



## Review

## Lignocellulosics as sustainable resources for production of bioplastics – A review



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## ABSTRACT

The bio-based economy requires a sustainable utilization of bioresources for production of a range of products, including pulp, paper, chemicals, biofuel and bioplastics. Currently, various types of bioplastics are produced industrially, competing in performance and price with the conventional fossil-oil based plastics. However, there is also a major interest in utilizing non-food crops, such as lignocellulosics, for production of drop-in polymers or new dedicated bioplastics. Lignocellulosic resources have a potential to replace plastics and materials, which have been traditionally based on fossil resources. This is important, as the development of high performance bio-based and renewable materials is one important factor for sustainable growth of the bio-based industry. However, production of bioplastics from forestry biomass requires a dedicated fractionation into the major components, i.e. cellulose, hemicelluloses and lignin, effective purification processes and cost-effective routes for conversion into monomers and platform molecules, utilized as a basis for bioplastics production. These processes are now technologically demanding and not profitable. The intention of this work was thus to review the current advances that have been made during the years within fractionation and purification of lignocellulosics and the processes that may be feasible for production of bioplastics, based on wood components.

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## Contents

1. Introduction .....	647
2. Methodology for data collection, selection and review .....	647
3. Biomass treatments for bioplastics production .....	648
3.1. Advances in fractionation of forest biomass .....	648
3.2. Separation and purification of components from different streams .....	649
4. Bioplastics .....	651
4.1. Major monomer-based bioplastics .....	651
4.1.1. Polylactic acid .....	651
4.1.2. Polyhydroxyalkanoates .....	652
4.1.3. Polyethylene .....	655
4.2. Wood-based platform molecules .....	656
4.3. Wood-based polysaccharides as bioplastics .....	657
4.4. Lignin-based routes .....	658
4.5. Forest-based components for the production of epoxy bioplastics .....	659
4.6. Bio-based thermosets from suberin monomers .....	660

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5. Some environmental aspects of bioplastics .....	660
6. Conclusion .....	661
Acknowledgement .....	661
References .....	661

## 1. Introduction

Society is moving towards a bio-based and circular economy. This implies a major focus on the appropriate and sustainable utilization of bioresources. Due to relatively high availability, effective management and sustainable exploitation, the forests constitute a major source of lignocellulosic biomass with potential within several industry sectors. Additionally, in places where forestry resources or their residues are limited, agro-industrial waste (e.g. sugar cane bagasse, cereal straw, other canes) is an important source of biomass. Lignocellulosics provide feedstocks for production of pulp fibers, nanofibers, lignin and biopolymers, having a range of industrial applications, e.g. paper products, biocomposites, rheology modifiers, food additives, biofuel and bioenergy production.

Additionally, bioplastics have attracted major attention as potential replacement of conventional fossil-based plastic products. Bioplastics are produced from renewable resources, today mainly from corn (e.g. polylactic acid, PLA), sugar cane (e.g. Biopolyethylen, BioPE) and waste fats and oils (e.g. 2nd generation BioPE). Presently, bioplastics can roughly be classified in two groups; dedicated polymers with a new chemical structure (e.g. PLA) and drop-ins (e.g. BioPE) (IfBB report 2016). Both chemical and biotechnological production routes are utilized in the production of bioplastics. As an example, polyhydroxyalkanoates (PHAs) can be produced by bacteria from sugar sources. Although, a bioplastic is characterized by being produced from a renewable resource, bioplastics are not necessarily biodegradable. BioPE is an example of a bioplastic that is similar to the fossil-based PE and thus not biodegradable, although the bioplastic can be recyclable. On the other side, PHA is an example of a bio-based and biodegradable bioplastic type (see e.g. Philp et al., 2013a). Hence, it is the chemical structure and not the origin that determines the biodegradability of the plastic.

Bioplastics may also be derived from non-food agroforestry resources (e.g. lignocellulosics from wood and agricultural residue, and components from bark). Some recent initiatives have appeared to produce bioplastics from alternative feedstocks, *i.e.* second-generation bioplastics (Lovett and de Bie, 2016). However, the processes for production are more demanding compared to the production of bioplastics from e.g. corn, starch or sugars. Lignocellulosics from forestry biomass requires a dedicated fractionation into the major components, *i.e.* cellulose, hemicelluloses and lignin. In addition, the biopolymers need to be deconstructed into monomers if the bioplastic shall be synthesized by polymerization (e.g. polyolefins, PLA, PHA). Hence, the production of bioplastics as a main product from forestry resources is demanding and presently not economically viable.

The interest in developing bio-based and environmentally sound polymer systems has increased over the last decade due to increasing environmental concerns for the current petroleum-based materials. Bio-based polymers have been reported to have a low environmental burden (see e.g. Kimura and Horikoshi, 2005; Narayan, 2012), although this may be difficult to estimate due to uncertainties with regard to logistics and availability of recycling systems and composting plants.

Lignocellulosic resources have a major potential to replace plastics and materials based on fossil resources. This is important, as the development of high performance bio-based and renewable materials is one important factor for sustainable growth of the bio-based industry. The success of the bio-based and circular economy relies on various aspects, including increased productivity, effective recycling, investments in innovation, technology development, access to capital, supportive stable policies and market opportunities (see e.g. Iles and Martin, 2013; Philp et al., 2013a, b).

Bio-based resources are renewable and expected to play a key role in the production of novel and bio-based materials, contributing to a reduction of the negative environmental impact of fossil-based products and thus addressing the bioeconomy of the future. However, commercial bio-based plastics are currently based on raw materials which production may take land from alternative food production (first generation feedstock). Cultivation of first generation feedstock stimulates concerns about direct and indirect effects on land-use and competition for arable lands (Nanda et al., 2015). The world's increased need for food production will therefore be an important driver towards production of bioplastics from renewable non-food sources, such as lignocellulosic biomass from forestry resources (see e.g. Broeren, 2013). Hence, the purpose of the present review is to focus on advances in the development of bioplastics from forestry resources. This review covers the main processes from fractionation to polymerization, delineating also four main routes for production of e.g. bio-based thermoplastics and bio-enriched thermosets.

## 2. Methodology for data collection, selection and review

Bioplastics production from forestry resources involves several steps, ranging from processes that have traditionally been developed for the pulp and paper industry (e.g. fractionation) to processes developed for the plastic industry (e.g. polymer polymerization). In this review, the data collection was divided into three main actions. Firstly, several databases were utilized, including Web of Science, Scopus, Academic Google and Ei Compendex. Secondly, the databases were extensively searched, and focusing on three relevant topics: i) Biomass treatments for bioplastics production, ii) Bioplastics, and iii) Environmental aspects. The literature search provided 500+ papers that were read and classified. Finally, this review includes results and opinions presented in national and international conferences.

Based on the extensive literature search (500+ papers), a number of studies were selected considering their relevance to the subject of the present review. One hundred and seventy three relevant papers were finally selected and reviewed. A number of reviews on bioplastics have been previously published and many of them focus on certain plastic types or on certain applications (e.g. Vilela et al., 2014; Auvergne et al., 2014; Jabeen et al., 2015; Arikan and Ozsoy, 2015; Sheldon, 2014; Kawaguchi et al., 2016). It is important to emphasize that in the present work we have narrowed down the scope of the review, focusing on bioplastics production from forestry resources. Hence, we intend to delineate routes that may have potential in sustainable forest-based production lines, considering the demanding processes involved and

recent technology that seems to be promising for e.g. fractionation and conversion. However, it is difficult to strictly limit the review to literature on forestry-based biomass. Considering this, we have subdivided the Bioplastic chapter of the review into sections ranging from relatively conventional monomers (irrespective of the biomass origin) for bioplastic production, to more specific components derived from trees. For clarity purposes, an overview of the present review is presented in Fig. 1.

### 3. Biomass treatments for bioplastics production

Lignocellulosic raw materials have a complex and heterogeneous structure and composition, which makes their utilization as a source for biochemical and bioplastic production demanding. Therefore, to achieve environmental, technical, and economic feasibility of a certain product from biomass, it is necessary to integrate its production with that of other components. In biorefineries, this involves the technology and processes for the extraction and conversion of different products, the separation and purification of the intermediates compounds and the end-products streams, and their full integration in the overall process. Such aspects will be discussed in the following sections.

#### 3.1. Advances in fractionation of forest biomass

The composition of lignocellulosic materials is variable depending on the species of plants (softwoods, hardwoods, or gramineous species). However, the main components are roughly 35–50% cellulose (polymer of glucose, which is the most abundant form of carbon on earth), 20–35% hemicelluloses (which main component is xylose, the second most abundant sugar in the biosphere), and 10–25% lignin (a complex aromatic structure, of high energy content and resistant to biochemical conversion). Lignocellulosic materials from agricultural residues have similar chemical composition than hardwoods, containing roughly 41–52% cellulose, 25–27% of hemicelluloses, 18–25% lignin, and 0.5–10% of other components as extractives and inorganics (Fengel and Wegener, 1989; Sjöström, 1993).

Fractionation involves the sequential removal of each chemical component. Fractionation treatments, mostly studied for bioethanol production, can be physical, chemical, physico-chemical, biological or the respective combinations (Alvira et al., 2010; Zheng et al., 2009; Kumar et al., 2009; Banerjee et al., 2010; Zhang and Shahbazi, 2011; Brodeur et al., 2011). The strategy and techniques used depend on the characteristics of each material. Raw materials have different chemical composition in quantity and quality, and different anatomical and structural characteristics. Hence, fractionation, products recovery, purification and conversion differ greatly between different raw materials. Hemicelluloses are chemically bound to lignin forming lignin-carbohydrate complex, lignin compacts the structure, and glucose is arranged forming cellulose, mainly in crystalline form. All these aspects hinder the processing, thus increasing its technological complexity. Most processes adapt well to angiosperm species (hardwoods, grasses, canes), and were widely studied, as shown by most of the references included in this section. Conifers in general, and particularly pines, are very interesting raw materials due to their high content of hexoses and their wide availability. However, the fractionation of conifers is the most complicated because of their highly crystalline cellulose and high lignin content. Most softwood species also have extractives (resin and fatty acids) which can produce pitch problems in the process (Stoffel et al., 2014).

The most studied fractionation treatments are included in Table 1. Even though all types of fractionation processes can be applied for bioplastic production, detoxification of hydrolysates is

needed when microorganisms are involved, as in PHA production (Obruca et al., 2015). Chemical treatments induce the breaking of hydrogen bonds in the crystalline regions of wood fibers to open up the structure and allow the passage of the hydrolytic agents. Dilute acid treatments are the most studied processes for hemicelluloses removal, as reported in various reviews (Zheng et al., 2009; Kumar et al., 2009; Banerjee et al., 2010; Zhang and Shahbazi, 2011; Brodeur et al., 2011; Stoffel et al., 2014). The main reason is that hemicelluloses can be hydrolyzed at temperatures of about 160 °C, whereas hydrolysis of crystalline cellulose requires temperatures in the order of 200 °C–240 °C. Importantly, an economic comparison of various treatments concluded that when the process does not include any integration, steam explosion and diluted sulfuric acid hydrolysis present the lower power requirements. However, when recycling is considered, liquid hot water process and ammonia explosion are also efficient (Conde-Mejia et al., 2012; Huang et al., 2010).

