Biorefinery Review: Wide-Reaching Products Through Kraft Lignin

Iara F. Demuner,[a,]* Jorge Luiz Colodette,[a] Antonio J. Demuner,[b] and Carolina M. Jardim [a]

This review details the structure of lignin and curates information on the characteristics that this polymer must have for each specific use. Lignin is a by-product of the pulp and paper industry and the second most abundant biopolymer after cellulose. Approximately 50 million tons of lignin are produced worldwide annually, of which 98% to 99% is incinerated to produce steam, process energy. Just 1% to 2% of the lignin, derived from the sulfite pulp industry, is used in chemical conversion to produce lignosulfonates. Biorefining is a promising approach to promote the wider use of kraft lignin. However, using kraft lignin to produce high value-added products is a great challenge, due to its complex structure, low reactivity, and low solubility, which are factors that limit the lignin's large-scale use in biorefineries. Recent studies show that kraft lignin can be used as lignosulfonates and dispersants, technical carbons, transportation fuels, bioplastics, and adhesives, but some technological hurdles must be overcome and several industrial tests must be developed to make these uses viable.

Keywords: Lignin; Biorefinery; Kraft; Chemical modification; Applications

*Contact information: a: Department of Forestry Engineering, Federal University of Viçosa, Av. P.H. Rolfs, s/n, Campus, 36570-900 Viçosa, Minas Gerais, Brazil; b: Department of Chemistry, Federal University of Viçosa, Av. P.H. Rolfs, s/n, Campus, 36570-900 Viçosa, Minas Gerais, Brazil; *Corresponding author: iarademuner@gmail.com*

INTRODUCTION

Lignocellulosic biomass (wood and non-wood) is the most abundant renewable material in the world, and its three main components are cellulose, hemicellulose, and lignin. The potential scarcity and increase in the price of fossil fuels, as well as increasing environmental restrictions, makes biomass an important source of renewable energy (Garcia-Maraver *et al.* 2015). Besides cellulose and hemicellulose, lignin is recognizable as a potential raw material to produce various products.

Lignin is found in large quantities in the cell wall of wood as a highly branched and amorphous biomacromolecule, and it can be diverse in composition, depending on the vegetal source (Sjöström 1993). It is an aromatic polymer with phenolic hydroxyl groups and is the main organic component present in black liquor of the kraft process (Zhu *et al.* 2014).

As a by-product of the pulp and paper industry, approximately 50 million tons of lignin are produced annually worldwide, of which 98% to 99% of the industrial lignin is incinerated to produce steam and energy, while 1% to 2%, derived from the sulfite pulp industry, is used in chemical conversion to produce lignosulfonates (Mohan *et al.* 2006; Gellerstedt *et al.* 2012; Inwood 2014; Norgren and Edlund 2014). Despite the fact that lignin becomes more valuable after its conversion into chemicals (Macfarlane *et al.* 2009), its application as a source of chemicals remains limited, and most of the kraft lignin in black liquor is combusted as a fuel as well as a reductant of sulfate in sulfur recycling.

The kraft and sulfite processes can effectively solubilize and extract lignin from the lignocellulosic biomass, and they are used all over the world. The kraft process is predominant in the pulp and paper sector, giving rise to sizeable amounts of lignin that could potentially yield high value-added products (Ouyang *et al.* 2009).

The lignocellulose biorefinery concept, based on the chemical separation of the major components (cellulose, hemicelluloses, and lignin) and their further individual processing, is an interesting approach to maximize the added value of the final products (Vila *et al.* 2016). The pulp industries have specific uses for lignin by-products. For example, the kraft pulp industry uses lignin as a fuel feedstock, while in the sulfite industry the lignin is sold to produce lignosulfonates, after a minor chemical treatment. Nevertheless, it is necessary for biorefinery processes to implement strategies to manage lignin and its by-products, which is essential for establishing the economic viability of the processes (Galkin and Samec 2016; Tian *et al.* 2017; Huang *et al.* 2018).

In this context, the biorefining of natural raw materials is a promising approach to promote the wider use of lignin. Such biorefining is based on the integration of biomass conversion, processes, and equipment to produce fuels, energy, and chemicals. In the last few years, the lignocellulosic biorefineries have focused on the valorization of cellulose and hemicellulose, the alleged sugar-based platform, whereas lignin was generally considered to be a low-value residue (Cherubini 2010; FitzPatrick *et al.* 2010; Doherty *et al.* 2011). Particularly in the case of the kraft pulp industry, removing part of the lignin from black liquor decreases the heat load to the recovery boiler. Therefore, more black liquor can be combusted in the boiler, and the pulp production can be increased if no other bottlenecks exist. In addition, high value-added products can potentially be obtained from the extracted lignin.

The conversion of lignin into valuable products is a way of unleashing its potential. However, according to Vishtal and Kraslawski (2011), the lignin's complex structure, low reactivity, and solubility are the main factors limiting its large-scale use in biorefineries. Additionally, lignin has a heterogeneous chemical structure and high polydispersity, which can lead to undesirable properties, impacting its applications in new products (Naseem *et al.* 2016; Roopan 2017; Park *et al.* 2018).

The use of kraft lignin to produce high-added-value products is a challenge due to the low yield, high costs, the validation of the new products by the performance testing, and the challenges involved in the integration of biorefinery (Wang *et al.* 2019). However, the combination of a growing market and the potential economic gains related to lignin biorefinery increases the interest in research to evaluate its large spectrum of applications. Kraft lignin can be used as lignosulfonates and dispersants, technical carbons (*e.g.*, carbon fibers), transportation fuels, bioplastics, adhesives, *etc.*

LIGNIN BIOSYNTHESIS AND STRUCTURE

Lignin is a natural macromolecule that is biosynthesized from a phenylpropanoid monomer structure, highly amorphous and branched with variable compositions depending on the plant source. In hardwood, lignin makes up 16% to 24% of the composition and 25% to 31% in softwood (Sjöström 1993; Klemm *et al.* 2002). In the cell wall, the lignin is chemically bound to carbohydrates by covalent bonds (benzyl esters, benzyl ethers, and phenyl glycosides), forming a structure of excellent resistance and durability (Smook

2002). The chemical structure of lignin is complex and can be described by the average empirical formula ($C_9H_{10}O_2(OCH_3)_n$), which is based on the phenylpropanoid unit (Kun and Pukánszky 2017).

