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# Cellulose and Lignin: The Abundant Renewable Polymers from Plant Biomass

Pietro Palmisano and Maria Chiara Piglione

**Abstract:** The conversion of several biomasses into renewable chemicals and fuels has received great attention in the last decade as a sort of parallel route to the classical petrochemical way of reaching an eco-friendlier and more sustainable economy. Many researchers have further focused their studies towards waste products coming from the agriculture and/or forest industry, and found out the different techniques used for the separation of the main constituents of a classical biomass—cellulose, hemicellulose and lignin—as well as their characterization techniques and analytical studies in order to better identify their physical and chemical characteristics for identifying the best way to transform them into valuable products. An overview of the most important developed processes has been widely coupled with a detailed list of the chemicals and fuels that a potential biorefinery could provide, simply by processing feedstocks that a few years ago were considered just waste.

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## 1. Introduction

Some of the main problems of today's world are climate change due to greenhouse gas emissions (GHG), resource constraints—particularly for fossil fuels—and population fast growth, which causes an increased energy, water and food demand. For these reasons, interest has been focused on studying new technologies and finding sustainable alternatives to the fossil feedstock dependence, developing the biorefinery concept. The idea is very similar to a petroleum refinery, in which petroleum is the starting source for the production of multiple fuels and a wide range of products. In the same way, a biorefinery is a chemical plant fed by biomass and/or renewable feedstocks as inputs, converting them to fuels (e.g., biodiesel and bioethanol), energy and a wide range of chemicals or different kind of materials that can have a multiple range of application fields (e.g., monoethylene glycol, *n*-butanol, xylenes, polyurethane, polyols).

One of the main strengths of a biorefinery is the number of different products and intermediates generated from the whole process that allow the maximization of the value of the biomass itself. Furthermore, big efforts are aimed at the energetic self-sustainability of the biorefinery in order to make their development and diffusion convenient.

It has also been widely demonstrated in the past 30 years of experimental studies that many fossil-derived industrial products could be partially or totally replaced using biomass sources as bio-based final products [1]. In the last decade, many scientific studies have been focused on the conversion of biomasses towards the main block molecules of the chemical and polymer industry, trying to better define the most promising and economically feasible route to get methanol, ethylene, propylene, butadiene, benzene, toluene and xylene from several kinds of biomasses instead of the complementary fossil-derived molecules.

Biorefineries can be fed with different feedstocks, such as perennial grasses, starch crops (wheat, maize, etc.), sugar crops (beet, cane, etc.), lignocellulosic crops as well as oil crops, aquatic biomass and organic residues (industrial, commercial and post-consumer wastes). First-generation biofuels achieved after transformation of food crops, in what we can define as I generation biomass plant, can generate several issues, such as negative energy balance coupled with a negative greenhouse gas emission, and most likely a vigorous increase in food prices. For this reason, the main focus of this section is on II generation lignocellulosic biorefineries, whose industry to date is still under development. Of primary importance in the development of these new technologies is assuring that new bio-based products have lower environmental impacts than their petrochemical equivalent. Another important aspect is the economical one, as in many cases bio-based chemicals and biofuels have higher production costs than their petrochemical equivalents, only partially justifiable with the complexity of their structure and with the heterogeneity and complexity of the starting feedstock (biomass).

If we focus on the historic standpoint, the transformation of the constituent part of woody biomasses is something well known and not new. For instance, cellulose can be used as precursor for textile fibers, paper, and film with different properties deriving from the industrial process. The impact of cellulose crosses different industrial applications as well as domestic life and civil construction [2]. Besides cellulose, lignin has been extensively studied in recent years. Its abundancy is directly connected with the pulp and paper industry (the order of magnitude is roughly millions of tons per year worldwide), where the residual part of the wood is not useful as cellulose fraction (i.e., black liquor coming from the Kraft processes or lignosulfonates coming from the sulfite processes, both of which are the platform for the production of pulp and paper) and it is actually employed as sacrificial fuel or binding agent for concrete. The increasing interest of academia in lignin is ascribable to its aromatic nature; that makes it a possible source of value-added aromatic chemicals, an aspect that will be described more thoroughly in the coming paragraphs.

For both cellulose and lignin, the interest is now focused on new value-added applications that can be combined to form the concept of a II generation platform,

in which the valorization of each constituent of the biomass is a condition sine qua non for achieving the self-sustainability of the entire process in terms of revenues (enlarging the range of potential products) and exploiting all the streams and sub-streams generable from the starting woody material trying to make a rather complex technical concept economically sustainable. A possible scheme for a lignocellulosic feedstock biorefinery is shown in Figure 1, in which a thermo-chemical platform is coupled with a biotechnological one. This general scheme highlights the possibility of obtaining fuels, chemicals, and building molecules for the polymer industry, as well as enough energy to achieve energetic self-sustainability. Products can be generated via thermo-chemical conversion or bioprocessing. In both cases, the structure of the natural monomers that constitutes the starting biomass are largely preserved instead of being transformed to obtain the final products.

The aim of this section is to highlight opportunities coming from the use of lignocellulosic feedstocks in order to obtain a number of value-added products through a number of different conversion processes.

