments and their effects in lignocellulosic biomass.
Source: Santos et al., 2013.

Pretreatment		**Composition Characteristics**		
		Cellulose	**Hemicellulose**	**Lignin**
Physical	Ball milling	Intense minimization of crystallinity	Does not remove	Does not remove
Chemical	Dilute acid	Low depolymerization	80-100 % of removal	Low Removal
	Sodium hydroxide	Significant swelling	Considerable solubility	Considerable solubilization>50%
	ARP, ammonia recycled percolation	Less <5% depolymerization	-50% of solubilization	-70% of solubilization
	Calcium hydroxide	Low depolymerization	Significant solubilization	Parcial solubilization ~40%
	Ozonolysis	There was no depolymerization	Low solubilization	Considerable solubilization>70%
	Organosolv	Significant swelling	Significant, almost complete	Significant
Biological	Biological	20-30% of depolymerization	Over 80% of solubilization	~40% of deslignification
Combined	Steam explosion	Low depolymerization	80-100% of removal	Low removal, but occurs structure change
	AFEX, ammonia fiber explosion	Minimization of crystallinity	Over 60% of solubilization	10-20% of solubilization

Figure 14. Top value products obtained from biorefinery by different platforms.
Sources: IEA Bioenergy Task 42 (2011); FNR (2012)



As presented by Figure 14 and as reported by IEA Bioenergy Task 42 (2011), the top chemical products which can be obtained from fermentation processes of *C5/C6 Sugar Platform* are succinic acid, itaconic acid, adipic acid, 3-hydroxypropionic acid/aldehyde, isoprene/farnesene, glutamic acid and aspartic acid. Moreover, these C5/C6 carbohydrates after passing through chemical transformation (dehydration, hydrogenation and oxidation reactions) can provide for example sorbitol, furfural, glurаric acid, hydroxymethylfurfural, levulinic acid and directly from glucose it can provide 2,5-furan dicarboxylic acid and p-xylene. *Plant-based oil platform* highlights that the glycerol is an important feedstock for fermentation, anaerobic digestion, and chemical conversion generating

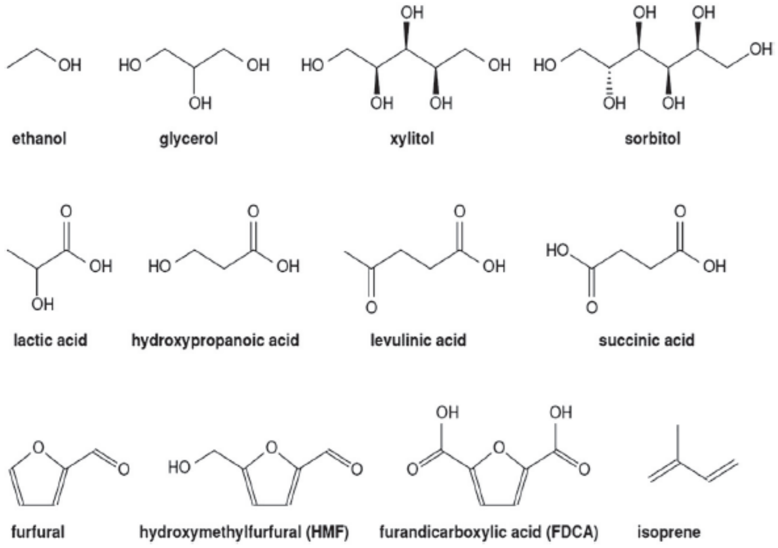


Figure 15. Proposed biobased platform molecules.
Source: De Jong & Jungmeier (2015)

epichlorohydrin, propylene glycol, 1,3-propanediol, 3-hydroxypropion aldehyde, acrylic acid, propylene and methanol which can be produced via syngas. Also, lignin native structure has being suggested as new chemical feedstock, *lignin platform*, mostly due the creation of supramolecular material and aromatic chemical. The potential products from lignin are divided into syngas products (methanol, ethanol, Fisher-Tropsh, etc.), hydrocarbons (benzene, xylene, toluene, styrenes, etc.), phenols (cresols, guaiacols, etc.), oxidized products (vanillin, cyclohexanes, aliphatic acids, aromatic acids, etc.), macromolecules (polymers extenders, thermoset resins, pharmaceuticals, etc.). Also, in medium to long-term, the production of value added chemical from lignin such as resins, composites, polymers, aromatic compounds and carbon fiber will depend on the quality and functionality of type of lignin that can be obtained. In the *pyrolysis oil platform,* initially the biomass is converted into pyrolysis oil, then the oil can be divided into different fractions, so it can be upgraded with a different technology to increase value to the final products such as phenols, organic acids, furfural and levoglucosan.

Some of these top value products are shown in Figure 15.

All primary and secondary products generated by biorefineries from natural resources can be part of another process which can produce chemicals such as fine chemicals, synthetic build blocks, organic acids such as lactic, succinic, propionic, itaconic, etc; polymers and amide resins such as, poly-ethylene, poly-propylene, poly-butadiene, phenolic resins, furanic resins; biomaterials (e.g. wood derived, paper, cellulose, ruminant food, fertilizers, cosmetic industry and perfumary) (RODRIGUES, 2011).