Among chemical treatments, chemical pulping and bleaching processes can be considered as the original fractionation processes. The main goal is to preserve the degree of polymerization of cellulose. These processes can be alkaline (NaOH), acid ( $\text{SO}_3^-$ ), or oxidative (e.g. oxygen, ozone.). Other processes that were developed for pulping, but found their greatest potential in fractionation processes, use organic solvents as delignifying agents (e.g. ethanol-water, acetone-water). In recent years, fractionation of the other main lignocellulosic components has been emphasized in the biorefinery context. Thus, several studies have been conducted about separation of hemicelluloses and partial lignin utilization (Al-Dajani et al., 2009; Yoon et al., 2010, 2011; Chirat et al., 2010; Schild et al., 2010). Importantly, some industrial ventures have been established, implementing some of these processes (Miller and Faleiros, 2016).

More recently, supercritical fluids and ionic liquids were proposed as fractionating medium (Gu et al., 2013). Technology based on supercritical fluids is an attractive alternative due to the short reaction time and the use of solvents that do not affect the environment. Supercritical conditions of treatment may remove lignin effectively thus increasing cellulose accessibility. The addition of a cosolvent such as ethanol may improve delignification. Supercritical-carbon dioxide (SC-CO<sub>2</sub>) is the most commonly used fluid because of its low critical temperature (31.1 °C) and pressure (73 bar). It is highly selective, non-toxic, non-flammable and easy to recover (Gu, 2013). In aqueous solution, the CO<sub>2</sub> forms carbonic acid, which favors the hydrolysis of biomass. CO<sub>2</sub> molecules can penetrate into the small pores of the lignocellulosic material, which is facilitated by the high pressure. The explosive release of CO<sub>2</sub> pressure disrupts the structure of cellulose and hemicelluloses increasing the surface area (Brunner, 2014), and thus facilitating the fractionation process.

Ionic liquids are salts composed of ions that are liquid at room temperature, which possess unique chemical and physical properties, such as low melting points, very low vapor pressure, and high thermal stability (Zhu et al., 2006). They have ability to dissolve both polar and non-polar solutes and can be structurally adapted for specific applications (Olivier-Bourbigou et al., 2010). Ionic liquids produce lignocellulosic biomass dissolution and promote structural changes in the regenerated biomass by reduction of cellulose crystallinity and lignin content (Costa Lopes et al., 2013). Cellulose dissolution is an industrially attractive application of ionic liquids, due to good solubilities (5–20 wt%, depending on the ionic liquid and the conditions). Recently, ionic liquid pretreatment using 1-ethyl-3-methylimidazolium acetate (EMIM-OAc) and alkali based (NaOH/urea) were combined to improve the enzymatic digestibility of forestry biomass, thus yielding an improvement of monosugar yield by 20–50% (Heggset et al., 2016). Both dissolved

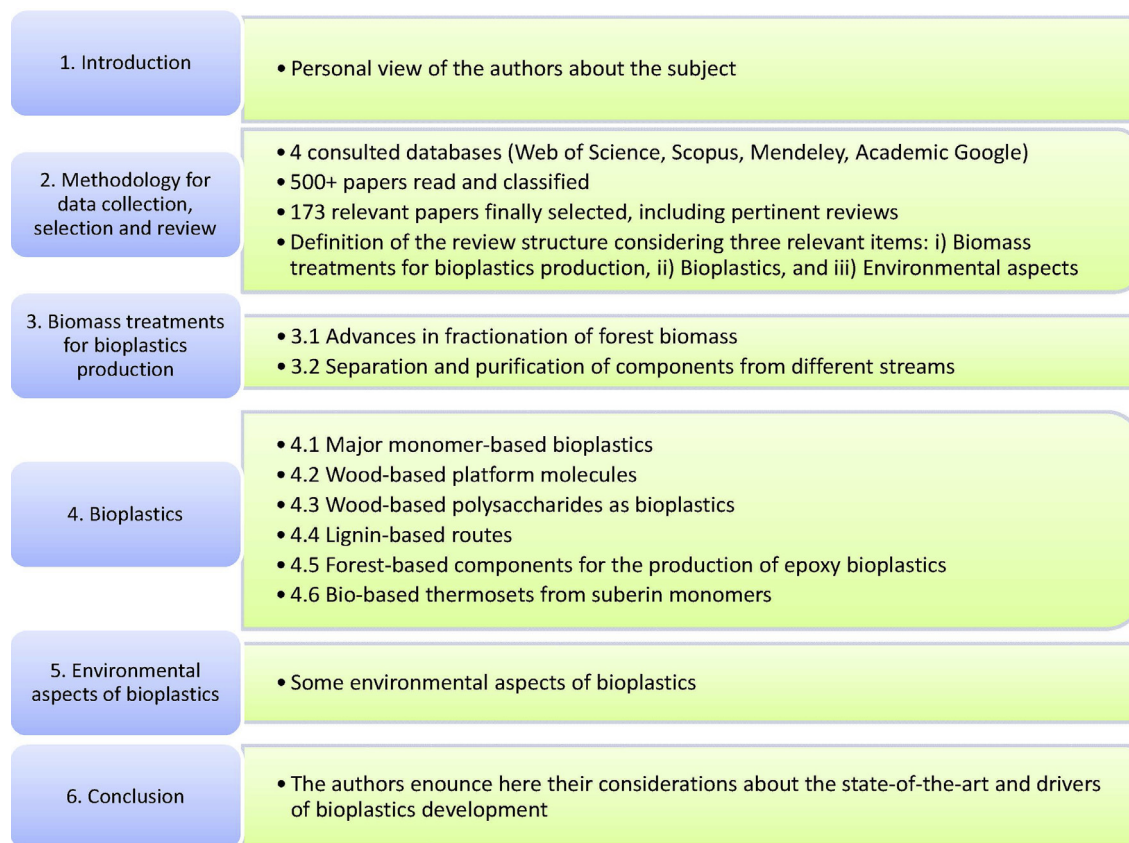


Fig. 1. Overview and structure of the present review.

lignocellulosic biomass and cellulose can be regenerated by addition of an anti-solvent like water. Although, this approach is considered as an interesting option for the manufacture of bioplastics (Chen et al., 2017), lignocellulose deconstruction with ionic liquids will only be successful if the ionic liquid can be recycled, due to the high solvent cost (Brandt et al., 2013).

Microemulsions have been recently studied as novel impregnation technologies that use green oil phases. Different microemulsions were formulated, e.g., 85% water and minority components consisting of oil (limonene) and anionic and nonionic surfactants (Carrillo et al., 2012, 2013), aqueous solutions of urea or ethylenediamine (Carrillo et al., 2014), and sodium dodecylsulfate (SDS)/pentanol/water/sodium chloride/dodecane (Du et al., 2016). Microemulsions seem to be economic, efficient, environmentally friendly and highly useful complex media for flooding/wetting substrates because of their low surface tension and viscosity (Du et al., 2016).

### 3.2. Separation and purification of components from different streams

Due to the characteristics and composition of the lignocellulosic materials and their potential conversion to multiple products, biorefineries requires the application of separation and purification techniques of components from different streams. The processes involved in their separation and purification can become about 20–50% of the total capital and operating costs of biorefineries (Huang and Ramaswamy, 2013). Separation and purification can involve (i) equilibrium-based processes, (ii) affinity-based separation, (iii) membrane separation, (iv) solid-liquid separation, and (v)

reaction-separation systems. Technologies involved in these processes are illustrated in Fig. 2. The characteristics and applications of the main techniques and processes of separation and purification of the different components of biomass are shown in Table 2.

Equilibrium-based processes consist on the introduction of a new phase to the system to allow that one or more components can distribute homogeneously between the phases. Recently, several extractive distillation systems at commercial scale have been built in the US (California, 2016), Brazil (Alagoas, 2014) and Italy (Crescentino, 2013), (Nhien et al., 2016b), to allow the reduction of costs of cellulosic ethanol production and to improve its competitiveness as compared with petroleum based fuels and corn ethanol (Adekunle et al., 2016).

The integration of a reversible reaction with the separation into a process unit allows removing potential by-products when the reaction still occurs. In fermentation, the products can inhibit the process limiting their concentration and leading to low fermentation yields. Therefore, higher product concentrations and yields can be achieved by systems in which products can be removed simultaneously with fermentation. These systems comprise hybrid reaction-membrane separation (filtration, electrodialysis, pervaporation, or distillation), fermentation extraction, reactive distillation, and absorptive distillation systems (Huang and Ramaswamy, 2013).

As described in this section, there are several types of fractionation and purification methods, each with techno-economical advantages and drawbacks. It is most important to find the right route to fractionate and purify e.g. carbohydrates and lignin in order to be used as feedstocks for profitable and environmentally sound production of bioplastics. Hence, the development of cost-