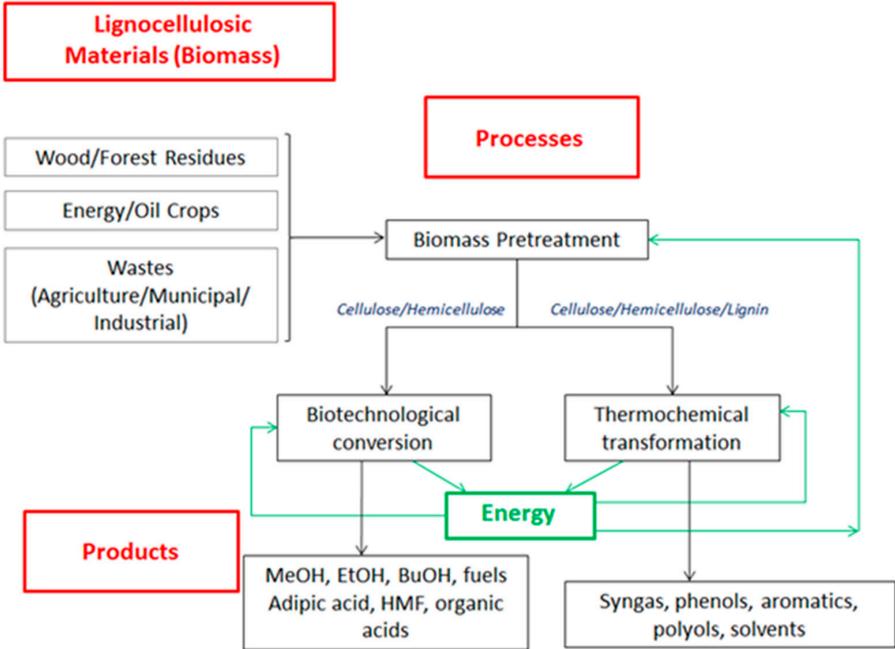
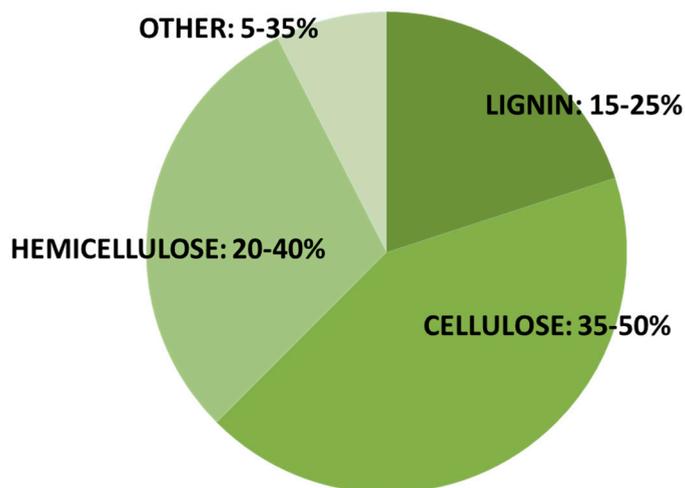


Figure 1. Concept block flow diagram for II generation biorefinery.

## 2. Lignocellulosic Feedstocks

Lignocellulosic biomass refers to inedible plant material with a complex polymeric generated by photosynthesis, whose main properties are structural

strength in combination with flexibility. Lignocellulosic feedstocks are in fact complex natural biopolymers built up by three main constituents—cellulose, hemicellulose and lignin—whose structures and compositions are affected by many factors such as plant species, cultivation regions and subsequently growth conditions [3]. A general composition of lignocellulosic feedstocks is shown in Figure 2.



**Figure 2.** Generic composition for lignocellulosic biomass feedstocks [4].

Cellulose and hemicellulose are carbohydrate polymers, while lignin is a phenolic polymer. Besides these three main constituents, lignocellulosic feedstocks also contain water and minor amounts of extractives and inorganic compounds (ashes). A general overview of lignocellulosic feedstock composition has been collected by Lee DK et al. Table 1 is taken from his monograph [4]. Nevertheless, it is important to remember that the growth in different environments has a significant effect on feedstock composition.

**Table 1.** Composition of residual lignocellulosic feedstock [4].

	Cellulose % of d.m.	Hemicellulose % of d.m.	Lignin % of d.m	Other % of d.m.
Corn Stover	38	26	19	17
Soybean	33	14	-	53
Wheat Straw	38	29	15	18
Rye Straw	31	25	-	44
Switchgrass	37	29	19	15
Miscanthus	43	24	19	14
Forage Sorghum	34	17	16	33
Sweet Sorghum	23	14	11	52
Bagasse	40	30	20	10

## 2.1. Cellulose and Hemicellulose

Cellulose is a long-chain linear polymer that contains predominantly crystalline arrangements with smaller amorphous regions. The cellulose polymers are arranged in micro fibrils that are organized in fibrils; these are combined into cellulose fibers which are responsible for the fibrous nature of lignocellulosic biomass cell walls. Hemicelluloses are shorter, or branched amorphous polymers, of five- or six-carbon sugars. Together with lignin, hemicellulose forms the matrix in which the cellulose fibrils are embedded. The hemicellulose acts as a connector between cellulose and lignin [5]. Its basic building block is celluliose, obtained from the linking of two molecules of  $\beta$ -D-glucose. Cellulose, shown in Figure 3, presents many polar -OH groups that form hydrogen bonds with adjacent chains and create hard, stable crystalline regions and microfibrils giving strength to the whole biomass structure. The length of the chains can vary greatly, going from a few hundred to over ten thousand sugar units, depending on the type of biomass.