Like most aromatic constituents of plants, the shikimic acid pathway related to carbohydrates and aromatic amino acids metabolism forms the lignin precursors, which provides the aromatic amino acid phenylalanine, a key step in the lignols biosynthesis (Cesarino *et al.* 2012; Liu 2012). In the course of the reaction, three hydroxycinnamyl alcohols (monolignols) are formed: p-coumaryl, coniferyl, and sinapyl, originating the lignins 4-hydroxyl phenyl (H), guaiacyl (G), and syringyl (S), respectively (Fig. 1). Their structure differ only regarding the methoxyl groups and its degree of substitution in the aromatic ring.

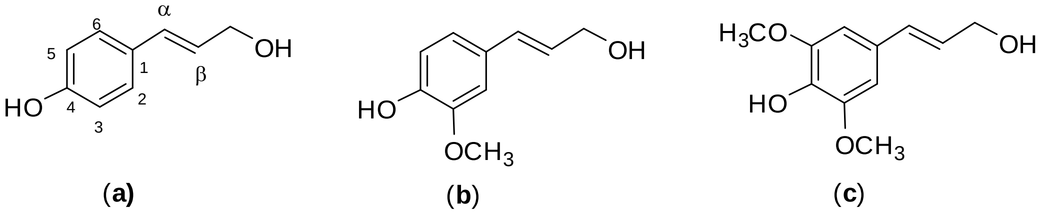

Fig. 1. Monolignol species: (a) *p*-coumaryl alcohol (H unit), (b) coniferyl alcohol (G unit), (c) sinapyl alcohol (S unit)

The lignin structure is formed through polymerization by enzymatic oxidation of these three monolignols. The radical sites are initiated by enzymes (*e.g.*, peroxidases or laccases), and the radical-radical combination between lignin monomers leads to the formation of the polymer (Davin *et al.* 2008; Vanholme *et al.* 2010). An important variety of inter-unit linkages is known, with the β-O-4 ether bonds indicating the most important and frequent type of connection between the lignin units in softwoods and hardwoods, representing approximately 50% and 60% of the bonds, respectively (Mašura 1982; Sjöström 1993; Chakar and Ragauskas 2004). In addition, other types of ether bonds (α-O-4, 4-O-5) are found in lignin with C-C covalent bonds (β-β, β-5, β-1, 5-5) (Fig. 2).

The lignin macromolecule carries multiple functional groups, which are responsible for its reactivity: hydroxyl (either phenolic or aliphatic), methoxyl, carboxyl, carbonyl, benzyl alcohol, hydrolysable ether linkages, and condensed units in C2, C5, and C6 (Sjöström 1993; Brunow *et al.* 1998; Wang *et al.* 2017). The chemical reactivity and branching degree of lignin is dependent on the ratio of the three monolignols (Boerjan *et al.* 2003; Nanayakkara *et al.* 2009). The different proportions of the monomers in lignin have a high range of variation depending on the type of plant material (*e.g.*, softwood, hardwood, and grasses) and the diversity in inter-unit linkages, resulting in a molecule with a high degree of complexity and heterogeneity (Norgren and Edlund 2014).

In softwoods, the G unit is dominant, while hardwood lignin normally contains both S and G units. In grasses, all 3 types of units are found, but the amount of H structures is less remarkable than the others (Gellerstedt and Henriksson 2008; Wang *et al.* 2009). The H/G/S ratio is 0:5/95:100/0 in softwood, 0:4/25:50/46:75 in hardwood, and 2-6/38:68/28:60 in grasses (Pinto *et al.* 2005; Notley and Norgren 2009; Del Río *et al*. 2012; Djajadi *et al*. 2018). Del Río *et al.* (2015) showed that the lignin from sugarcane bagasse is rich in syringyl units (H/G/S molar ratio of 2/38/60), the lignin from sugarcane straw is rich in guaiacyl units (4/68/28), and that both are different in their abundances of the unit linkages.

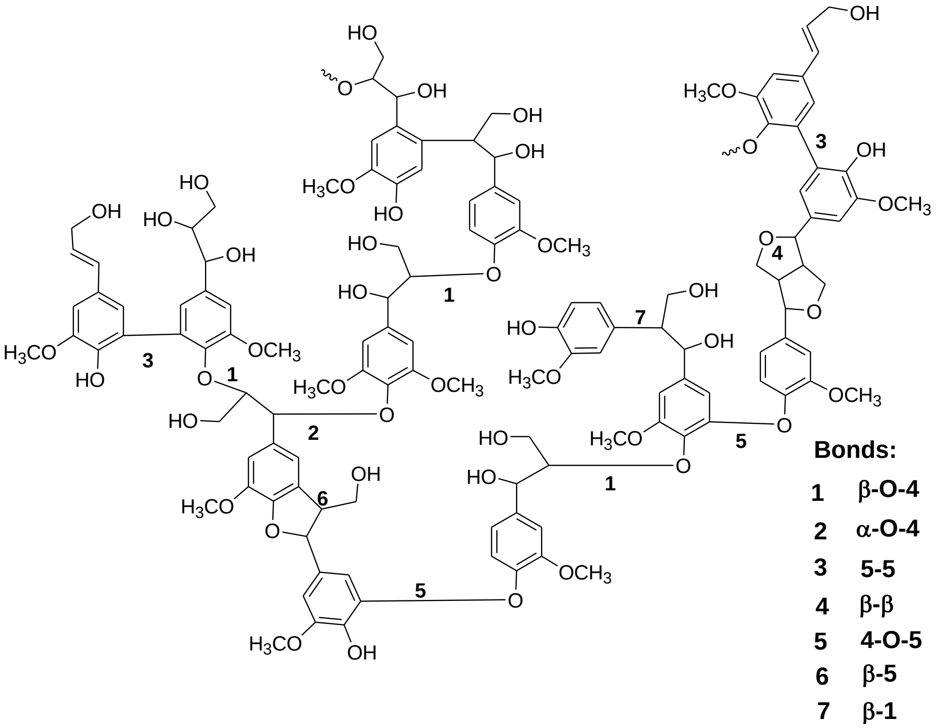

Fig. 2. Main linkages in a softwood lignin. Figure adapted from Windeisen and Wegener (2012).