**Table 1**  
Comparison of main fractionation processes applied to lignocellulosic materials.

Type	Mechanism	Characteristics/Advantages	Disadvantages	References
<b>Physical treatments</b>				
Mechanical (ball, hammer, blade, and rollers mills)	Splits lignocellulosic material into fine particles.	Decrease of particle size. Increase of specific surface area. Reduction of polymerization degree. Reduction of cellulose crystallinity. Low investment costs. Applicable to various lignocellulosic biomasses.	High mechanical energy input and costs. High operational costs. No extraction of compounds.	Bajpai, 2016
Gamma irradiation	Breaks bonds of the molecular chains of cellulose and links between hemicelluloses and lignin.	Cellulose is degraded to oligosaccharides and low molecular weight oligomers.	Complex and expensive facilities required to apply the high-energy demand. Radiation doses >100 Mrad imply high processing costs. Difficult application at industrial scale.	Saini et al., 2015 Chen, 2015
Ultrasound	Enhances chemical treatments to extract hemicelluloses and lignin, resulting in increased delignification and porosity.	Moderate treatment conditions (25 °C, 60 min).	Superficial effect on biomass.	Ur Rehman et al., 2013
Microwave	Causes localized heating which produces a disruption of lignocellulose material. Cellulose and hemicellulose become more accessible to enzymatic hydrolysis.	Low power consumption and low cost treatment. Effective when applied in combination with chemicals. Treatment times are proportional to the power of the microwave oven. Efficient and environmentally friendly. Less or no solvents are required.	Energy-intensive and expensive.	Bajpai, 2016 Zhu et al., 2005 Ooshima et al., 1984
<b>Physico-chemical treatments</b>				
Steam explosion	Uses high-pressure steam by direct injection of saturated steam followed by a sudden decompression to atmospheric pressure. The rapid evaporation of capillary water produces a combination of physical changes (breakdown of lignocellulosic fibers) and chemical (depolymerisation and breaking of C-O-C bonds).	High temperatures and short residence times (270 °C, 1 min) or low temperatures and long-times (190 °C, 10 min) can be applied. Hemicelluloses are extracted as oligomers or sugars, depending on the treatment conditions. Cellulose undergoes minimal depolymerisation whereas lignin can be removed virtually unchanged. Using chemicals improves the hemicelluloses removal.	Residual solid should be washed by water to remove the inhibitory materials. Inhibitors production for microbial growth, enzymatic hydrolysis, and/or fermentation.	Chen, 2015 Bajpai, 2016 Singh et al., 2015 Jacquet et al., 2015
<b>Chemical treatments</b>				
Auto- hydrolysis	Liquid hot water (LHW) is an auto-catalyzed treatment based in the auto-hydrolysis mechanism. The effect is due to chemical hydrolysis of the acetyl residues of xylans producing acetic acid, which catalyzes the hydrolysis of hemicelluloses (auto-hydrolysis) and partially destroys lignin-carbohydrate bonds.	No chemicals are used. Hot water at temperatures between 150 and 250 °C, in a pressurized reactor, for moderate times can hydrolyze 80–100% of hemicelluloses as oligomers. High amount of solubilized products and less degradation products that steam explosion. Limited equipment corrosion. Reduction of capital and operational costs. High recovery of solids, higher content of cellulose with increased enzymatic digestibility.	Incomplete destruction of lignin–carbohydrate complex. Condensation and precipitation of soluble lignin (biomass less digestible). Degradation of hemicelluloses at high temperatures, (formation of fermentation inhibitors). Lower concentration of solubilized products as compared to steam explosion.	Vallejos et al., 2016
Dilute acid	At moderate temperature, hemicelluloses and cellulose are direct saccharified with low yields because of sugar decomposition. High temperatures are favorable for cellulose hydrolysis	Usual concentrations ranges are between 0.2 and 1.0% acid by weight and temperatures between 150 and 190 °C. Hemicelluloses and cellulose are degraded in sugars by glycosidic bonds breaking. High hemicelluloses yield. Low cost of the catalyst.	Neutralization of acidic hydrolyzates is necessary before sugars fermentation. Gypsum is formed when acid is neutralized with inexpensive calcium hydroxide. Equipment corrosion. Particle size reduction is required.	Bajpai, 2016
Alkaline	The reactions involve saponification of the esters of xylans and lignin, resulting in swelling of the biomass due to the solvation of the generated ions. Produces splitting of lignin-carbohydrates bonds.	Low temperatures and pressures Hemicelluloses are solubilized. Lignin solubilization depends on the alkalinity and temperature. Less sugar degradation compared with acid processes.	High alkali consumption. Conversion of alkali into irrecoverable salts and/or the incorporation of salts into the residual solid.	Kim et al., 2016 Bajpai, 2016

Organosolv	<p>The effectiveness of these treatments depends on the lignin content of the feedstock.</p> <p>Includes a catalyst (HCl or H<sub>2</sub>SO<sub>4</sub>) to break the internal bonds between lignin and hemicelluloses.</p> <p>The solvent facilitates the dissolution of lignin increasing the accessibility of the acid into the fibrils.</p> <p>Without catalyst, the medium is acidified by the deacetylation of the hemicelluloses.</p>	<p>Increase of internal surface area.</p> <p>Decrease of degree of polymerization and crystallinity of cellulose.</p> <p>The solvent allows decreasing the severity of the reaction conditions.</p> <p>Sulfur-free lignin with high purity and low molecular weight apt for bioplastics manufacture can be obtained.</p> <p>Easy recovery of organic solvents by distillation for reuse, reduce chemical consumptions and process costs.</p> <p>Largely studied for sugarcane bagasse and grasses.</p> <p>Ozone pressures range from 0.6 to 1.5 bar and times between 15 and 30 min.</p> <p>Removal of lignin.</p> <p>Low toxic compounds concentration.</p>	<p>Requires high-pressurized reactors (volatile organic liquid at high temperature).</p> <p>Risks of fire or explosion.</p> <p>Concerns of safety, environmental, and health.</p>	<p>Zhao et al., 2009</p> <p>Zhang et al., 2016</p>
Ozone	<p>Removes lignin and gradually hemicelluloses at ambient pressure and temperature, yielding a purified cellulosic solid with increased reactivity.</p>	<p>Organic molecules are decomposed into CO<sub>2</sub>, H<sub>2</sub>O, and simpler and more oxidized organic compounds, especially low molecular weight carboxylic acids.</p> <p>The residual solid is cellulose with low lignin content.</p>	<p>Low O<sub>3</sub> pressures are not effective to penetrate fibers.</p> <p>High O<sub>3</sub> pressures cause biomass degradation.</p> <p>High production costs because of the high ozone requirements.</p>	<p>Sugimoto et al., 2009</p> <p>García Cubero et al., 2009</p> <p>Chen, 2015</p>
Wet oxidation	<p>Uses water in the presence of oxygen or air at high temperatures (about 200 °C) and pressures (up to 2 MPa).</p> <p>Oxidizes oxidizable organic and inorganic compounds.</p> <p>High temperatures cause substantial fragmentation and oxidation, mainly of lignin.</p>	<p>Generation of low amounts of furfural and HMF (inhibitors in the fermentation).</p> <p>Large amounts of hemicellulosic sugars are lost.</p> <p>Exothermal process, requiring control of process parameters.</p>	<p>Requires high-pressurized reactors (volatile organic liquid at high temperature).</p> <p>Risks of fire or explosion.</p> <p>Concerns of safety, environmental, and health.</p>	<p>Bajpai, 2016</p> <p>Martín Medina et al., 2008</p> <p>Banerjee et al., 2009</p>

efficient and dedicated fractionation and purification processes is essential for the implementation of competitive processes for bioplastic production.

#### 4. Bioplastics

The classification of plastics into thermoplastics and thermosets refers to plastic compounds which can be melt-molded (i.e. thermoplastics) and plastic resins which polymerize and cross-link upon heating to form unmoldable thermosets. Examples of thermoplastics from the petrochemical feedstock are polyolefins (PE, PP), polyethylene terephthalate (PET) and polycarbonate. Common thermosets include phenol formaldehyde resin (PF) and polyurethane (PUR). The mentioned plastics can be either replaced or enriched with biobased components as described in the present review.

The first generation compostable bioplastics, polylactic acid (PLA) and compounds based on starch (thermoplastic starch) and cellulose (e.g. cellulose acetate and cellulose xanthate/cellophane) represent major categories of bio-based plastics. Although growing, the bioplastic market still constitutes less than a percentage of the total market of plastics. The global production capacity of bioplastic comprised approximately 1.7 million tons in 2014 (Aeschelmann and Carus, 2015). For comparison, the global thermoplastic market was over 215 million tons whereas the production of thermoset plastics was more than 30 million tons in 2012 (Mordor Intelligence LLP, 2016a; Mordor Intelligence LLP, 2016b).

The production of bioplastics can be described by different production routes, the most important ones for bioplastics based on forestry biomass are described in Fig. 3.

##### 4.1. Major monomer-based bioplastics

Three monomer-based bioplastics on the market are PLA (e.g. produced from corn by NatureWorks™), BioPE (e.g. produced from sugarcane by Braskem in Brazil) and PHA. The monomers for the production of PLA, PE and PHA can be produced from forest-based raw materials. However, corn and sugarcane have an advantage over wood-based lignocellulose since their sugars have a lower degree of polymerization and therefore they are more easily extracted from the plants. Using wood-based lignocellulose in production routes involving monomeric sugar (routes 2 and 3 in Fig. 3), requires pretreatment to separate the polysaccharides from other wood components. Additionally, conversion steps are necessary to degrade the polysaccharides to monomeric sugar, as described previously. However, it is a challenge to perform the degradation without simultaneously producing compounds that have an inhibitory effect on the microorganisms used in subsequent process steps (Almeida et al., 2009).

##### 4.1.1. Polylactic acid

PLA is an aliphatic polyester produced by polymerization of lactic acid (Route 3, Fig. 3), which separation and purification require electro dialysis, solvent extraction, adsorption, reverse osmosis, and reactive distillation (Huang and Ramaswamy, 2013). The costs of separation and recovery can be reduced by the increase in concentration of raw material, but this also involves an increase of fermentation and enzymatic hydrolysis costs. After fermentation, proteins in the fermentation broth can be removed by ultrafiltration. The electro dialysis unit converts lactate to lactic acid and sodium hydroxide by bipolar membranes. Lactide is purified by vacuum distillation. Polylactic acid can be obtained by the condensation and polymerization of lactic acid or by the chain growth ring-opening polymerization of lactide (Lim et al., 2008).

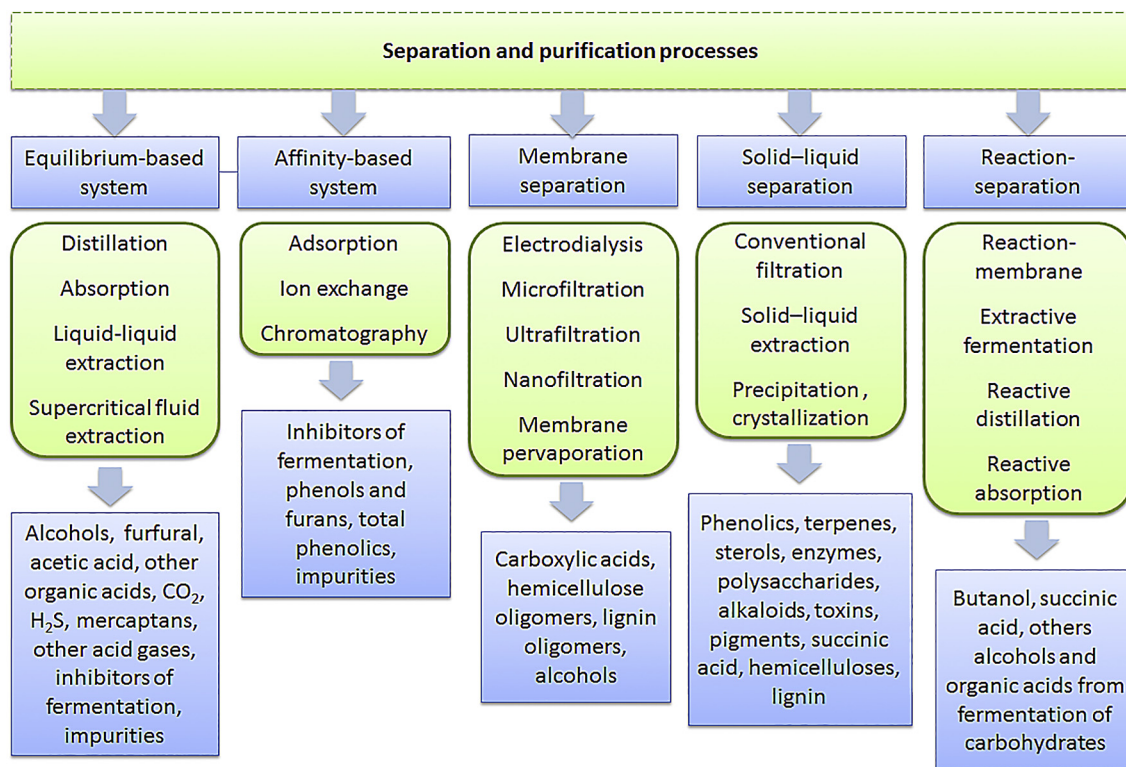


Fig. 2. Main separation and purification techniques and processes of components from biomass.