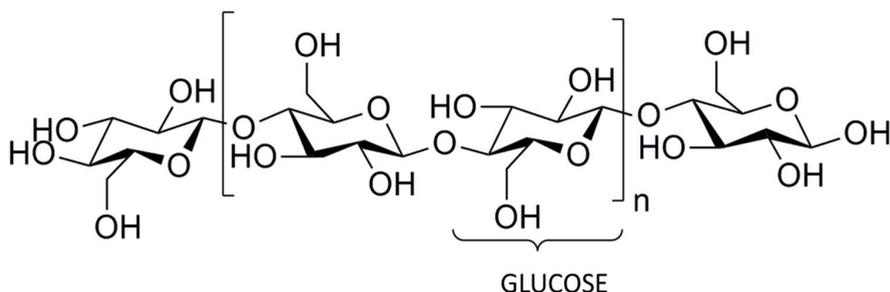
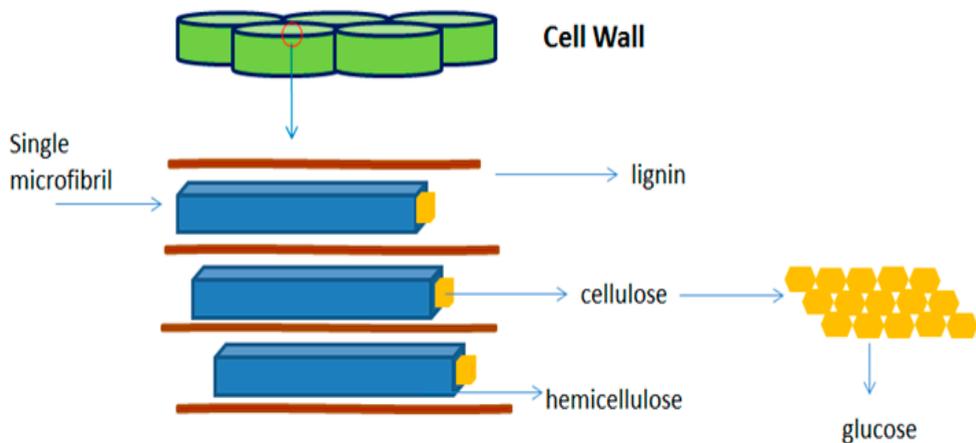


Figure 3. Molecular structure of cellulose.

Referring to Figure 4, it shows that cellulose is arranged into walls that constitute the plant cell.

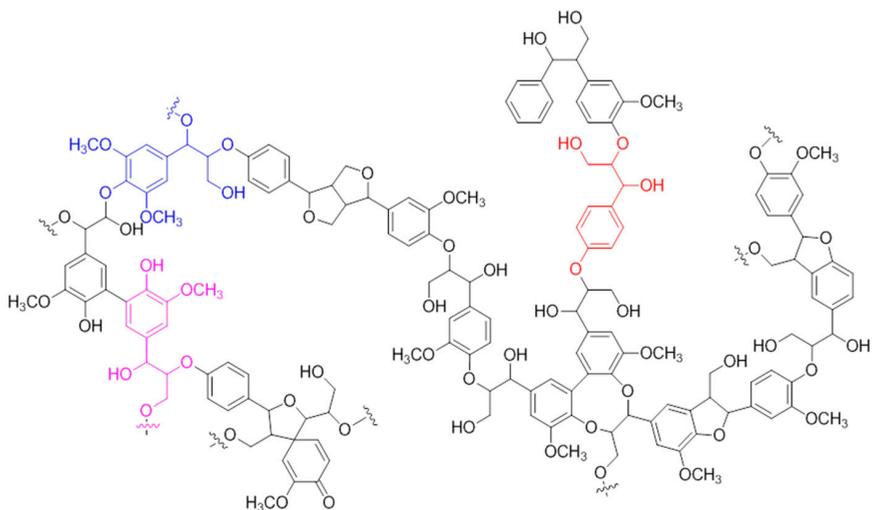
The hemicelluloses in deciduous woods (hardwoods) and agricultural herbaceous products such as wheat straw, cornstover and switch grass predominantly consist of D-xylose units (xylans), whereas coniferous (softwood) hemicellulose is mainly made up of D-mannose (mannans), L-arabinose (arabinans) and D-galactose (galactans) [5]. Xylans are the main hemicelluloses in hardwood and they also predominate in annual plants and cereals, making up to 30 per cent of the cell wall material. Hardwood xylan (*O*-acetyl-4 methyl-glucuronoxylan) is substituted at irregular intervals with 4-*O*-methyl- $\alpha$ -D-glucuronic acid groups joined to xylose by  $\alpha$ -1,2-glycosidic linkages. On average, every tenth xylose unit has a uronic acid group attached at C2 or C3 of xylopyranose [6]. Using hydrolysis, both cellulose and hemicellulose can be disrupted in C5 and C6 sugars. Hydrolysis can be done more readily on hemicellulose than on cellulose, due to its branched, amorphous nature.