The G unit has no methoxyl groups linked on the C5 of the aromatic ring, leading to a greater possibility of C-C bonds in this position (Sjöström 1993). Therefore, softwood lignin is more condensed than hardwood lignin, and it is less reactive during kraft processes. According to Norgren and Edlund (2014), the lignin isolation from native sources is accomplished by the cleavage of bonds between different lignin monomers, resulting in the chemical modification and formation of fragments of different sizes, with C-C bonds proving more difficult to be broken.

LIGNIN INDUSTRIAL EXTRACTION PROCESS

The pulp industry is the main commercial source of lignin, which is considered a potential by-product of adding value within the concept of biorefinery (Thakur *et al.* 2014; Jiang *et al.* 2018). The pulping processes are used to separate the lignocellulosic biomass components. The main processes are kraft, sulfite, soda, and organosolv (not commercial). These lignin extraction processes occur in acid and alkaline media or organic solvents, where lignin is progressively broken into low molecular weight fragments, resulting in changes in its physical-chemical properties (Doherty *et al.* 2011).

The various processes cause significant degradation and change the structure of the native lignins with a reduction in the amounts of aliphatic OH groups, β-O-4, and β-β bonds. Additionally, it is possible to observe an increase in the quantities of phenolic hydroxyl groups, carboxylic acids, and carbonyl groups, and in the degree of condensation, due to the formation and/or accumulation of condensed lignin structures (Capanema and Balakshin 2015). Therefore, the structure of the technical lignins is typically dependent on the extraction method and the raw material of origin (softwood, hardwood, or grasses)

(Berlin and Balakshin 2014; Capanema and Balakshin 2014).

Currently, the sulfite process is responsible for the generation of lignosulfonates, but the kraft process is the most widespread and dominant worldwide. For these reasons, these two processes are detailed below.

Sulfite Process

Regarding pulp production, the sulfite process is quantitatively less noticeable when compared to kraft process, but it is the most important in terms of marketable lignin, *e.g.* lignosulfonates with an annual production of approximately 1.8 million tons (Aro and Fatehi 2017).

Traditionally, lignosulfonates are obtained as by-products of sulfite cooking. The wood delignification is carried out by SO_2 and HSO_3^- (acid sulfite), HSO_3^- (bisulfite), or HSO_3^- and SO_3^{2-} (neutral sulfite), usually in the presence of a cation, such as sodium, calcium, magnesium, or ammonium, noting that the solubility of each specific sulfite salt is dependent on pH (Fan and Zhan 2008; Calvo-Flores and Dobado 2010).

The pulping reactions are generally conducted between 140 °C and 160 °C, and the process pH is between 1.0 and 2.0 (acid sulfite), 3.0 and 5.0 (bisulfite), and 6.0 and 7.0 (neutral sulfite). The proportions of sulfite, bisulfite, and sulfur dioxide depend on the pH of the reaction medium, and this affects the path of lignin degradation (Sjöström 1993; Smook 2002).

In the sulfite process, the main reactions that cause lignin solubilization are sulfonation and acid hydrolysis (Elumalai and Pan 2011). The mechanisms involve the loss of a hydroxyl group or the cleavage of the ether bond (α-O-4), generating quinone methide intermediates by means of a resonance-stabilized benzylic cation (Fig. 3) (Doherty *et al.* 2011; Matsushita 2015). Subsequently, large amounts of sulfur become covalently bonded with the lignin as sulfonate groups ($-SO_3^-$) attach to α-carbon in amounts ranging from 0.4 to 0.5 sulfonate groups per C9 unit (Goring 1971; Sjöström 1993; Gellerstedt and Henriksson 2008; Lora 2008; Calvo-Flores *et al.* 2015).

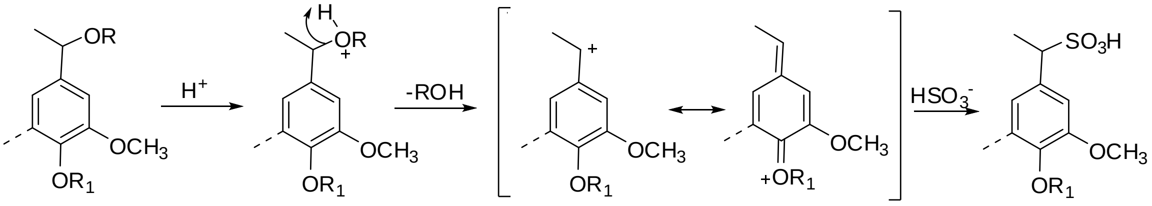

Fig. 3. Sulfonation reaction occurring during acidic sulfite pulping. Figure adapted from Matsushita (2015).

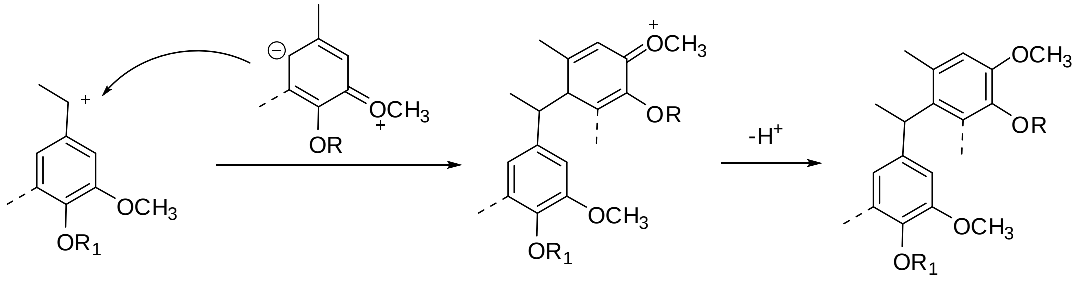

Fig. 4. Condensation reaction occurring during acidic sulfite pulping. Figure adapted from Matsushita (2015).