The most commonly used route is by ring-opening polymerization of the intermediate dilactide. Direct condensation of lactic acid is a more challenging process, which gives lower molecular weights and poor mechanical properties of the PLA (Vink et al., 2003; Mehta et al., 2005). Bio-based lactic acid and lactide is produced by fermentation of sugar (commonly corn-based sugar). Hydrolysis of lignocellulosic woody biomass represents an attractive route for lactic acid/lactide production provided that adequate and cost-efficient technological solutions to the challenges described above are developed. PLA is thermoplastic and can be converted to end products using modified industrial equipment for thermoforming, such as injection molding, blow molding, foaming, film extrusion and fiber extrusion. The processing temperatures of PLA are low compared to conventional thermoplastics. Synthesis, processing and modification of PLA have been reviewed by several researchers (e.g. Rasal et al., 2010; Mehta et al., 2005). PLA can be used in a wide range of applications including geotextile, agricultural film, packaging, as binder fiber for cellulosic non-wovens and recently as one major thermoplastic for 3D printing, using the fused deposition modeling method (Fig. 4). Since it can be bioresorbed by human body and is biocompatible (i.e. compatible with human body) (Lasprilla et al., 2012), it has been used in absorbable sutures and prosthetic devices (Auras et al., 2004). PLA has been commercialized by NatureWorks™. The global demands for lactic acid and PLA were 714 and 361 ktons in 2013 (Grand View Research, Inc, 2015), which represents a minor fraction of the total plastic consumption worldwide.

#### 4.1.2. Polyhydroxyalkanoates

PHAs is a collective denotation of a large class of bio-based polyesters. Like PLA, PHAs can be thermoformed and are produced from renewable feedstocks (e.g. glucose, sucrose, fatty acids) via biotechnological routes applying different microorganisms

(Route 2 in Fig. 3) (Kawaguchi et al., 2016). Depending on carbon source, choice of microorganism, process conditions and additives, polymers with various monomeric compositions and different characteristics (such as crystallinity, chain length, brittleness and elasticity) are obtained (Keenan et al., 2006). Suriyamongkol et al. (2007) and Kawaguchi et al. (2016) reviewed the biotechnological production routes of PHAs.

PHA granules of significant purity can be produced by bacterial fermentation, breaking the bacterial cell and solubilizing the cellular material. The digestion method using low cost chemicals or enzymes is an efficient and economical recovery process. Equipment is the main cost in PHA production, but its concentration also has important effects on the economics of the process (Snell and Peoples, 2009). After separation of cells from the broth, the enzymatic treatment to release the intracellular PHA granules can be carried out with e.g. lysozymes, exonucleases and proteinases (Wang et al., 2014). High purity PHA can be obtained by solvent extraction (e.g. chloroform, methylene chloride). However, this method has some disadvantages, e.g. i) the high viscosity of the extracted polymer solutions (PHA > 5% w/v), ii) the difficulty of cell residues removal, and iii) the use of toxic and volatile solvents (Choi and Lee, 1999). Continuous centrifugation of broth with low cell concentration is an expensive separation method due to its high-energy requirement.

Several companies worldwide have been producing different types of PHAs, including poly-(R)-3-hydroxybutyrate (PHB) and the copolymer of the monomers (R)-3-hydroxyvalerate and (R)-3-hydroxybutyrate (PHVB). Possible bioplastic applications of PHAs include packaging, textiles and medical implants. However, there has been no significant implementation of PHAs in bioplastic products (Chen, 2009) and one cause is believed to be the high production cost of PHAs. There have been some efforts to find alternative and less costly feedstocks for PHAs. An example is the

**Table 2**

Characteristics and applications of the main techniques and processes of separation and purification of the different components of biomass.

Type	Mechanism	Characteristics/Applications	References
<b>Equilibrium-based processes</b>			
Distillation	Separation of liquids with different boiling points by evaporation and subsequent condensation.	It is a mature method used in many industries, which can be applied to extract light components whose vapor pressures are relatively high, and to separate light components of essential oils and bioactive compounds from lignocellulosic material, to obtain value-added by-products. Furfural and acetic acid can be separated by distillation from the same stream. Ordinary and azeotropic distillations are usually used for separation and dehydration of ethanol.	<a href="#">Lei and Chen, 2013</a> <a href="#">Liu et al., 2013</a> <a href="#">Nhien et al., 2016a</a>
Absorption	Removal of components from a gas by contacting with a solvent in which it is dissolved. The solvent is regenerated and recycled.	It is used to remove CO <sub>2</sub> , H <sub>2</sub> S, mercaptans, and other acid gases at different levels of concentration (even ppm or ppb) from a gas or vapor stream into a liquid stream by chemisorption or physisorption. Selexol™ and Rectisol™ are the most used processes to extract these gases from CH <sub>4</sub> mixtures, such in synthesis gas.	<a href="#">Groeger et al., 2015</a> <a href="#">Huang and Ramaswamy, 2013</a> <a href="#">Sadhukhan et al., 2014</a>
Liquid-liquid extraction	Extraction of components from the liquid phase to one or more solvents phase.	It can be used to separate: (i) bioalcohols and carboxylic acids from their fermentation broths, (ii) compounds toxic to microorganisms from biomass hydrolyzates used for fermentation and (iii) impurities as soap, methanol, and glycerol in biodiesel. Organic acids (succinic, maleic, lactic, and itaconic acids) can be extracted from the fermentation broths by reactive extraction with amine extractants. Ionic liquids can be used as agents for the separation of selected compounds, for example, the dehydration of ethanol–water mixtures, the extractive separation of biofuels or lactic acid from the respective fermentation broths, and the removal of volatile organic compounds or carbon dioxide from gaseous biorefinery effluents.	<a href="#">Huang and Ramaswamy, 2013</a> <a href="#">Peleteiro et al., 2015</a>
<b>Affinity-based processes</b>			
Adsorption, ion exchange, and chromatography	Selective transference of adsorbates from the fluid phase to the surface of insoluble, rigid particles suspended in liquid in a vessel or packed in a column.	Adsorption and ion exchange are efficient to eliminate inhibitor compounds from lignocellulosic hydrolyzates. Ion exchange and activated carbon can remove a great proportion of furans and total phenolics from hydrolyzates. Regeneration of the adsorbents is critical. Simulated moving-bed chromatography has better performance (higher throughput and less solvent requirement) than traditional batch chromatography.	<a href="#">Berrios et al., 2013</a> <a href="#">Venkatesan, 2013</a>
<b>Membrane separation</b>			
Electrodialysis	Selective extraction of ions from one solution to another solution, through ion-exchange membranes based on electric potential difference.	It can be used for the separation of organic acids or carboxylic acids from fermentation broths (acetic acid, oxalic acid, citric acid, gluconic acid, succinic acid, others). Anion exchange membranes can remove inhibitors from the hydrolyzates prior to fermentation, such as acetic acid generated from hemicelluloses acetyl groups during hydrolysis.	<a href="#">Huang and Ramaswamy, 2013</a>
Nanofiltration	Pore size is of 1 nm (molecular weight cut-off of 300–500 Da). In contact with aqueous solution, membranes are slightly charged (dissociation of surface functional groups or adsorption of charge solute).	It can be applied to separate small molecular weight hemicelluloses oligomers from hydrolyzates. Hydrophobic molecules (as lignin and resins) can foul hydrophobic membranes whereas hydrophilic membranes had no fouling problems. This technique can also be used for separation and purification of ionic liquids.	<a href="#">Huang and Ramaswamy, 2013</a> <a href="#">Mohammad et al., 2015</a>
Ultrafiltration (UF) and Microfiltration (MF)	Pore size of 0.08–2 μm for MF membranes and 0.002–0.1 μm for UF membranes.	These are cost-efficient and environmentally friendly separation processes for biorefineries.	<a href="#">Huang and Ramaswamy, 2013</a>

*(continued on next page)*



Table 2 (continued)

Type	Mechanism	Characteristics/Applications	References
Pervaporation	The membrane in contact with a liquid mixture allows the removal of one of the components from the mixture (higher affinity with, and/or quicker diffusivity).	<p>These processes do not require pH or temperature adjustments of the feed and the separation can be fine-tuned by the choice of appropriate membranes and operating conditions.</p> <p>These techniques can be used to separate colloids and macromolecular matter, and to fractionate polydisperse compounds as lignin and hemicelluloses, according to their molecular mass.</p> <p>This is a promissory technique for molecular-scale liquid/liquid separations in biorefineries due to its high selectivity, cost, and safety.</p> <p>Inorganic membranes and organic–inorganic hybrid membranes prevail for alcohol dehydration.</p> <p>Polymeric membranes with higher flux and separation factors in a harsh operating environment are in demand. For alcohol recovery, the development of novel hydrophobic materials is needed.</p>	<p>Wang et al., 2013a Shao and Huang, 2007</p>
<b>Solid–liquid separation</b> Filtration	Applied to recover solid (cake) or liquid (filtrate) phases. The suspension is pushed (either by pressure or vacuum), through a screen to obtain a stream of filtrate. The solid is collected on the surface (cake layer).	<p>It is a mature method used in many industries.</p> <p>In biorefineries, the processing of solid lignocellulosic materials involves numerous solid–liquid separation stages to extract valuable compounds from solid feedstocks with a solvent or solvent mixture.</p> <p>This technique can be assisted by ultrasound, microwave, and pressure.</p> <p>Value-added co-products as phenolics, terpenes, sterols, enzymes, polysaccharides, alkaloids, toxins, and pigments can be extracted for nutraceutical and pharmaceutical industries by filtration</p>	<p>Abidin et al., 2013 Huang and Ramaswamy, 2013.</p>
Precipitation	Formation of an insoluble compound by reaction or by temperature change affecting the solubility of the compound. It may also take place if solute concentration surpasses its solubility limit.	<p>Ethanol precipitation is used for hemicelluloses recovery from hydrolyzates in biorefineries.</p> <p>Succinic acid can be crystallized and isolated from its fermentation broth whereas lactic acid, acetic acid, and formic acids are miscible in the solution.</p> <p>In pulp mills, acidification to pH 2 of spent liquors with CO<sub>2</sub> or sulfuric acid allows lignin precipitation and extraction from kraft black liquors.</p>	<p>Huang and Ramaswamy, 2013</p>
<b>Reaction - separation</b> Reaction-membrane	Removal of potential by-products after reversible reactions. The rate and the yield are limited by the reaction equilibrium.	<p>It is a biocatalytic process together with an efficient membrane separation: the biocatalyst (microorganism or enzyme) is retained by the membrane, which allows the preferential permeation of smaller substrates or products.</p> <p>It is a highly selective method with relatively low energy requirements, which combines the catalytic features found in biological systems and the separating properties of membrane systems.</p>	<p>Huang and Ramaswamy, 2013.</p>
Extractive fermentation	Separation of products <i>in situ</i> (within the bioreactor) or <i>ex situ</i> (circulation of the broth through an external separation unit).	<p>A technology that can be used in the slipstream method for the recovery of fermentation products (carboxylic acids and alcohols). Since the inhibitory fermentation product as removed as being produced it prevents its accumulation to a level toxic to the microorganism.</p>	<p>Yang and Lu, 2013</p>