**Figure 4.** Structure of plant cell walls.

## 2.2. Lignin

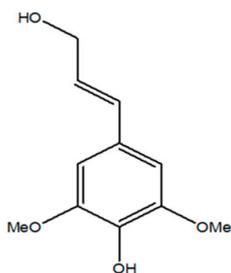
Being one of the most abundant natural polymers, together with cellulose and hemicellulose, lignin forms part of the secondary cell walls of plants and helps maintain the integrity of the cellulose/hemicellulose/pectin matrix. The most complete structural model of lignin was proposed by Adler in 1977 (Figure 5) [7]. The variable molecular mass of this biopolymer is a consequence of the random cross-linked polymerization of phenolic monomeric units, originating from radical-coupling reactions between phenolic radicals [8,9]. It is generally accepted that there are three basic phenol derivatives, the so-called monolignols that make up almost all types of lignin found in nature—*p*-coumaryl alcohol (H-phenolic group)—coniferyl alcohol (G for guayacylic phenolic group), and sinapyl alcohol (S for syringilic phenolic group)] [10]. The scientific literature has defined lignin as a phenolic-propanoid polymer providing structural support for the plant, giving strength, rigidity and resistance to environmental stresses [11]. Of course, as well as cellulose and hemicellulose, the lignin content in biomass varies depending on biomass typology (softwood vs. hardwood vs. herbaceous plants), harvesting time and zone, biomass treatment.



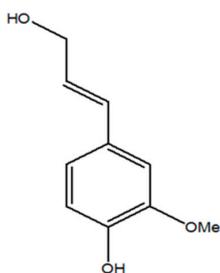
**Figure 5.** Lignin structure by Adler [7].

If the lignin can retain a generic propanoic polymer, it becomes crucial to identify its monomer distribution and concentration relating them to the three basic precursors mentioned above and shown in Figure 6 [9].

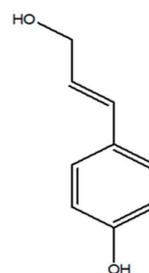
**S - Syringyl Alcohol**



**G - Guaiacyl Alcohol**



**H - Hydroxyphenyl Alcohol**



**Figure 6.** Lignin precursors.

The chemistry of lignin is complex compared to other biopolymers such as proteins or carbohydrates, which are linear chains or, at the most, branched polymers. Lignin contains a range of chemical functional groups, which is partly the result of the extraction method. The main groups in unmodified lignins are hydroxyl (aromatic and aliphatic), methoxyl, carbonyl, and carboxyl [9]. Lignin is composed of a three-dimensional network, lacking the regular and ordered repeating units of other biopolymers such as cellulose. The majority (approximately two thirds) of

chemical bonds in the native lignin polymeric network are of the C-O-C ether linkage type between the phenylpropane units, predominantly  $\beta$ -O-4, while about one third consists of C-C bonds between these units. Furthermore, lignin also includes branched and cross-linked structures. Typical bonds and their recurrence in different types of lignin are shown in Table 2 [11].

**Table 2.** [Typical bonds and their recurrence in different types of lignin each 100 bonds] [11].

Name Bond	Type	Softwood (%)	Hardwood (%)
$\beta$ -O-4	Etheric	40–50	50–60
$\beta$ -5	Etheric	10–12	3
4-O-5	Etheric	3	3
5-5	carbon to carbon	13	3
$\beta$ - $\beta$	carbon to carbon	3	3

### 3. II Generation Biomass Conversion

#### 3.1. Pretreatment Methods

Until recently, the last pilot and demo-scale plant developments have defined pretreatment as the most important step for the conversion of II generation biomass towards chemicals and fuels. The goal of this step is the separation of the cellulose from the other natural polymers as well as the cellulose accessibility to the subsequent process steps such as the enzymatic hydrolysis or any thermic or catalytic chemical transformation. A strong separation from the lignin is needed. At the same time, it is important to allow valorization of the production of a lignin by-product with high purity. For both streams, the purer they are, the better can be retained. From this standpoint, it should also be considered that pretreatment should be tuned compatibility with feedstocks, enzymes and organisms that will be injected later on be in the bioprocessing and/or the needings for thermo/catalytic/chemical operations. Another important aspect that needs to be taken in account is the pretreatment cost, which also includes the costs related to the handling of feedstock and of solid and liquid streams generated, handling of waste and the potential production of co-products. The basic aim of this step of the procedure involves firstly the cleavage of hydrogen typically present in the crystalline cellulose as well as disrupting hemicellulose and secondly lignin matrix disrupting a remarkable increment of porosity as well as surface area of cellulose in order to make the enzymatic/chemical attack more effective [11,12]. The literature presents four pretreatment approaches to reach the goal: physical, physico-chemical, chemical and biological [13].

### 3.2. *Physical Biomass Pretreatment*

Physical pretreatment consists of mechanical processing for size reduction and specific surface increase. Examples of physical pretreatments are grinding, milling, microwaving and extrusion. Typically, these methods are expensive for their energy requirement [13].

### 3.3. *Physico-Chemical Biomass Pretreatment*

Physico-chemical pretreatments include steam explosion, catalyzed (SO<sub>2</sub> or CO<sub>2</sub>) steam explosion, ammonia fiber explosion (AFEX), liquid hot water and microwave-chemical pretreatment [14,15]. The steam explosion biomass is treated with high-pressure saturated steam and then the pressure is suddenly reduced, which makes the materials undergo an explosive decompression [16]. This kind of explosion allows efficient cellulose separation from the woody matrix as well as making for a good characteristic for the subsequent cellulose hydrolysis, degradation of hemicellulose, an impact modification of native lignin structure. In this last aspect steam explosions usually affect the molecular weight of lignin towards its decrement as well as a reduction of its etheric bonds (C-O-C) despite an increment of biphenilic (C-C types) ones. It requires low capital investment, it has been proven on different feedstocks and it also has a low environmental impact [17]. Ammonia fiber explosion is very similar to steam explosion, but in this case lignocellulosic biomass is exposed to liquid ammonia instead of steam. The AFEX process demonstrates attractive economics compared to several leading pretreatment technologies [18] and the ammonia used during the process can be recovered and reused.