Instead of sulfonation, there may be a condensation reaction involving the benzylic carbon of one molecule and another electron-rich carbon atom due to the presence of the benzylic cation (Fig. 4). This condensation tends to block the sulfonation reaction from occurring in the α-position (Doherty *et al.* 2011; Matsushita 2015).

Sulfite pulping does not selectively remove lignin; thus, carbohydrates are highly solubilized (particularly hemicelluloses). The liquor resulting from the sulfite process contains a high content of sugars and chemicals used during the process. The sugar content is an important property of the industrial lignosulfonates because their presence may have negative implications in some applications (Forss *et al.* 1985). Several purification steps are necessary to obtain lignosulfonates with a higher purity and added value, including fermentation to convert the residual sugars into ethanol, membrane separation, and ultrafiltration (Lora 2008; Aro and Fatehi 2017).

The lignosulfonates generated by the sulfite process have two main ionizing groups, the sulfonates (pKa ≤ 2) and the phenolic hydroxyl groups (pKa ~ 10), in addition to approximately 5% by weight of sulfur content (Doherty *et al.* 2011). The high water-soluble characteristic attributed to lignosulfonates is due to the low pKa of the sulfonate groups, the variety of functional groups, and other structural characteristics that provide unique colloidal properties to these lignins (Areskogh *et al.* 2010; Areskogh and Henriksson 2011; Duval and Lawoko 2014).

When compared to kraft lignin (MW = 1,000 to 5,000 g/mol), lignosulfonates generally have higher molecular weights, since only a small part of the more frequent β-O-4-ether bonds reacts in the pulping process (Aro and Fatehi 2017; Kun and Pukánszky 2017). However, molecular weights may also vary depending on the raw material, with hardwood lignosulfonates exhibiting lower molecular weights (MW = 5,700 to 12,000 g/mol) compared to softwood lignosulfonates (MW = 36,000 to 61,000 g/mol) (Braaten *et al.* 2003).

The conditions of the pulping process result in different physicochemical properties of lignosulfonates (Aro and Fatehi 2017). For example, the use of sodium cations produces extended lignin chains, which are more suitable for use as dispersants, while calcium cations produce compact lignin chains (Doherty *et al.* 2011). The lignosulfonates generally have a wide range of uses, such as dispersants, surfactants, animal feed, pesticides formulation, petroleum drilling additives, stabilizers in colloidal suspensions, and as plasticizers in concrete mixtures, which comprise cement, sand, and aggregate (Lora 2008; Fatehi and Ni 2011; Vishtal and Kraslawski 2011; Zhou *et al.* 2013).

Kraft Process

Kraft is the world's dominant pulping process. During the kraft process, wood is converted into pulp using a solution of Na_2S and NaOH (white liquor) at a temperature of 155 °C to 175 °C. In addition, the lignin macromolecule must be degraded and solubilized to a large extent, and the pulping conditions are highly dependent on the chemical structure of the macromolecule (Potthast 2006).

During pulping under alkaline conditions, the degradation or dissolution of phenolic lignin units involves the ionization of phenolic groups and the formation of the quinone methide, an unstable intermediate species (Fig. 5). The bisulfide ions (HS^-) are strong nucleophiles. When present in the liquor, they react with the quinone methide, resulting in the hydrolysis of β-aryl ether bonds (Gierer 1980). A common characteristic of the kraft process is the nucleophilic reaction of species such as HO^-, HS^-, and S^{2-} (their nucleophilicity increases in the order $HO^- < HS^- < S^{2-}$) with electron-deficient centers in the lignin molecule, resulting in the cleavage of lignin interconnections and a higher hydrophilicity of resulting lignin fragments and thus, a better dissolution in the cooking liquor (Potthast 2006). Additionally, the breakage of β-aryl ether bonds occurs in non-phenolic structures of lignin under specific conditions (*e.g.*, the presence of an HO^- group in the α-carbon) (Fig. 6).

The hydrolysis of the β-aryl ether bonds is important because it comprises 40% to 70% of the lignin interunit linkages. However, the hydrolysis of the α-aryl and α-alkyl ether bonds occurs during the kraft pulping process, in addition to the β-aryl ether bonds (Gierer 1980).

The reactivities of the lignin subunits differ greatly, with the phenolic lignins being noticeably more reactive than the non-phenolic lignin units. Additionally, softwood lignin is less reactive than hardwood lignin, which is due to the G-lignin containing higher amounts of C-C bonds at the C5 position (Sjöström 1993). In general, the kraft lignin contains characteristics that differentiate it from both native lignin and other classes of lignins. Kraft lignin has abundant phenolic hydroxyl groups, which arise due to the extensive breakage of β-O-4 linkages during the kraft cook (Chakar and Ragauskas 2004).

In addition to the degradation reactions of lignin, condensation reactions occur during kraft pulping, which increase the molecular size of the lignin fragments. Despite having the opposite effect in the delignification process, these two types of reactions are closely related because they proceed through common intermediates (Gierer 1980).

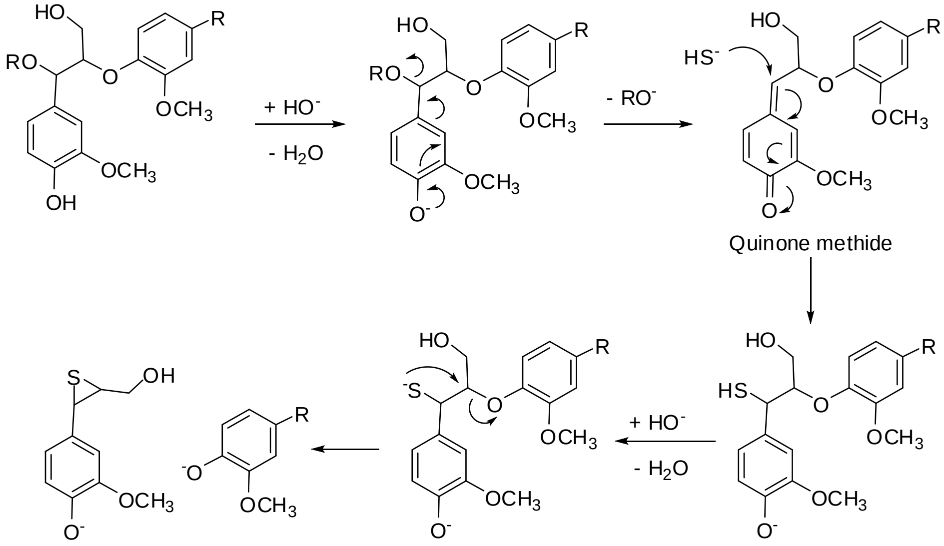

Fig. 5. Cleavage of phenolic β-O-4 linkages during kraft process. Figure adapted from Gierer (1980)