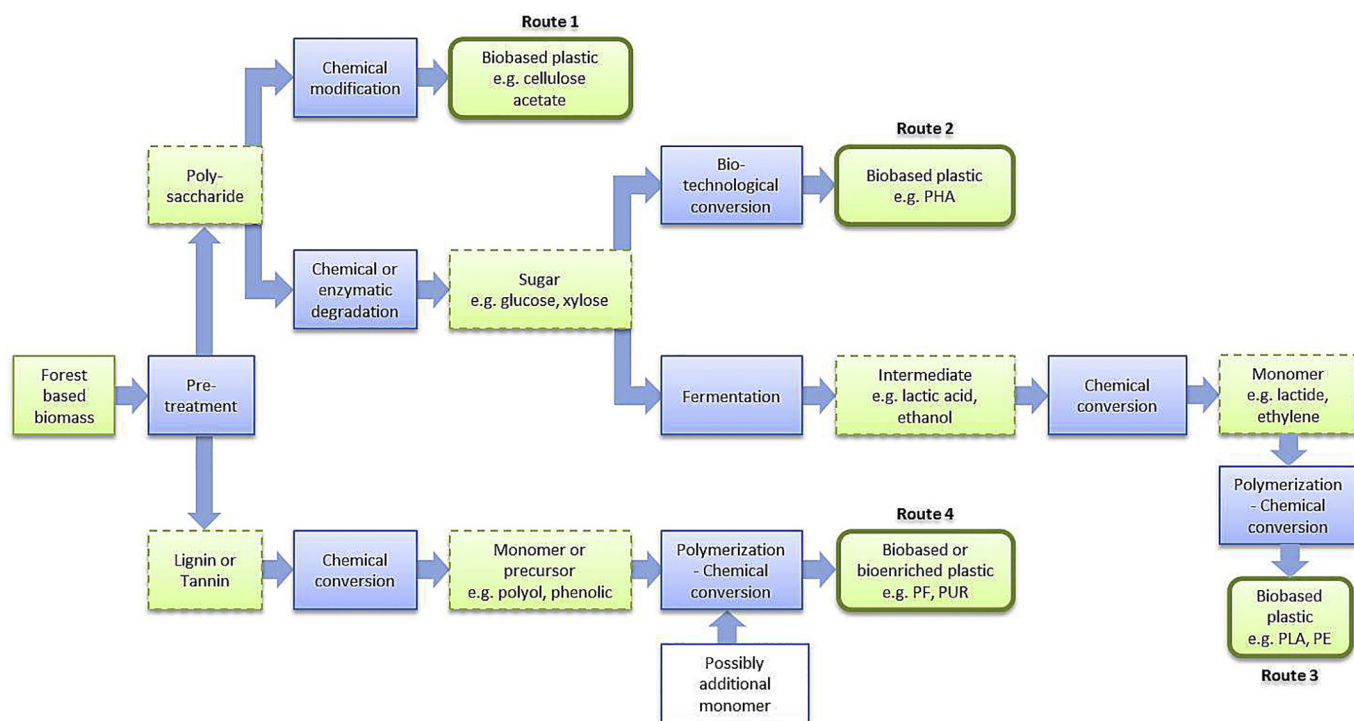


Fig. 3. The main production routes to forest-based bioplastics.

usage of hemicelluloses sawmills extracts since wood-based poly-saccharides can be used in bacterial production of PHA (Silva et al., 2007).

#### 4.1.3. Polyethylene

PE is an aliphatic polyolefin produced by polymerization of ethylene (Route 3 in Fig. 3) and represents more than 30% of the global plastic market (Hutley and Ouederni, 2016). Bio-ethylene, made from ethanol based on biomass, represents a chemically identical alternative to ethylene from petrochemical feedstock. However, the overall production process of ethylene from sugar-based ethanol has to be further optimized. The most well developed production routes for bio-ethanol are fermentation of sucrose (e.g. sugarcane feedstock) and hydrolysis followed by fermentation of starchy biomass (e.g. corn feedstock).

The bioethanol production defines the final production cost of bio-ethylene. For example, the use of Brazilian or European ethanol results in 85 and 91% of total production cost, respectively (Haro et al., 2013). This means that the origin of bioethanol is crucial in the processes. The cost of petrochemical ethylene is around USD 600–1300 per ton. Brazil produces cost-competitive ethanol for

ethylene production at current market prices due to the availability of cheap sugarcane feedstock and their extensive experience in ethanol production (Broeren, 2013). Production cost in Brazil is around USD 1200 per ton of sugarcane ethylene, whereas in the United States, the cost is estimated as USD 1900–2000 per ton of cellulosic ethylene. The impact of cellulosic ethanol on bioethanol commercial price (now involving 1st generation) is unknown, because it is still in development (Broeren, 2013).

The dehydration of ethanol to ethylene is commercially available and established technology. It is based on preheat of the blend of ethanol and water (1:1 M ratio) to produce dehydration in a reactor (350 °C, 5 bar, usually), and further cooling and compressing of the gas stream for ethylene recovery by fractionation columns. The final product stream contains 99.99% (on a weight basis) ethylene, with methane as main impurity (Haro et al., 2013).

Forest-based lignocellulosic biomass can also be used, but the conversion of biomass to ethanol precursors is more challenging and costly. A techno-economic study of a biorefinery producing polymer-grade ethylene, organosolv lignin, biomethane and hydrolysis lignin from wood showed that a heat integrated biorefinery concept is not yet profitable and that profitability strongly depends on the assumptions of the price of raw material and the selling prices of the products. The minimum selling price obtained for ethylene was 1349 € per ton, close to the price of fossil-based ethylene (Nitzsche et al., 2016).

As an example, the Norwegian company Borregaard produces approx. 20 million liter ethanol from hemicellulose from softwood (*Picea abies*) (Valles, 2015). Presently, the 2nd generation lignocellulosic bio-ethanol is used in paint/varnish, car care products and fuel in diesel engines (Rødsrud, 2012). 2nd generation lignocellulosic bio-ethanol requires less land use, which is an environmental advantage (see e.g. Broeren, 2013). Unfortunately, the worldwide production of 2nd generation bio-ethanol is low and the price is high due to several reasons, including expensive production routes (Carriquiry et al., 2010). This limits the use of lignocellulosic bio-

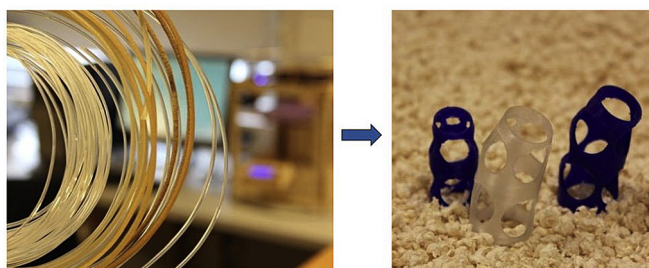


Fig. 4. PLA-based filaments containing wood fibers for 3D printing by fused deposition modeling (left). PLA-based 3D printed finger orthosis (right).

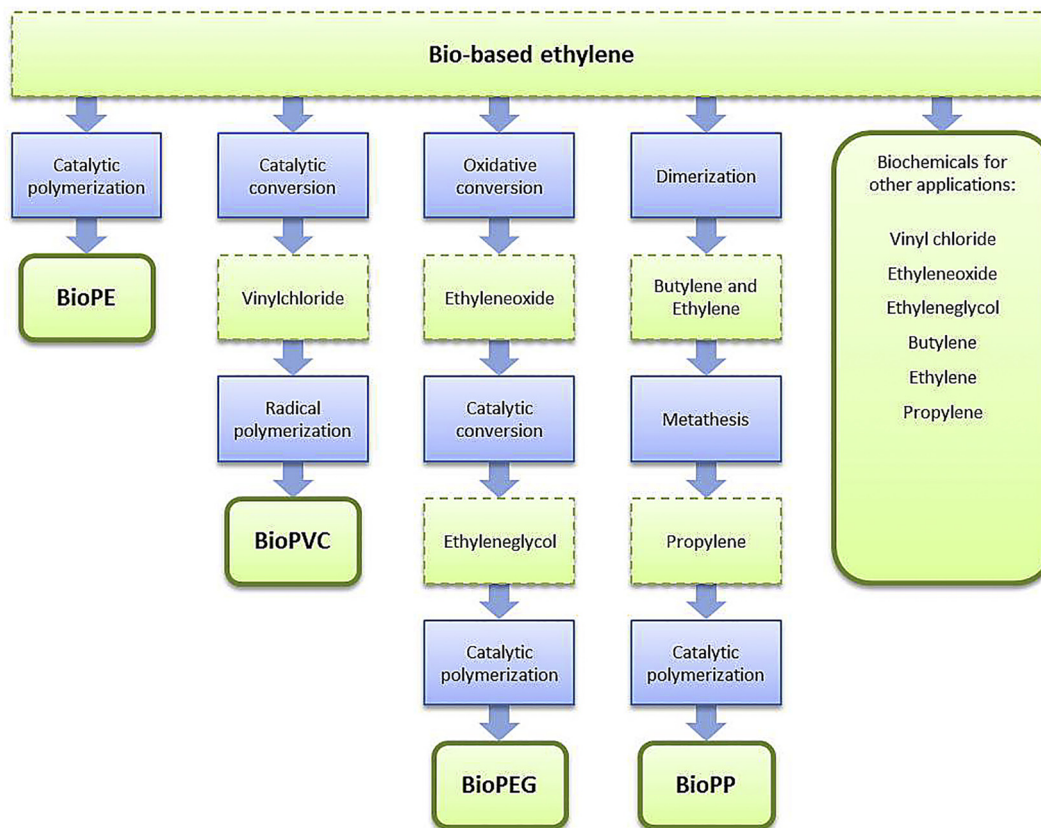


Fig. 5. Bioplastics produced from the bio-ethylene platform.

ethanol for production of bioplastics and emphasizes the necessity of technological advances and breakthroughs in the area.

An alternative processing route for polyolefins from the forest-based feedstock, is by catalytic fast pyrolysis of biomass into olefins (mainly ethylene and propylene) (Carlson et al., 2011) followed by separation of the olefins and polymerization into PE and polypropylene (PP). PP can also be produced by biochemical and thermochemical routes, based on metathesis of butane and ethylene to produce the propylene monomer.

The replacement of conventional fossil-oil plastics (PE, PP) with drop-in polymers is not necessarily the only alternative from a bioeconomy point of view. According to Nova-Institute, the production of 1 kg of BioPE and PLA requires 4.0 and 1.6 kg of fermentable sugar, respectively. Additionally, from 1 ha of sugar cane (or sugar beet), 2–3 and 6–7 tons of BioPE and PLA, respectively, can be obtained (Carus, 2016; see also IfBB report, 2016). However, keep in mind that PLA and BioPE are two polymers with different properties (e.g. mechanical). Additionally, they differ with respect to their durability and can be used in different applications. Dedicated polymers from biomass (e.g. PLA) are considered good demonstrators of a successful development of alternative bioplastic products (Carus, 2016). However, increased production of bioplastics will probably require accessibility to biomass from non-food resources, where lignocellulosics can play an important role.