In the case of liquid hot water pretreatment (LHW), biomass undergoes high-temperature cooking in pressurized water [19]. LHW helps enhance cellulose digestibility, sugar extraction, and pentose recovery, and the product contains little or no inhibitor of sugar fermentation [20]. Moreover, this kind of pretreatment does not require biomass size reduction, as particles are broken apart during pretreatment itself. Finally, microwave/chemical pretreatment is very effective as it accelerates reactions during the pretreatment process [16,21].

### 3.4. *Chemical Biomass Pretreatment*

Today, these types of pretreatments are mainly employed in the pulp and paper industry where the cellulose delignification is a must in order to achieve high quality in terms of pulp purity (lignin here retains a sort of undesired product or a real poison) and so a high quality of final products (paper). It is important to note that the chemical wood/biomass pretreatment must provide a cellulose having high crystalline degree and molecular weight, and biodegradability of the product.

Among the commercial routes actually used, the Acidic pretreatment foresees the use of concentrated and diluted acids (typically dilute sulfuric acid,  $H_2SO_4$  and  $Na_2S$ ) with a good hemicellulose removal. Alkaline pretreatment is more focused on lignin separation. The chemicals needed are basically potassium, calcium, and ammonium hydroxide. In any case, a good quality of cellulose is generally achieved. Depending on the starting material origin, type (softwood vs. hardwood) and aging, the tuning of each process parameter (pressure, temperature, residence time, and above all chemical choice and their weight ratio with respect to the biomass) must be defined preliminarily in order to get high cellulose/hemicellulose/lignin separation.

Generally alkaline pretreatment is performed at lower temperature/pressure (almost in environmental conditions) and for a longer residence time than the acid one. In both cases the de-structured biomass needs a washing step where lignin and all the inhibitors for the subsequent hydrolysis must be removed.

Ionic liquids (green solvents) have recently been used for dissolution of several woody biomasses. These pretreatments seem more sustainable in term of energy requirement, less impacting from an environmental standpoint, simple enough in terms of equipment and operating conditions [22], but more study must to be done in order to use them for commercial applications [23].

### *3.5. Chemical Biomass Pretreatment*

Biological pretreatment uses wood-degrading microorganisms to modify the chemical composition and/or structure of the lignocellulosic biomass in order to facilitate enzyme digestion. This kind of pretreatment has multiple limitations but also many advantages, including no chemical requirement, low energy input, mild environmental conditions, and environmentally friendly working parameters [24,25].

## **4. Cellulose and Hemicellulose Conversion to Sugars**

Cellulose and hemicellulose obtained from biomass pretreatment is then hydrolyzed to soluble fermentable sugars using enzyme systems (mainly cellulases and hemicellulases). Several process configurations can be applied: separate hydrolysis and fermentation (SHF), simultaneous saccharification and fermentation (SSF), simultaneous saccharification and co-fermentation (SSCF) and consolidated biomass processing (CBP) [16].

SHF is composed by two steps conducted at different conditions to each other and does not need any washing of pretreated biomass or nutrient supplementation [26]. The first one foresees a biomass hydrolysis to sugars via enzyme injection, followed by a second step where the sugars are fermented to ethanol with the help of various yeasts [27].

During SSF, pretreated biomass hydrolysis to sugars and sugar fermentation to ethanol take place in the same vessel. The difficulty with this solution is the optimizing of all the various conditions governing the two different processes (pH, temperature, substrate concentration, etc.) [28]. On the other hand, its strength is in the removal of end-product inhibition, which causes enhanced hydrolysis rate. The cellulose conversion can be favored only with a washing step where the inhibitor has to be taken out [29].

SSCF is mainly used for xylose-rich lignocellulosic materials and is carried out by genetically engineered microbes.

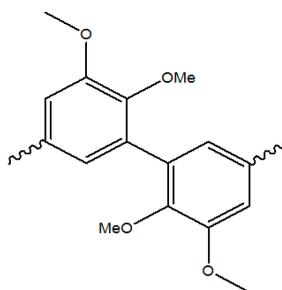
CBP is characterized by the occurring of the three main bio-transformations involved in lignocellulosic bioprospecting in a single process: production of enzymes, hydrolysis and fermentation. In the first step, cellulase and hemicellulases enzyme production is achieved; simultaneously it is possible to get sugars such as pentose and hexose (from hemicellulose and cellulose) as well as their fermentation. This kind of method allows avoiding the costs associated with cellulose production, but the “engineering” of a culture with many microbial tasks.

## 5. Lignin Separation Technologies

As already widely discussed in this section, there are distinct lignin separation processes [30] already implemented on the commercial scale for several purposes. Most of them are directly connected to the pulp and paper industry where the lignin is considered a by-product, and in the best case a co-product. Moreover, due to the different properties (molecular weight, dryness, particle size distribution, surface area, presence of sulfonic groups) intensely dependent on the separation processes of origin, we can have different kinds of products and just not a simple lignin with native characteristics. Despite this dilemma, nowadays in the pulp and paper industry 98% of the material coming out from the delignification processes is still burnt in the same factories to generate energy and steam for the energetic sustainability of the entire process. Lignosulfonates are the only products related to the pulp and paper industry that have a market, but they represent no more than 2% of the total amount of lignin product available (in terms of mass, no more than 1 Mton/y). The reduced availability of lignosulfonates on the market is mainly due to the fact that Kraft process has gradually replaced sulfite process in the last 50 years. Today, the amount of lignin extracted and separated from black liquor in the Kraft process is one order of magnitude less than that of lignosulfonates, but a strong effort has been made by some pulp and paper companies in order to obtain high-value products, lowly affected from impurities and sulfur traces [31].