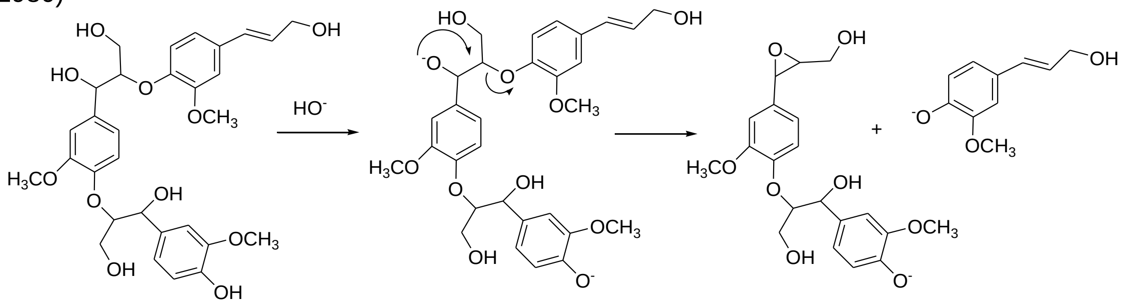

Fig. 6. Cleavage of non-phenolic β-O-4 linkages during kraft process

Black liquor is generated by the kraft process as a residual liquor, characterized by the presence of inorganic components as well as organic components that have been removed from the wood. The organic material consists of lignin fragments and hydroxy acids derived from carbohydrates (mainly hemicelluloses) that have been degraded by alkali-catalyzed reactions. According to Krotscheck and Sixta (2006), the black liquor chemical composition depends on the wood species, the composition of and amount of white liquor (solution of Na_2S and NaOH), the unbleached pulp yield, and the volume of recycled filtrates from the oxygen delignification stage (O-stage). This O-stage uses alkali and oxygen to remove a substantial portion of the residual lignin in the unbleached pulps before a bleaching process. In the pulp mill, the filtrate from the O-stage can be incorporated into the chemical recovery system together with the black liquor, if the recovery boiler has sufficient capacity to handle the extra load (Kvarnlöf and Germgård 2015).

In pulp and paper mills, black liquor is burned in the recovery boiler, which serves as a source of steam for electricity generation and for the drying of paper. Through the kraft recovery cycle, it is possible to recover the inorganic chemical compounds used in the cooking process, providing lower production costs and a considerable reduction of effluents production (Reeve 2002; Tran and Vakkilainen 2008).

The isolation of lignin from black liquor is an important step when converting the pulp mill into a biorefinery to improve the pulp mill throughput and increase the added value of lignin *via* the generation of usable products (Zhu *et al.* 2014). Several methods have been evaluated for the separation and purification of lignin (Jönsson *et al.* 2008; Bhattacharjee *et al.* 2006; Arkell *et al.* 2014). The extraction process should be simple and easy, producing a high-yield, isolated lignin, that is free of contaminants (Lin and Dence 1992). Currently, the most commercialized process to recover lignin from black liquor is known as “LignoBoost” (Theliander 2008).

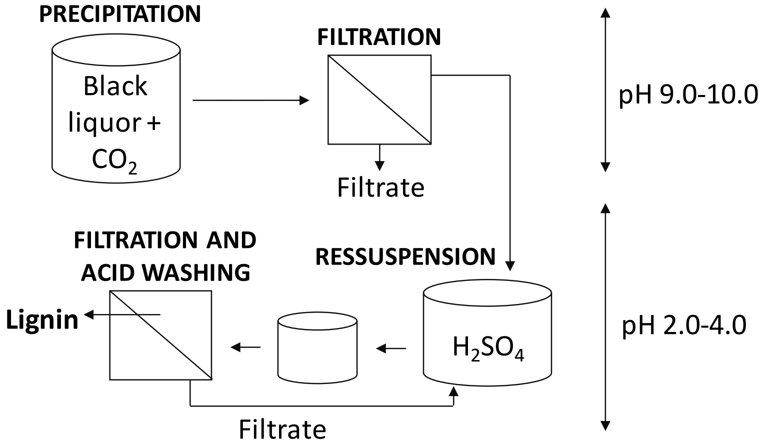

Fig. 7. The LignoBoost process for isolation of kraft lignin

In this process, a black liquor stream is withdrawn from evaporators of the kraft process recovery (dry solid content of 30% to 45%) and is acidified with CO_2 to a pH of 9.0 to 10.0 at 60 °C to 80 °C. The lignin is precipitated at this pH in a precipitation tank and filtered. The precipitated lignin is re-dispersed in an acidic filtrate suspension tank with pH controlled at 2 to 4 (Fig. 7). The resulting lignin is then filtered and washed by acid displacement washing (pH of 2 to 3) (Kalogiannis *et al.* 2015). Unlike the lignin separation process during a single stage, the change in pH, ionic strength, and lignin solubility occur mainly in the re-dispersion tank and not during the final stage of lignin washing, and this improves the properties of the precipitated lignin (Öhman *et al.* 2007; Tomani 2010; Fatehi and Chen 2016).

The LignoBoost process has a high lignin yield, high-purity lignin with low ash and carbohydrate contents, low investment costs due to reductions in acid wash volume, and low operating costs due to a reduction in the amount of H_2SO_4 required (Tomani 2010). According to Hu *et al.* (2018), the plant at the Stora Enso Sunila Mill (Kotka, Finland) and the plant at the Domtar Plymouth Mill (Plymouth, NC, USA) manufacture 75,000 tons of kraft lignin per year using the LignoBoost process.