#### 4.2. Wood-based platform molecules

Platform molecules are chemicals that can be converted into a large number of chemicals, materials and plastics. Bio-based platform chemicals that can be produced from wood-based feedstocks include e.g. succinic acid, 2,5-furandicarboxylic acid (FDCA), 5-

hydroxymethyl furfural (HMF), ethylene, levulinic acid, adipic acid and sorbitol (Bozell and Petersen, 2010; Bechthold et al., 2008; Vardon et al., 2015). Ethylene can be produced both from petrochemical and bio-based feedstocks and is one of the most important platform chemicals in use today. In addition to being the monomer of PE, other important monomers can be obtained by derivatization of bio-ethylene, such as propylene (the monomer of polypropylene), vinylchloride (precursor of PVC) and ethylene glycol (monomer used for production of bio-PEG) (Fig. 5).

HMF is another example of a platform chemical that can be produced from bio-based carbohydrates (Fig. 6). Much of the research on the production of HMF from carbohydrates has been focused on the conversion of fructose (van Plutten et al., 2013; Sheldon, 2014). As mentioned above, the most abundant 6-carbon carbohydrate in lignocellulosic resources such as wood is glucose, being the monomer of cellulose as well as some hemicelluloses. Its conversion into HMF has been considered more challenging compared to fructose due to its more stable ring structure and the formation of more by-products (van Plutten et al., 2013; Zhao et al., 2007). There are however, processes to convert glucose as well as cellulose into HMF at good yields using metal halide and ionic liquid catalysis (Zhao et al., 2007; Su et al., 2009). The direct conversion of cellulose into HMF is interesting since it removes the challenging process step of hydrolyzing cellulose into glucose (Su et al., 2009).

HMF can be used in the production of different bio-based polyesters and polyamides, but it is also an intermediate in the production of other platform chemicals, i.e. levulinic acid (LA) and 2,5-furandicarboxylic acid (FDCA) (Eerhart et al., 2012).  $\epsilon$ -Caprolactone, the monomer of the polyester polycaprolactone (PCL), is synthesized industrially by oxidation of cyclohexanone (Labet and

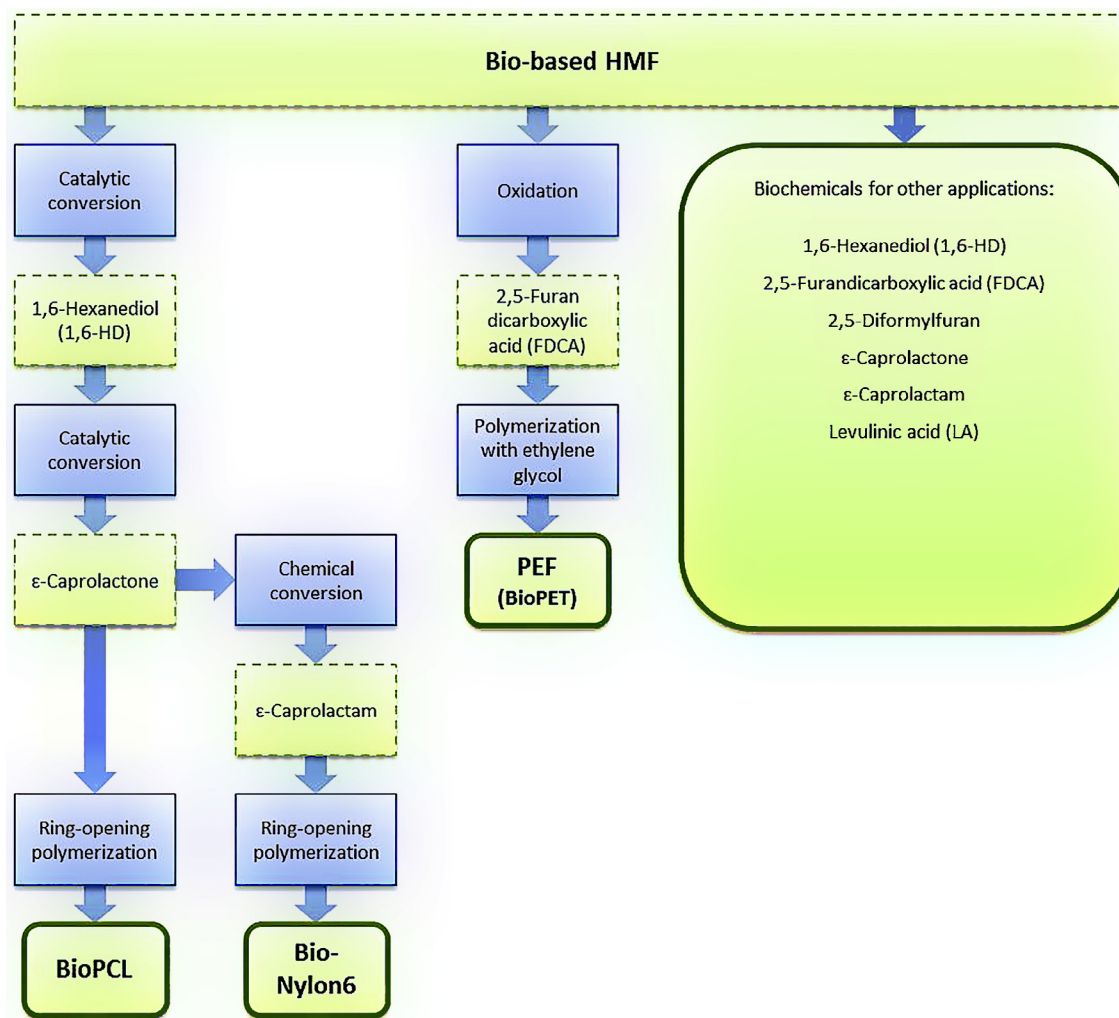


Fig. 6. Bioplastics produced from the HMF platform.

Thielemans, 2009), but can also be produced from wood and other lignocellulosics via 1,6-hexanediol from the HMF platform (Buntara et al., 2011). Poly-ε-caprolactone (PCL), the equivalent amide (poly-ε-caprolactam, *i.e.* Nylon 6) and the polyesteramide copolymer, are produced commercially by ring-opening polymerization from the monomers (Fang et al., 2002). The bio-based amide monomer (*i.e.* ε-caprolactam) may be produced from lysine via fermentation from glucose (Frost, 2005) but also by reaction of ε-caprolactone with ammonia (Buntara et al., 2011). Another molecule that can be synthesized from HMF is adipic acid, which is one of the monomers in the polyamide Nylon 66 (*i.e.* poly(hexamethylene adipamide)) (Dros et al., 2015). HMF can also be converted into polyethylene furandicarboxylate (PEF), the bio-based counterpart to the common petroleum-based plastic polyethylene terephthalate (PET) (Eerhart et al., 2012). In the final process step, FDCA is polymerized with ethylene glycol (EG) into PEF. By selecting a bio-based EG from the ethylene platform a fully bio-based PEF is obtained.

#### 4.3. Wood-based polysaccharides as bioplastics

Bioplastics based on naturally occurring and slightly modified polymers such as cellulose have long history and were used before the petrochemically based plastics were introduced to the market. As stated above, lignocellulosics wood fibers consists of roughly

35–50% by weight of cellulose and 25–35% by weight of hemicelluloses. These polysaccharides can be shaped into *e.g.* films after dissolution. Cellulose films possess good strength, toughness, and transparency, and high surface gloss (Yano et al., 2005). In many cases, the cellulose is modified chemically during the dissolution process to ease the disintegration of the polymeric chains. To produce *e.g.* cellulose esters or ethers the hydroxyl groups of cellulose are reacted chemically, whereas the polymer backbone is intact. The cellulose derivative is obtained as a polymer solution that can be regenerated *e.g.* as film (*e.g.* for packaging and other barriers) or fiber (*e.g.* for textiles). Plastic materials made of cellulose derivatives are produced by route 1 in Fig. 3. Cellulose xanthate (also referred to as viscose) is produced by the reaction of cellulose with carbon disulfide and alkali (Paunonen, 2013). Films produced from cellulose xanthate (also referred to as Cellophane) are transparent films often used in food packaging. Cellulose acetate is optically clear and printable films used as polarized films for liquid crystal displays (LCDs), as film base in photographic film and in sunglasses. It is considered biodegradable, since many microorganisms have acetyl esterase enzymes and are capable of deacetylation (Puls et al., 2011). Methylcellulose and carboxymethyl cellulose can be regenerated as edible films for packaging. Additionally, bio-based thermoplastic of a new class was successfully fabricated from cellulose hydrogels prepared in an alkali hydroxide/urea aqueous

solution by changing the aggregated structure via a hot-pressing process (Wang et al., 2013).

Hemicelluloses are a group of less structurally ordered, amorphous polysaccharides in lignocellulose. Hemicelluloses are the most hydrophilic polymers of wood, and have the lowest thermal resistance (Hosseinaei et al., 2012). Polymeric and oligomeric hemicelluloses can be extracted from wood by different methods including microwave assisted water extraction (Gulbrandsen et al., 2015) and alkaline extraction (Jiang et al., 2014). They can also be obtained from the processing water from pulp mills (Hartman et al., 2006). Films made from hemicelluloses are brittle but with the addition of plasticizers materials with high toughness, low oxygen permeability as well as flexibility have been reported (Hartman et al., 2006; Gröndahl et al., 2004). The low oxygen permeability makes the films interesting for packaging applications. The films are also biodegradable, provided that bio-based and naturally occurring polymers and additives are used. Both the softwood hemicelluloses O-acetyl-galacto-glucomannan and the hardwood hemicelluloses glucuronoxylan have been used in mixtures with bio-based plasticizers to prepare films with good flexibility and oxygen permeability (Hartman et al., 2006; Gröndahl et al., 2004). However, the films were susceptible to moisture. The addition of high molecular weight biopolymers (carboxymethylcellulose or alginate) provided better resistance to humidity as well as high mechanical toughness, but on the expense of flexibility (Hartman et al., 2006).

#### 4.4. Lignin-based routes

Lignocellulosic wood fibers consist of 10–25% by weight of lignin. Lignin is a cross-linked phenolic polymer that performs the role of adhesive bonding the components of the cell wall together. It has been estimated that the current lignin production in the existing pulp and paper industry is between 50 and 60 million tons per year of which 98% is burned as a low cost fuel in the chemical recovery boiler and only 2% is used commercially (Christopher, 2013). This represents an underutilized resource with major added-value potential. A potential advent for lignin as a low cost additive would be its use in polyurethane (PUR) formulations to displace petroleum-derived compounds and thereby improving thermal and mechanical properties of the PUR (van Heiningen, 2006; Christopher, 2013). PUR is used in a versatile number of applications as solid plastics, coatings, foams and binders with major end-use being in furniture/bedding, construction, automotive and electronic products. The global market for PUR was estimated at 13 million tons in 2010 with revenue of \$33 billion (Christopher, 2013).