### 5.1. Kraft Lignin

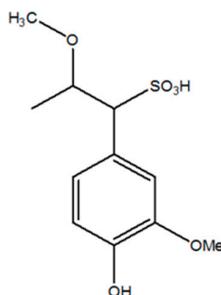
The Kraft process consists of a chemical pretreatment of wood in a range of 155–175 °C, using a solution of Na<sub>2</sub>S/NaOH that allows the delignification of the raw material after several hours of decanting time. The solid (cellulose) stream is then separated from the fluid (black liquor) fraction. If isolation of Kraft lignin is desired, the black liquor is precipitated by neutralization with at very low pH by adding some acidic agent. In order to get the solid powder of lignin, a drying process needs to be implemented at a large scale [32]. Kraft lignin could be considered a hydrophobic material, with a molecular mass around 1000 Da, affected from an abundance of biphenilic bonds (C-C') among propylphenols monomers [33] as reported in Figure 7. This separation process makes lignin water-insoluble, and/or soluble in basic phase.



**Figure 7.** Main structure identified in Kraft extracted lignin [33].

### 5.2. Lignosulfonates

This kind of lignin is generally extracted from liquid residues at the end of the sulfite-pulping process. The raw material generally used for this technology consists of softwoods, and the lignin extraction procedure foresees the use of sulfurous acid (sulfites or bisulfites) followed by the addition of magnesium, ammonium or sodium salts [34] for neutralization and precipitation. The chemical structure of this product presents hydrophobic and hydrophilic properties. In this kind of extraction, the less aggressive and severe conditions ensure a product with a higher molecular weight than Kraft lignin, and a quite important presence of etheric groups among the propylphenolic aromatic monomers. Comparing this polymer matrix with the native lignin, the presence of the sulfonic group attached to the lignin monomers creates a new and completely different physical and chemical behavior with respect to the original one (see Figure 8).



**Figure 8.** Typical monomer formulation of lignosulfonate.

### 5.3. Organosolv Lignins

Organosolv treatment applied to the raw biomass has been one of the most studied processes in the field of lignin extraction. Many literature papers have highlighted the influence of delignification parameters (temperature, pressure, type of solvent, basically ethanol or acetic acid, solvent concentration in the aqueous phase, addition of a small amount of acid dose) on the fraction of lignin extracted in a batch or in a continuous process. In any case, the aim of the process is solubilizing part of the original lignin. In a subsequent step, lignin separation from the solution is obtained by acidic precipitation (pH ~2), and then solvent recovery is achieved by distillation of the solution. Nowadays there are several processes producing commercial Organosolv Lignin. Most of them are summarized in Table 3, also specifying the solvent adopted in order to achieve them. Usually working temperature is between 180 and 200 °C, working pressure between 2 and 5 bar and solvent concentration in water close to 60% *w/w*. Usually lignin yields are quite low and the pureness of the obtained product (sulfur, ash and salt free, abundance of etheric bonds among monomeric units as well as high concentration of guayacilic, siryngilic and phenolic monomers) is combined with low molecular weight (around 1000 g/mol) [35].

**Table 3.** Organosolv Lignin Commercial/Patented Extraction [10].

Lignin Type	Solvent
Alcell [36]	Ethanol/water
Alcetocell [37]	Acetic acid/water
Acetosolv [38]	Acetic acid/HCl pulping
ASAM [39]	Alkaline sulfite/anthraquinone/methanol
Batelle [40]	Phenol/acid/water
Formacell [41]	Acetic acid/formic acid/water
Milox [42]	Formic acid/hydrogen peroxide
Organocell [43]	Methanol pulping/NaOH/anthraquinone pulping

#### 5.4. Steam Exploded Lignin

If biomasses are treated at high temperature/pressure (i.e., 180–200 °C), followed by a sudden decompression in presence of some chemicals, hydrolysis of lignin is reached. In these conditions a water-insoluble lignin material with a low level of residual carbohydrates and extractives is obtained [10]. Depending on the severity of the explosion and on the acidity level of the hydrolysis, the molecular weight of the product can be affected.

#### 5.5. II Generation Bioethanol Lignin

In recent years the development of 2<sup>nd</sup>-generation bioethanol plants has made it possible to get a new source of lignin as a by-product of the entire process. In this case, the lignin is a sulfur-free product due to the fact that these processes do not foresee the use of acid or basic attack to the inlet feedstock (mainly agricultures residues like wheat or rice straw or energy crops grown in marginal land). Furthermore, the chemical structure of the obtained lignin is very close to the native one because in this case smart cooking used for biomass pretreatment is less severe in terms of temperature and vapor condition than steam explosion.

### 6. Lignin Derivatives and Their Applications

As shown in a previous paragraph, liginosulfonate is the only lignoderivative with a wide commercial use due to its capabilities as a binder. Nevertheless, to date, new routes are becoming interesting in terms of application although they remain limited in terms of market dimensions. These routes are the ones of eco-friendly renewable materials [44], moisture-retention agent and dust suppressors, gypsum-board manufacture, asphalt stabilizers, dyes, and pigment emulsions [45]. In the last 5 years, many studies and granted projects worldwide [46,47] have been focused on the use of different lignins (Organosolv, Kraft, steam exploded) as co-polymers, additives for making new and functionalized composite polymers, formaldehyde resins, polyester polymers, polyurethane foams, bio-plastics, epoxy resins. The scientific approach to make feasible the realization of these new products with enhanced mechanical and thermal properties (with respect to their petrochemical equivalents) consists in the functionalization of the starting lignins, obtained by chemical modification. This goal can be achieved by the insertion of a specific group into the polymeric matrix by alkylation, dealkylation, amination, sulfonation, silylation, acylation, halogenation, nitration or methylation [48,49].