The pH of black liquor is high (pH of 13 to 14), contributing to a high solubility of lignin due to the ionized phenolic groups present in the molecules. The lignin precipitation results from the acidification of black liquor, which results in the protonation of these ionized phenolic groups, reducing the electrostatic repulsive forces between lignin molecules, and making them less hydrophilic (Sundin 2000; Vainio *et al.* 2004). Protonation takes place to a greater extent at a given pH, in cases where the pKa value is higher, which is influenced by the temperature, the ionic strength of the solution, and the molecular structure of the lignin (Rudatin *et al.* 1989; Norgren and Lindström 2000; Ragnar *et al.* 2000).

The structural difference of softwood and hardwood lignins, according to the type of monolignol units present [softwood (G) or hardwood (G and S)], has implication for the reactivity of lignin during kraft pulping, and for the kraft lignin extracted properties. Due to availability of the C5 position, G-type lignins contain more C-C bonds, *e.g.* β-C5 and C5-C5, when compared to S-type lignins (Sjöström 1993). According to Zhu and Theliander (2015), precipitated softwood lignin specimens contain lower amounts of methoxyl groups than a mix of hardwood and softwood lignin.

In addition, kraft lignin properties can be altered according to the conditions used during the LignoBoost process. A lower pH and/or lower temperature and a greater ionic strength in black liquor results in a higher precipitation yield. Under these conditions, the precipitated kraft lignin has a lower average molecular weight and the lignin has a higher number of phenolic groups (Zhu and Theliander 2015).

The main factors that limit the large-scale use of precipitated lignins in biorefineries are the large chemical and molecular variation, their complex structure, low reactivity, and low solubility (Vishtal and Kraslawski 2011; Park *et al.* 2018). Studies in order to improve solubility and reactivity of lignin may be developed to potentiate the production and generation of high value-added products.

To improve homogeneity and reduce the complexity of lignin, fractionation techniques by an eluotropic series of organic solvents and precipitation by the pH effect are potential solutions (García *et al.* 2009; Wang and Chen 2013; Li and McDonald 2014; Santos *et al.* 2014; Duval *et al.* 2015). In addition, the use of ceramic membranes having different cut-offs has been widely researched (Wallberg *et al.* 2003; Toledano *et al.* 2010). These techniques allow lignin to be produced with more uniform molecular weights and low polydispersity fractions (Francuskiewicz 1994; Li and McDonald 2014; Duval *et al.* 2015; Jääskeläinen *et al.* 2017).

Based on the chemical and molecular variations of the precipitated lignins, many possibilities of modifying its structure have been studied to increase the reactivity, to enhance its applications, and to increase the added value of this pulp industry by-product (Hu *et al.* 2011; Laurichesse and Avérous 2014).

KRAFT LIGNIN MODIFICATION

Kraft lignin has limited industrial applications, and it requires modifications to increase its potential for use as a starting material for polymer and chemical synthesis. However, due to the structural complexity and heterogeneity of lignin, such modifications are challenging. Without any modification, the most reactive site in the kraft lignin is the α-position of the phenylpropene subunits (Heden and Holmberg 1936). However, this reactive α-site can be occupied by ether bonds (*e.g.*, α-O-4 aryl), or be sterically hindered because of β-O-4 linkages and other interconnecting bonds, lowering the reactivity of kraft lignin (Inwood 2014).

According to Laurichesse and Avérous (2014), the chemical modification of lignin can be performed through the fragmentation of lignin, the chemical modification of hydroxyl groups, and the creation of new chemically-active sites. To increase the reactivity of the lignin, various methods have been described for modifying its structure, including demethylation, oxidation, hydrolysis, reduction, phenolation, and hydroxymethylation (Li and Geng 2005; Effendi *et al.* 2008; Hu *et al.* 2011; Inwood 2014; Dai *et al.* 2016; Zuluaga *et al.* 2018).

In the lignin structure, the C3 e C5 positions of the aromatic ring can be substituted by one or two methoxyl groups (-OCH_3), and these groups can interfere with the reactivity of the free phenolic hydroxyl group. The demethylation results in lignin with free phenolic groups instead of modifying lignin to form catechol groups (Okamoto *et al.* 1996; Hu *et al.* 2011). Sulfur-mediated demethylation and enzymatic oxidative cleavage can remove the methyl groups (Wu and Zhan 2001; Filley *et al.* 2002). However, in recent studies, a thermal treatment of black liquor prior to the lignin extraction was performed to obtain a significant level of demethylation and demethoxylation in the kraft lignin, a technology known as catechol (CAT) lignin (Wikberg *et al.* 2017). During the CAT lignin process, a lignin rich in catechol is produced, thus increasing the number of reactive sites. According to Leppävuori *et al.* (2017), in hardwood lignins, the methoxycatechol units that are formed primarily by demethylation and the demethoxylation will activate the *ortho* positions of the lignin phenolic unit (C3 and C5).

Lignin oxidation is one way to obtain phenolic derivatives, and the oxidative lignin depolymerization increases the reactivity of lignin through selective bond cleavage of the β-O-4, aryl ether, and C-C types (Dai *et al.* 2016). The application of different oxidants (*e.g.*, nitrobenzene, oxygen gas, hydrogen peroxide, and metal oxides) allows the production of functionalized products that range from aromatic aldehydes (vanillin and syringic) to acids (vanillic and syringic). Nitrobenzene is the aromatic oxidant that promotes the highest yield of derivatives from lignin (Laurichesse and Avérous 2014). To obtain fractions with high value-added compounds, lignins are oxidized under the optimized conditions of temperature, time, and air pressure, with vanillin being considered the most well-known and valuable product from lignin.

The formation of an aldehyde through the oxidative degradation of lignin using alkaline nitrobenzene has been described as a one-electron transfer process (Nandanwar *et al.* 2016; Fache *et al.* 2016; Tarabanko and Tarabanko 2017). This process is demonstrated in Fig 8 with nitrobenzene, but another oxidant can be used. According Fache *et al* (2016), there are many parameters influencing the process, which increase the complexity of the mechanism.