Polyurethanes are prepared by a two-component system based on the polymerization of polyols and isocyanates forming urethane linkages. The substitution of polyols in polyurethanes with bio-

based ones prepared from vegetable oils, have already reached some commercial importance. However, lignin derived from wood resources can be used as a renewable and bio-based alternative to replace some of the fossil-based polyols in the PUR formulation (Thring et al., 1997). It is necessary to combine the rigid lignin polyols with flexible aliphatic polyols to obtain PURs with good properties. With unmodified organosolv lignin, tough polyurethanes with satisfactory mechanical properties were obtained at lignin concentrations of 15–25 wt% (Thring et al., 1997). However, at higher lignin contents the polyurethanes were hard and brittle. In addition, many of the hydroxyl groups of the macromolecular lignin polyol are entrapped within its structure, making their reactivity towards isocyanate poor. Chemical modification with alkyloxides (often oxypropylation) is a common approach to introduce more available hydroxy groups in lignin (e.g. Li and Ragauskas, 2012). By this method, aliphatic chains with hydroxy groups in their ends are attached by ether linkages to former lignin hydroxy groups (Cateto et al., 2009). These flexible aliphatic chains are less sterically hindered making the new hydroxy groups more available for polymerization with isocyanates. Since alkyloxide homopolymers are formed simultaneously with oxyalkylation, a lignin that is already mixed with a more flexible polyol is obtained (Cateto et al., 2009). Li and Ragauskas (2012) found that compressive properties of PUR foams with oxypropylated lignin polyols were best when no other polyol was used. This was attributed to the rigid structure of the lignin polyol (Li and Ragauskas, 2012). Alkoxylation also makes hydrophilic lignin-types (i.e. lignosulfonates) soluble in organic solvents (Mozheiko et al., 1981). The reaction conditions have been optimized for usage in rigid PUR foams using commercial lignins from several raw materials (hardwood, softwood and non-wood) and extraction methods (kraft lignin, soda lignin and organosolv lignin) (Cateto et al., 2009).

Another way to make more flexible and uniform lignin polyols is liquefaction. Liquefaction of lignin has been illustrated for enzymatic hydrolysis lignin and autocatalyzed ethanol-water lignin by sulfuric acid catalyzed reaction of lignin in polyethylene glycol (PEG) and glycerol (Xue et al., 2013; Jin et al., 2011). By this method, lignin is hydrolyzed in a medium of PEG and/or glycerol and the smaller lignin fragments will be well mixed with the flexible polyol. Jin et al. (2011) reported that the hydrolyzed lignin polymers self-polymerize (i.e. recondensation) after blending.

Beside its use in polyurethanes and polyesters, lignin can replace phenolic compounds in the synthesis of phenol-formaldehyde (PF) resins. Kraft lignin has been used to replace up to 70% of the phenol required for PF resins (Alonso et al., 2004). PF resins are partly polymerized formulations, which form thermoset plastics in a second reaction step (Ibeh, 1999). A Resole resin is formed by a base-catalyzed reaction and with a high molar ratio of formaldehyde to phenol. The reaction is stopped by cooling to yield the resin, which can be stored and at a later point heated to allow

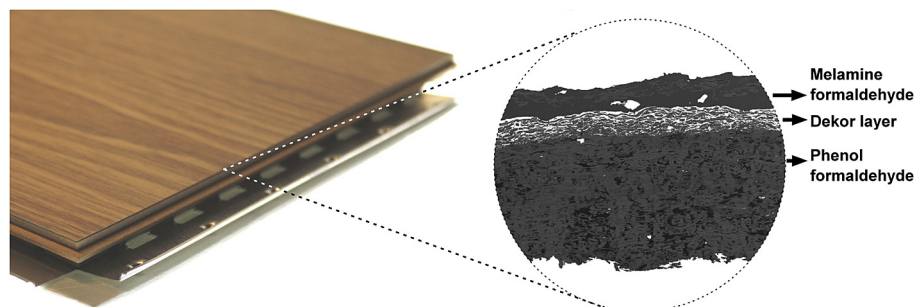


Fig. 7. High-pressure laminate for flooring applications, with PF and MF highlighted.

the reaction to proceed until a thermoset is obtained. Acid catalysis and a low molar ratio of formaldehyde to phenol are used in the production of a Novolac resin. Due to the shortage of formaldehyde reaction stops spontaneously and the partly polymerized resin has a high degree of cross-linking, a low molecular weight and is thermoplastic. The full reaction to obtain the thermoset can be obtained by addition of more formaldehyde. Often hexamethylene tetraamine (hexa) is used as a formaldehyde source (for details see [Ibeh, 1999](#)). PF is used as binder for wood-based products such as fiberboard and as thermoset matrix in paper-based laminates (see e.g. [Kouisni et al., 2011](#); [Brodin et al., 2015](#) and [Fig. 7](#)). Lignin can be used as a bio-based replacement for some of the phenol in the fossil-based phenol formaldehyde resin ([Kouisni et al., 2011](#)).

Steric hindrance of the functionalities in lignin limits its reactivity towards formaldehyde in lignin-based PF resins ([Raquez et al., 2010](#)). The curing chemistry of lignin-PF resins based on lignosulfonates was studied by [Turunen et al. \(2003\)](#), but in general, kraft lignins are more reactive compared to lignosulfonates. By chemical modification of the lignin by phenolation, the hardening time of the lignin-PF resins could be decreased below the hardening time of both unmodified lignin-PF resins and of commercial PF resins ([Cetin and Özmen, 2002a](#)). When used in particleboard panels lignin-PF resins with phenolated lignin imparted better mechanical and physical properties than unmodified lignins ([Cetin and Özmen, 2002b](#)). Methylation of lignin has been reported to increase the reaction time of lignin-PF resin and to perform well in plywood board ([Vázquez et al., 1997](#)). Additionally, kraft lignin has previously been applied as binder in fiberboards, yielding good mechanical and water resistance properties ([Mancera et al., 2011](#)).

It is important to keep the formaldehyde emissions down in indoor environments, medical devices and other products used in human vicinity, due to the carcinogenic properties of formaldehyde. This has promoted the development of alternative cross-linkers in cured plastics and adhesives ([Moubarik et al., 2010](#)). Non-formaldehyde yielding hexamethylenetetramine (often referred to as HEXA) and un-toxic glyoxal are alternatives that can be used in lignin based PF-type resins ([Perez et al., 2011](#); [Lei et al., 2008](#)). Recently, the production and usage of lignin based-aldehydes as alternatives to formaldehyde in phenolic resin production was reported ([Foyer et al., 2016](#)). Reactive aromatic precursors with two aldehyde moieties were prepared from lignin-based monomers (i.e. 4-hydroxybenzaldehyde and vanillin) and bromoalkylacetals. It should be mentioned that the bromoacetals are toxic reactants, although unreacted molecules are removed after synthesis of the precursors. Resole-type thermosets were prepared using the lignin-based aldehydes and thermal stabilities and char yields comparable to PF prepared with formaldehyde were presented (for details see [Foyer et al., 2016](#)). The lignin-based monomers, vanillin, is produced commercially from wood-based lignosulfonates by Borregaard in Norway (see [Rødsrud, 2013](#)) and is according to the best of our knowledge the only aromatic chemical produced in large amounts from lignin. The scientific efforts on the production of bio-based polymers from vanillin and lignin have been reviewed in recent years ([Fache et al., 2015](#); [Laurichesse and Avérous, 2014](#)).

Hydrolysable and condensed tannins are classes of phenol-based compounds found in wood and bark of different trees (e.g. bark from *Acacia* and *Pinus* species and in wood from *Schinopsis* species) ([Pizzi, 2006](#)). Tannin adhesives extracted from wood and other plant sources have been already applied in the production of plywood and particleboard ([Ogunwusi, 2013](#); [Mosiewicki et al., 2004](#)). Processed tannins with polyphenolic molecular structures were found to have higher chemical reactivity toward formaldehyde than phenol and could be used to partially replace phenol for synthesizing phenolic resins ([Zhao et al., 2013](#)). In another study,

50% of the phenol in the manufacture of PF resins was successfully replaced by hydrolysable tannins ([Christopher, 2013](#)). As with lignin PF-resins, non-formaldehyde emitting tannin-based PFs can be made using HEXA or glyoxal ([Lei et al., 2008](#); [Moubarik et al., 2010](#)). Flavenoid tannins have also been found to harden through autocondensation in the presence of small amounts of electron accepting chemicals (Lewis acids) ([Meikleham et al., 1994](#)).

#### 4.5. Forest-based components for the production of epoxy bioplastics

Bio-based epoxy resins can be manufactured from several resources, including lignin, vanillin (derived from lignin), suberins (derived from bark) and levulinic acid (derived from cellulosic biomass). Manufacture of bio-based epoxy resins usually includes the modification of the bio-based molecule, to attach an epoxy functionality ([Koike, 2012](#)). Epichlorohydrin (ECH) is the most common epoxidizing molecule for commercial epoxy resins. It is derived from glycerin, which is an available byproduct from the biodiesel production. The availability of bio-based ECH has driven a development of bio-based epoxy resins using ECH to functionalize bio-based monomers. The monomers are then polymerized by step-wise or chain-growth polymerization with comonomers (often amines) to form the thermoset product ([Auvergne et al., 2014](#)). Indeed, bio-based diphenolic acid produced from levulinic acid was used commercially for the production of its diglycidyl ether, until the fossil-based equivalent Bisphenol A became the less expensive and most widely used option ([Auvergne et al., 2014](#)). Several routes to prepare levulinic acid from lignocellulosic biomass have been suggested, including its conversion from HMF ([Gallezot, 2012](#)). The usage of monomeric wood-based moieties in epoxy plastics also includes different modifications of lignin-based vanillin ([Fache et al., 2015](#)). Biobased epoxy has been produced from vegetable oils such as castor oil, soybean oil and linseed oil. These compounds are limited in their use due to their low aromatic content and as a consequence, poor thermal and mechanical performance ([Koike, 2012](#)).

Lignin-based epoxy resins have a high aromatic content, can provide good thermal and mechanical performance, and have been used successfully as replacement of some of the conventional components in epoxy materials ([Koike, 2012](#); [Feldman et al., 1991](#); [Feng and Chen, 2012](#); [Zhao et al., 2001](#)). The addition of kraft lignin to a conventional amine-cured diglycidylether-Bisphenol A resin resulted in an increased adhesive shear strength of the epoxy material with an optimum at 20% addition of lignin ([Feldman et al., 1991](#)). At higher addition levels (30%), the Tg characteristics indicate a poor miscibility of the blends. [Feng and Chen \(2012\)](#) reported similar results for the addition of a modified lignin used in a conventional Bisphenol A diglycidylether epoxide. A polymeric acetic acid lignin from eucalyptus, that had been phenolated and epoxidized with ECH was used to replace fractions of Bisphenol A diglycidylether. After cross-linking with triethylene tetramine the plastics possessed better adhesive shear strength compared to plastic without the lignin component (optimal addition level was 20%). At higher fractions of the epoxidized lignin, the plastic became more inhomogeneous and agglomeration and pores could be seen on SEM images ([Feng and Chen, 2012](#)). The modification of lignin with poly(propylene oxide) copolymers (i.e. oxyalkylated lignin) has also been epoxidized and used in epoxy resins ([Hofmann et al., 1993](#)). However, it is important to emphasize that the presence of unreacted material as well as several different reaction products limit the performance of the bio-based epoxy ([Hofmann and Glasser, 1993](#); [Zhao et al., 2001](#)). With fractionation of the reaction mixtures materials with different properties could be obtained ([Hofmann and Glasser, 1993](#); [Zhao et al., 2001](#)), which

indicates that a better selectivity between reaction paths could provide more homogenous materials.