#### 6.1. Resins

As an alternative to the commercial phenol-formaldehyde resins, lignin-formaldehyde resins seem to be promising materials if used as adhesives

for plywood, chipboard, fiberboard, rubber products, and refractory and friction materials. The synthesis of this new type of resin occurs in acidic or basic media [50]. In order to get this new kind of resin, Organosolv or hydrolyzed lignin has been retained as the most performing replacements for phenols coming from fossil sources [51]. The economic and technical evaluation of this new product as adhesive is considered positive for its application and commercialization [52].

Referring to epoxy-resins, a previous modification of the lignin is required before its introduction in the polymer structure as cross-linking agent instead of the bisphenol-A [53]. Generally, the modification foresees a phenolation of the lignin matrix in order to get diphenolic moieties that perform as well as the bisphenols during the epoxidation of the resin precursors [54]. In this type of application, the best performing feedstocks have been identified in lignosulfonates and Organosolv lignin.

### *6.2. Polyurethane*

Due to the large use of this material in the construction and building industry, the substitution of these fossil-derivatives with green sources has been widely investigated. In this case, the Organosolv lignin has been demonstrated as the best substitute of the aromatic isocyanates (in particular the methyl diphenil isocyanate, MDI) for reacting with polyols (PEG or PPG). The products achieved could be considered good in terms of physical properties (both sheets and foams) [55]. Economic evaluations are undergoing in order to ascertain a comparison cost production with the fossil derivatives.

### *6.3. Polyolefin Polymers*

The high resistance to biodegradability of polypropylene (PP) and polyethylene (PE) has led to new research towards a blend of both these polyolefin polymers with natural polymer lignin. However, the optimization of good products, especially referring to the HDPE and PP, in terms of mechanical properties, seems to be still far off [56].

### *6.4. Bio-Plastics from Lignin*

Remarkable results have been achieved for the production of an alternative thermoplastic material in which sulfur-free lignins can be mixed with natural fiber or additives in order to obtain a plastic granulated called ARBOFORM [57] that can be melted and molded as a petrochemical thermoplastic material that can replace the plastic used in household industries.

### *6.5. Carbon Fibres*

The relatively low cost of some lignin sources has oriented many researchers in considering these materials as precursors for preparing carbon fibers by carbonization

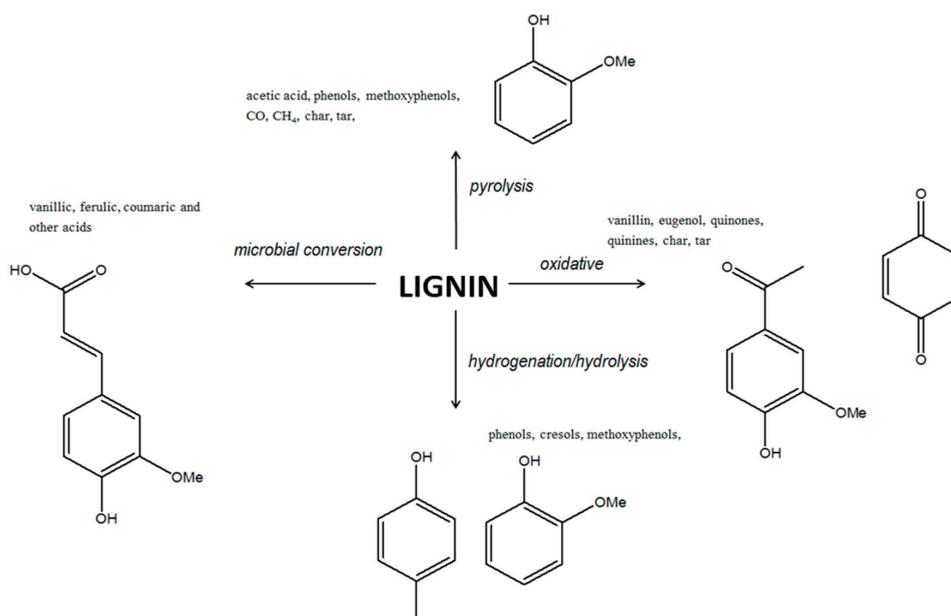
of dry-spun fibers. A basic aqueous solution needs to be prepared and added during the plasticized treatment with polyvinyl alcohol or glycerol. Due to the high-purity lignin required for melt-spinning (sulfur, sugar and ash free), this application seems to be quite far from an immediate realization [58].