Hydrolysis is a method to break the ether bonds of lignin, which results in the production of low molecular mass phenolic compounds (Hu *et al.* 2011). This process can be performed with near- and super-critical water using a batch type reactor and an alkaline treatment with NaOH (Nenkova *et al.* 2008; Wahyudiono *et al.* 2008). Despite the fact that hydrolysis increases the lignin reactivity, it decreases the molecular weight, which is undesirable for some applications, *e.g.*, flocculants and dispersants.

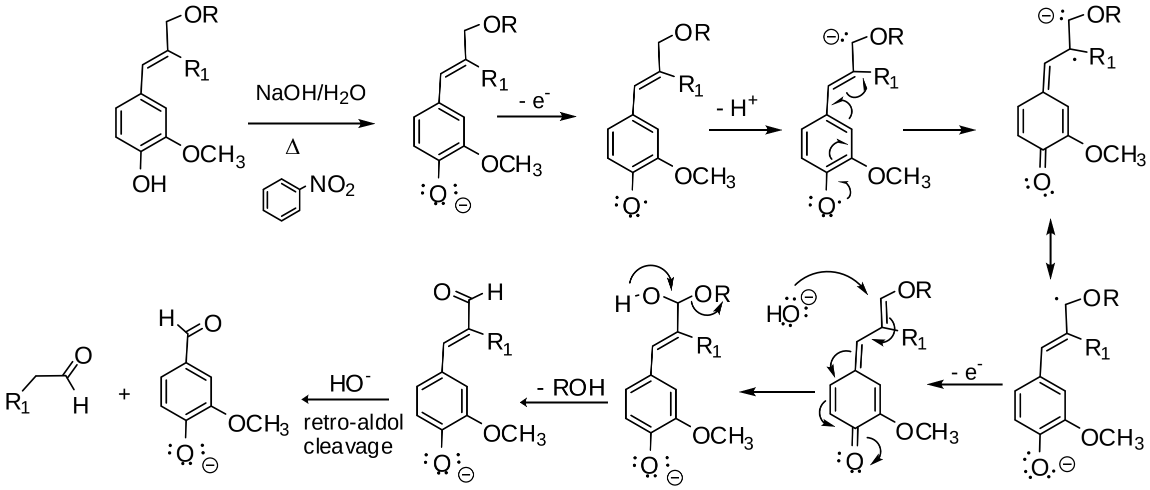

Fig. 8. Reaction pathway of softwood lignin oxidation giving rise to vanillin. Figure adapted from Fache *et al.* (2016).

The reduction of lignin takes place during the production of alcoholic groups through the reduction of aldehydes and ketones in the lignin. Some reducing reagents that can be used in this process are lithium aluminum hydride ($LiAlH_4$) and sodium borohydride ($NaBH_4$). According to Li and Geng (2005), a demethylated lignin reaction with $NaBH_4$ can form catechol groups, which are regarded as having a higher reactivity than phenol. A strong reagent for hydrogenation (*i.e.*, lithium aluminum hydroxide) can be used to reduce certain groups such as acid and ester, in addition to the aldehydes and ketones into alcohol, although this reagent is selective and does not react with the C-C bonds in lignin (Hu *et al.* 2011).

The phenolation process consists of the treatment of the lignin with phenol in a solution of organic solvents, *e.g.*, methanol or ethanol (Effendi *et al.* 2008). During the phenolation process in an acidic medium, the phenol condenses in the lignin's aromatic ring at the *ortho* site relative to the hydroxide group through aromatic substitutions as well as within the chain at the α position (Fig. 9) (Brunow 2005; Inwood 2014; Jiang *et al.* 2018). Gao *et al.* (2019) demonstrated that the phenolation of lignin also can occur at the reactive γ position by substitution of aliphatic hydroxyl groups. The phenolation reaction is an acidolytic process, where electrophilic substitution reactions of phenolation and condensation occur simultaneously (Huang *et al.* 2017; Gao *et al.* 2019).

According to Hu *et al.* (2011), the phenolation process, as well as hydroxymethylation, are more effective at increasing the reactivity of lignin when compared with reduction, oxidation, and hydrolysis. The goal of the hydroxymethylation process is to introduce hydroxymethyl groups ($-CH_2OH$) to lignin molecules (Fig. 10), which increases the reactivity of the *ortho* bonding site in relation to the hydroxide group on the phenyl propene subunit (Yasuda *et al.* 1999; Zuluaga *et al.* 2018).

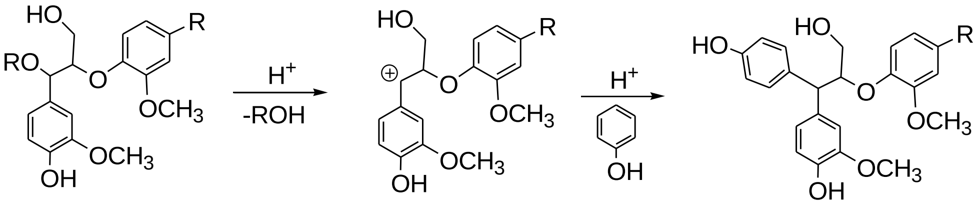

Fig. 9. Reaction pathway of the phenolation of β-O-4 structure of lignin. Figure adapted from Jiang *et al.* (2018).

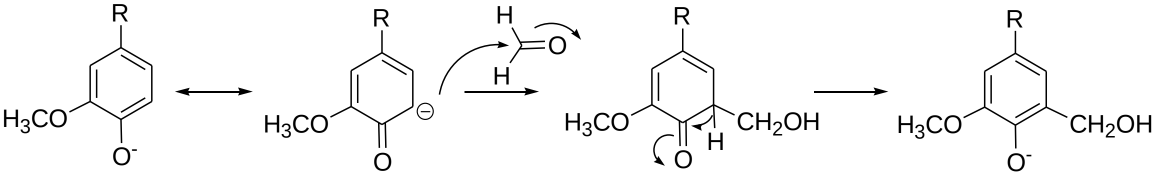

Fig. 10. Reaction pathway of the hydroxymethylation of lignin. Figure adapted from Zuluaga *et al.* (2018).