Oligophenols from bark can also be used as resources for epoxy resins (Kuo et al., 2014). The lower molecular weight of the aromatic polyphenols from bark extractives compared to those of lignin, could potentially be a benefit from the processing perspective. There is a limited amount of work on bark extractive-based epoxy resin in the literature. However, a recent article concluded that epoxy with good thermal and mechanical properties could be prepared from bark extracts. Chemical analysis of the epoxidized extracts suggested that those contain significant amounts of epoxidized tannins, lignin fragments and coniferyl alcohol (Kuo et al., 2014).

#### 4.6. Bio-based thermosets from suberin monomers

Suberin polymers provide hydrophobic and antimicrobial protection to tree, and are found in especially in oak cork and birch outer bark. It contains aromatic and aliphatic regions, and can be depolymerized into aromatic and aliphatic monomers by cleavage of ester bonds (Garça and Pereira, 2000). Especially the aliphatic monomers have received interest as precursors for bio-based polyester. One aliphatic monomer that can be isolated from birch outer bark is 9,10-epoxy-18-hydroxyoctadecanoic acid (Torron et al., 2014). This suberin monomer has several chemical functionalities (epoxide, carboxylic acid, alcohol) and by selective polymerization of these, thermosets with varying thermal and dynamic mechanical properties could be obtained (Torron et al., 2014; Olsson et al., 2007). Sousa et al. used the suberin depolymerization mixtures to prepare novel polyesters (Sousa et al., 2011). With polycondensation and polytransesterification schemes, in some cases by combinations with non-suberin monomers, polyesters with properties that resembled those of petroleum-based polyesters were developed.

### 5. Some environmental aspects of bioplastics

Wood-based feedstocks have a vast advantage over fossil-based feedstocks due to their much shorter carbon cycle, resulting in a balance between atmospheric carbon (carbon dioxide) and carbon bonded in organic material. Additionally, according to cradle to gate studies (OECD report, 2013), the greenhouse gas (GHG) emissions of some bioplastics (e.g. PLA, BioPP and BioPE) tend to be lower

than the fossil-based polymers. However, although the cradle to grave results also suggested GHG emissions savings for biobased products, the results were not conclusive (OECD report, 2013).

One approach to decrease the environmental load of a material is to use renewable resources. As an example, polyols derived from plant oils are used commercially to substitute fossil-based polyol in polyurethane plastics. Another concern is that bio-based polymers (e.g. polyols from vegetable oils) may cause land-use change and thus compete with food production (Álvarez-Chávez et al., 2012). The usage of polymers (e.g. lignin-based polyols) from wood can represent a bio-based alternative that does not compete with food production, since wood may be grown in areas unsuitable for food production.

The type of application of the bioplastic matters to the choice of waste treatment. Bio-based materials may be used in durable applications such as construction materials and vehicles that are more easily reused or recycled (Song et al., 2009). Hence, plastics durability can be a virtue, if the end-of-life solution can be energy recovery during incineration or recycling, considering GHG emissions savings as the primary purpose of the application (Philp et al., 2013b). Biodegradable materials may be suitable for usage in short service life applications such as packaging and food disposals, (e.g. PLA, PHA). However, this statement has to be taken with care as some studies have shown that this is not always the case (Yates et al., 2013). According to the same authors, the environmental performance of bioplastics can be improved by using alternative feedstocks, e.g. waste- or by-products. Hence, new opportunities for residual biomass from e.g. agro-forestry resources or industrial side-streams may arise, if the technology required to process the biomass is environmentally sound and cost-efficient.

Biodegradation is an environmentally sound waste treatment method. The term 'biodegradation' refers to the degradation performed by naturally occurring microorganisms in nature (Briassoulis and Dejean, 2010). Under aerobic conditions, the microorganisms produce water and CO<sub>2</sub>, whereas methane is formed rather than CO<sub>2</sub> under anaerobic conditions. Unfortunately, the term 'biodegradable' is used generously for bioplastics, and not only where it would apply if it was kept more strictly defined. According to OECD report (2013), the measurement of biodegradability is not the result of a single test, and misinterpretation may result in error labeling of plastic products. This is problematic since it may confuse end-users and result in waste materials ending up where they may harm the environment. Some plastics are not biodegraded into water and CO<sub>2</sub>/methane for very long time, but are degradable or fragmentable into small fragments that are invisible to the naked eye. The very slow biodegradation of these plastics results in the accumulation of plastic debris in the oceans, which has become a considerable environmental concern (Hidalgo-Ruz et al., 2012). Hence, it is important that 'degradability' (or 'partial biodegradability') is distinguished from complete biodegradability (illustrated in Fig. 8). An example of such a fragmentable plastic is PE with pro-oxidant additives, which are added explicitly to cause degradation of the plastic into invisible fragments. However, it has not been possible to biodegrade the invisible PE fragments (Briassoulis and Dejean, 2010; European Bioplastics, 2015). Plastic fragments such as high surface area plastic residues may migrate into water and other compartments of the ecosystem (Song et al., 2009). According to Thompson et al. (2009), substantial quantities of plastic debris contaminate marine habitats, which is a major environmental concern.

Compostability defines complete degradation of a material into water, CO<sub>2</sub> and/or methane under controlled conditions using industrial or household systems. In the composting system, microorganisms degrade the plastics under optimized conditions to reduce the degradation time compared to many natural systems.

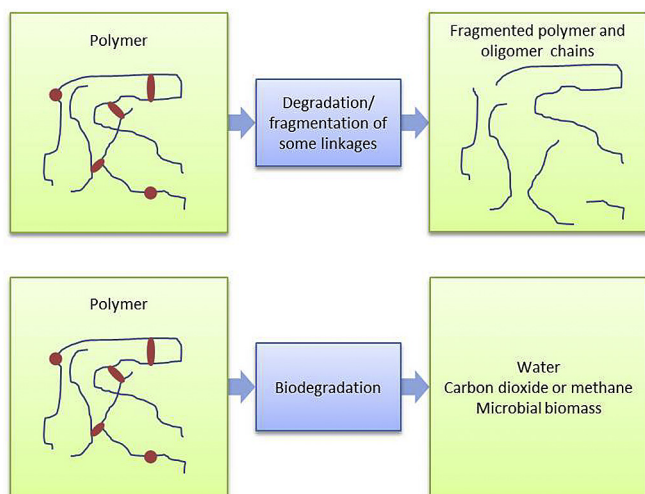


Fig. 8. The difference between degradation/fragmentation and biodegradation.

The complexity of the definition and standardization of biodegradability and compostability may be confusing not only to plastic industry but also to household users and policy makers (European Bioplastics, 2015). However, proper definitions, labeling of products and waste collection systems may pave way for these promising waste treatment methods.

The sustainability of a given bioplastic depends on several factors including biodegradability, recyclability, reusability, application, local infrastructure for harvesting feedstock and for collection and reuse at end-of-life and raw material feedstock. Keep in mind that recycling of some bioplastics (e.g. PLA) may not be practical in established recycling systems, and infrastructure for composting bioplastics is not widely available (Álvarez-Chávez et al., 2012; Philp et al., 2013b). Other bioplastics such as BioPE can enter the existing plastics recycling infrastructure (Philp et al., 2013b). Understanding the cradle-to-grave life of bioplastics is thus necessary to avoid creating a potential waste problem (Kale et al., 2007). Hence, it is important to emphasize that long-term sustainability will depend on the flexibility and development potentials in any given material and technology. A proper assessment of sustainability is complex and extensive, and requires a dedicated case-by-case study, which was outside the scope of this review. Here we intended to give a general overview and some directions and aspects to consider. For interested readers, various aspects of sustainability of bioplastics are discussed in the OECD report (2013) and additional studies and reviews (e.g. Kale et al., 2007; Álvarez-Chávez et al., 2012; Philp et al., 2013a,b; Iles and Martin, 2013; Yates et al., 2013).

Finally, it is important to emphasize that the implementation of industrial processes for the production of bioplastics should not only address the technology development, but also essential societal and political framework conditions, address sustainability and raw material availability, and promote the use of sustainable bioplastic and biobased materials in society (see e.g. Iles and Martin, 2013).

## 6. Conclusion

Bioplastics production from lignocellulosic materials involves processes as pre-treatment, saccharification, detoxification of liquids, fermentation, conversion, separation, and purification. This review intended to give an overview of the advances in the different processes. Defining a specific production route is difficult as the appropriate route to develop a given bioplastic depends on the availability of biomass, type of biomass feedstock, raw material yield costs, recovery costs and available infrastructure, which may determine the specific bioplastic to develop.

We have considered the production of conventional bioplastics such as PLA, PHA, BioPE and discussed its production in relation to the potential production from forestry biomass. One aspect to consider is the production of novel and dedicated bioplastics instead of focusing on drop-in polymers. Additionally, wood-based platform molecules such as HMF are another example of a platform chemical that can be produced from carbohydrates. HMF can be the basis for various bioplastics such as BioPET, BioPA and BioPCL. However, a viable utilization of HMF as a platform molecule requires processes to convert cellulose into HMF at good yields and thus avoiding the challenging processing step of hydrolyzing cellulose into glucose. Some advances have been reported in this respect.

Specifically, it is worth to emphasize the following points:

1. Use of ionic liquids is an interesting fractionation option to increase monosugar yield for bioplastic production, if the ionic

liquids can be recycled to reduce costs. Microemulsions are also a plausible alternative.

2. Depending on the chemical structure the thermo-bioplastics can be either durable (e.g. BioPE), compostable (e.g. PLA) or biodegradable (e.g. PHA).
3. Each type of bioplastics has advantages and drawbacks and their use depend on specific applications (e.g. construction, infrastructure, packaging, biomedical).
4. Drop-ins such as BioPE can be advantageous for durable applications. Additionally, BioPE can be recycled in conventional PE recycling streams.
5. Efforts have to be made to implement specific collecting and recycling streams to fully exploit dedicated compostable and biodegradable bioplastics.
6. Lignin offers various opportunities to bio-enrich thermosets such as PF and PUR.
7. The production of bioplastics from lignocellulosics is presently demanding and expensive. Further advances and breakthroughs are necessary to reduce production costs.

Finally, it is important to keep in mind that this review focused on forestry resources. However, the technology and processes can be applied in most cases to alternative biomass (e.g. agro-industrial residues). In general, sustainable and profitable production of bioplastics from forestry resources requires the consideration of three main aspects: 1) the development of innovative and economically viable technology to produce bioplastic from renewable sources, 2) the definition of political and environmental drivers for production and use of bioplastics and 3) the development of business models based on sustainable and profitable processes within a bioeconomy framework. These additional considerations will facilitate the adequate conditions for production of bioplastics from forestry biomass.

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