## 7. Lignin Depolymerization Technologies

In competition with the direct application of lignins in the products/materials listed and described before, there is the transformation of lignin to several families of remarkable chemicals, mainly aromatics, which might substitute products coming from standard petrochemistry. Conversion technologies are based on the depolymerization concept that transforms the starting matrix structure to monomers or dimers having a good relevance in terms of chemical product demand: phenols, cresols, benzene, toluene and xylenes as well as quinones or polyols. From this perspective pyrolysis of lignin can be seen as the oldest and most widely studied depolymerization/cracking technique since the 60s for transforming wood or lignocellulosic feedstocks to chemicals and fuels [59]. Independently from reactor choice (fluidized bed, ablative cone, Auger) [60] the main product achieved by thermocracking (usually 500 °C in inert atmosphere) is an oil with a large amount of substituted phenols (monomeric, dimeric and trimeric), with a huge water, oxygen and acid content, unstable along the time that requires an immediate upgrade process in order to get monomeric phenols/cresols or aromatics like benzene toluene and xylenes. Besides oil, pyrolysis also foresees an important production of char (yields can oscillate between 20 and 40% *w/w* of the starting materials) and gases. Both these products need to be burnt in order to make energetically self-sustainable the entire operation. If the thermocracking occurs in an oxidative atmosphere, the oil is richer in vanillin and eugenol than phenols and methoxyphenols (guaiacols and syringols). Both these products have a good way out market as flavorings for the food and cosmetic industries and some application in the pharmaceutical industries. If the oxidative atmosphere is brought to a higher concentration respect to the inert carrier (especially if the fluidized bed configuration is used as reactoristic choice) the distribution of products loses the aromaticity to facilitate the formation of quinones or quinines (C6-cyclic dione structure). In both cases, the inert or oxidative atmosphere represents a limitation for making continuous and scalable processes. The huge amount of TAR formation during the condensation of the vapors coming out from the cracker reactor seems to be detrimental for the large scale development [61]. Due to this limit, in recent years, the catalytic cracking of lignin in a reducing atmosphere (presence of hydrogen) has been more and more studied, in order to avoid the formation of undesired products (char and tar), maximize the useful oil fractions, minimize its acidic content (in order to get it stable), and maximize its concentration in monomeric phenols [62,63]. If we refer to the char by-product, in the last three

years many studies have been made for a possible upgrade of the char towards useful compounds like active carbon or as a simple soil amendment compound. From this perspective the valorization of the char could make the pyrolysis more attractive for its further development in bigger scale. Alternative depolymerization routes are also represented by microbial conversions for producing vanillic, ferulic and coumaric acids, the enzymatic oxidation for the production of pigments [64,65].

The controlled breaking of different linkage types in lignin needs detailed information on the stability of the bonds under different conditions and knowledge of the mechanisms of lignin decomposition. The etheric  $\beta$ -O-4 bond that crosslinks more than 50% of the phenolic monomers can be cleaved between 200 and 400 °C. At higher temperatures secondary reactions could bring radicalic carbons crossing over with formation of diphenilic C-C bonds much more stable. A very bad consequence might be the TAR formation as unsuitable effect. For this reason, lignin treatments typically yield oligomers, rarely a single monomer, so the cleavage can be promoted using a reducing atmosphere. In all these cases the use of functionalized catalysts that allow the simultaneous cleavage of etheric and diphenilic bonds, and the hydrogenation of the radicals generated by the thermal cracking seem to be a keyword in order to get the goal. In Figure 9 are shown the products that can be obtained with the various depolymerization techniques, depending from the atmosphere in which they take place.



**Figure 9.** Summary of lignin depolymerization thermocracking [66].

If we refer to the sources of lignin available on the market, lignosulfonates still represents the most important product with a huge use as plasticizer in the concrete industries [67,68] as well as many others like emulsifiers but with lower impact in terms of tons sold to the tons produced [66]. In any case, the high concentration of sulfur and salts in its structures has strongly limited the valorization of this ligno-derivatives towards other applications, in particular its depolymerization towards valuable monomers [66]. Nowadays the development of second generation bioethanol plants has made possible to foresee in the near future alternative sources of very pure types of lignin products, sensibly less affected from sulfur or salts, so easier to transform in high valuable compounds and/or pure chemicals. From this perspective, the valorization of the lignin residues coupled to the second generation bioethanol plants makes it possible a new and more versatile scheme of a biorefinery platform in which the lignin transformation becomes more profitable than its energy valorization [69]. Many studies made in the past upon different kind of lignins (differing for the extraction process, because each extraction process can affect differently lignin native structure, its bond functionalities and its polymerization grade), have been revalued and deepened in order to better identify new and alternative routes for the production of emulsifiers [70], chelating agents for heavy metals removal from industrial effluent [71], active carbons (after activation by gasification) [72] as well as several depolymerization technologies via many catalytic, thermic or thermocatalytic cracking processes able to convert this feedstock to high value products having lower molecular weight [73].

## 8. Conclusions

The developments and the main results achieved during the scale-up at commercial scale of second-generation biorefineries is becoming more important with every year. If everything starts from the three components that constitute the feedstocks for this kind of concept plant—cellulose (in part and hemicellulose) and lignin—a plethora of processes have been separately developed for being later integrated among them in order to:

- Separate the main components
- Depolymerize or use as they are the components that are retained, which are a huge source of different chemicals, able to be entered in basic chemistry or other more complex applications

If the cellulose can open a route towards a plethora of chemicals, it is mandatory to operate in the inlet part of the biorefinery concept a series of operations able to depolymerize the starting matrix in order to get pure and low molecular weight sugars that can be then converted towards the desired chemicals, a route already widely known from the I generation biorefinery concept. If the conversion

of cellulose and its derivatives can be considered a quite well-known pathway, lignin and its valorization is still undergoing. However numerous direct applications seem to be close to their first scale-up from small quantity to almost commercial amounts, as well as the scale-up of several depolymerization processes from pilot to semi-commercial scale.

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