8 SOCIOECONOMIC, TECHNOLOGOGIC AND ENVIRONMENTAL ASPECTS

The global production of plastics achieved 299 million tons in 2013. This sector has increased for more than 50 years and it is responsible for innovation of many products and technologies in different sectors of the economy (e.g. healthcare, energy generation, aerospace, automotive, maritime, electronics, packaging or textile). Also none of these sectors could developed as much as they did without plastic materials and new technologies. Furthermore, the European plastic industry provides 1.45 million direct jobs, the turnover was 320 billion euro and 6.6 million tons of plastic were recycled in 2012 (PLASTICS EUROPE & EPRO, 2015). In addition, global bioplastics production capacity is set to grow 300% by 2018, the expectance is reaching 6.7 thousand metric ktons (EUROPEAN BIOPLASTICS, 2013). Therefore, to reduce the use of nonrenewable fossil resources which are draining hastily, there are significant developments dedicated to bio-based sustainable processes, which make use of renewable feedstock.

Biopolymers are biologically safe alternatives to conventional polymers due their biodegradable nature and their origin from renewable resources, so bio-based products and processes can provide alternative for fossil/mineral based products and chemical processes. For instance, the use of the economical lignocellulosic wastes could diminish the production cost of biopolymer production process and they will attract more industries (NOVAK *et al.*, 2014). Recent analyses present the ability of recycling biomass through the use of wastes and residues and support crop yield growth through investments in infrastructure and development capacity in agriculture and forestry (SANTOS *et al.*, 2013; SCOPE, 2015). Moreover, the importance of bio-economy is linked to all areas, in which waste biomass derived from crop residues from different fonts such as food and feed production, fermentation process wastes, food/beverage processing wastes, marine crops and processing wastes, forestry residues, municipal waste, biological process-derived wastes, and manure and animal products are potential candidates towards the achievement of a bio-based economy (NOVAK *et al.*, 2014). Thus, energy and chemicals derived from biomass, are directly linked by the biorefinery concept, adding value to residues of the main production proving a sustainable system (ZHANG *et al.*, 2010).

Bioplastics are economically innovative and have high potential to increase economy regarding to the reduction of greenhouse gas emissions and carbon footprint of products, yet it can contribute to increase resource efficiency through biomass use cascades and rural development (EUROPEAN BIOPLASTICS, 2013). Among all the *benefits* and *opportunities* it possible to point up: new areas of economic growth and development (especially rural areas); formation of new innovative business sectors and entrepreneurial skills; improved energy security, by diminishing necessity on nonrenewable resources; enriched economic and environmental linkages

between the agricultural sector and sustainable industrial sector; reduction of GHG emissions; employment creation and rural development; avoiding the competition of land used (NOVAK *et al.*, 2014). The land use for bioplastics were 0.6 million ha in 2013, and the projections for 2018 are to reach 1.3 million ha, equally 0.02% of global agriculture area considered arable land (EUROPEAN BIOPLASTICS, 2013). It is important to highlight that the land availability for biomass will exceed 500 million ha in 2050 after allowing for food production, protected areas, urban expansion, and increased biodiversity protection (SCOPE, 2015).

One of the major problems faced by biorefineries is *food security.* Between the reasons for food insecurity there are losses of access land, local of food and feed production undermined by cheaper, poorly developed infrastructure, degraded land, conflict or instability. Thus, poverty and hunger mainly result from insufficient supplies of food and from a lack of income, considering that the majority of the rural people depend on farming and use a large portion of their income for food. Bioenergy/bioproducts production can motivate rural development broadly and outcome in increased food security by improving rural incomes (SCOPE, 2015).

The main part of *sustainable development* involves a system approach and integration on different levels: assessment, long-term policies and strategies, and business models consistent with policies for climate, rural and industrial development, and energy and food security. Besides, the main issue for an ideal biomass supply chain is to guarantee a stable and continuous supply of suitable feedstock at competitive prices. Also, it becomes important to deliver technical and financial supports to innovate efficient biomass supply systems that are fully compatible with different production scales, feedstock quality and their processing (SCOPE, 2015).

Although all steps of biorefinery processes, such as second generation biofuels production, are demonstrated, the challenge of integrating these processes in the existent industry and the continuous need of costs reduction remains. Technologies involving the improvement of sugars conversion in biofuels, increase in production efficiency, increase in production and use of enzymes and processes that enable inputs and microorganisms recycle need to be developed. The development of biorefineries depends on technical-scientific challenges that need to be overcome in feedstock production, industrial processing and integration of regional productive chains (VAZ JR., 2011).

9 FINAL CONSIDERATIONS

The interest in replacing fossil based energy and materials for a biobased economy has grown in the last years aiming the development of a sustainable society, and an effective management of greenhouse emissions, waste treatment and disposal. Facing the growing concerns over climate changes, lignocellulosic biomass has been vastly studied in the concept of a biorefinery as feedstock to produce a variety of high value added bioproducts, which are promising replacements for fossil-based products. Lignocellulosic biomass is an interesting feedstock since it is a largely available natural resource derived from plants, animals, as well as, from industrial and municipal wastes. Among the high value added products which can be obtained from lignocellulosic biomass, biopolymers have been the topic of several researches, once nowadays most of plastics are produced from petrochemicals and are not biodegradable, generating a huge environmental problem concerning their disposal.

Biopolymers derived from natural resources are categorized according to their chemical structural as polysaccharides, proteins, lipids, polyesters, natural fibers and composites, which can be used in different industrial sectors in several applications as packaging, medical equipment, electronics, containers and many others. When studying biopolymers it is important to characterize their physicochemical properties in order to evaluate the different applications each type of biopolymer can be employed. Another important factor to be evaluated about biopolymers is their degradability by microorganisms, oxygen or natural processes during composting procedures, so that the biopolymer degradability can be carefully considered according to the type of application, it will be used.

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