KRAFT LIGNIN AS HIGH VALUE-ADDED PRODUCT

Kraft lignin has a combination of a growing market and a high-level purity in its end-product, which increases its potential for applications in high value-added products. Based on the biorefinery concept, several studies are being carried out to develop wider uses for kraft lignin. In many cases, it is necessary to tune the extraction process or add a process step to reach a specific requirement. When the goal is to improve the reactivity and homogeneity of kraft lignin to compete with petroleum products, depolymerization techniques and chemical modification should be adopted.

Lignin as Lignosulfonates and Dispersants

The production of lignosulfonates from kraft lignin through sulfonation reactions give rise to a wide range of lignins with different degrees of sulfonation, molecular weights, and functional groups. Although kraft lignin dissolves readily at a high pH, it exhibits poor solubility at a near-neutral pH, and this hinders its use in many systems involving aqueous solutions (Helander *et al.* 2013). Due to the presence of sulfonic groups, the lignosulfonates are both anionically charged and water-soluble, improving the properties of solubility and charge density of kraft lignin (Aro and Fatehi 2017).

Due to the limited production of lignosulfonates by the sulfite process, an increasing amount of studies focusing on acid sulfonation or sulfomethylation of technical lignins have been performed for the generation of water-soluble sulfonated lignin to satisfy the market demand (He and Fatehi 2015; Konduri and Fatehi 2015). Acid sulfonation consists of the treatment of kraft lignin with sulfuric acid at high temperatures (Inwood 2014). According to Dilling (1991), depending on the degree of sulfonation, the sulfonated lignin may exhibit complete solubility in water at all pH levels.

In this sulfonation, the $-SO_3H$ groups are linked to the aliphatic side chain of the lignin molecule, and the reaction occurs at the α-carbon of the phenyl propane unit (Fig.11) (Inwood 2014; Sjöström 1993).

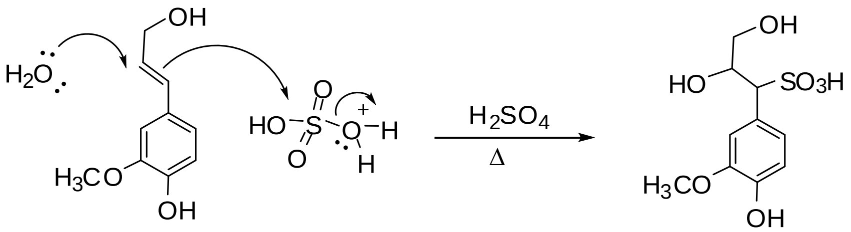

Fig. 11. Sulfonation of kraft lignin with sulfuric acid (-SO_3H groups linked on the aliphatic chain). Figure adapted from Inwood (2014).

According to Gao *et al*. (2019), the -SO_3H groups can also be linked to aromatic groups, in H and G units of kraft lignin (Fig. 12). A disadvantage of acid sulfonation is that kraft lignin may form condensed structures in the acidic conditions, impairing an extent of lignin sulfonation and its reactivity (Huang *et al.* 2017).

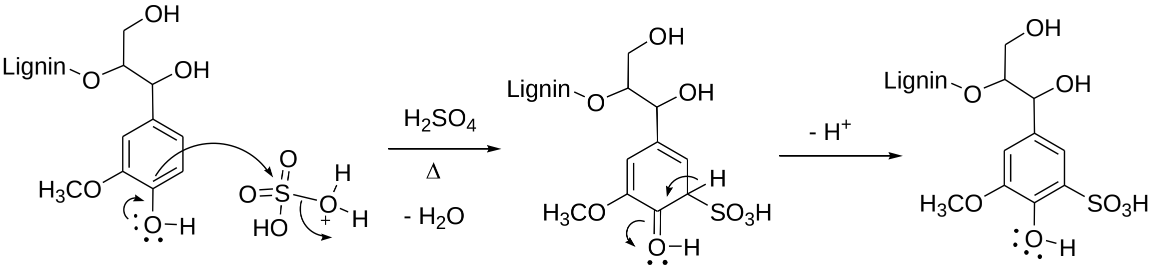

Fig. 12. Sulfonation of kraft lignin with sulfuric acid (-SO_3H groups linked on the aromatic groups). Figure adapted from Gao *et al.* (2019).

Sulfomethylation is another alternative to produce sulfonated kraft lignin, and it consists of the treatment of purified lignin with sodium sulfite or sodium bisulfite in the presence of an aldehyde (formaldehyde). Therefore, hydroxymethylation occurs through the addition of formaldehyde, and sulfonation occurs through use of sodium sulfite or sodium bisulfite (Yu *et al.* 2013). The sulfomethylation reaction of the kraft lignin introduces -CH_2SO_3H groups into the aromatic ring of the lignin structure, according to the mechanism proposed in Fig. 13. Note that lignosulfonate production through sulfomethylation runs through a mechanism completely different from those of the sulfite pulping process and acid sulfonation, in which the sulfonic acid groups are in the aliphatic chain (Berlin and Balakshin 2014). According to Kamoun *et al.* (2003), in the sulfomethylation reaction, the introduction of sulfonate groups into the aliphatic side chain of the lignin molecule may also occur in the presence of excess sulfite.

However, the sulfomethylation reaction in the aromatic ring is possible only in the guaiacyl lignin present in black liquor, which has the aromatic carbon at the C5 position available for sulfomethylation. Therefore, the sulfomethylation of hardwood kraft lignin is a challenging process due to the high content of low reactivity syringyl lignin present in the kraft liquor.

The kraft lignin can be sulfonated to various degrees, depending on the process conditions. Each water-soluble sulfonated lignin is evaluated through solubility, molar mass distribution, and hydrophilic character (Kamoun *et al.* 2003). Several applications have been suggested for sulfonated lignins, and the dispersants and additives for concrete (plasticizers) seem to have the most potential.

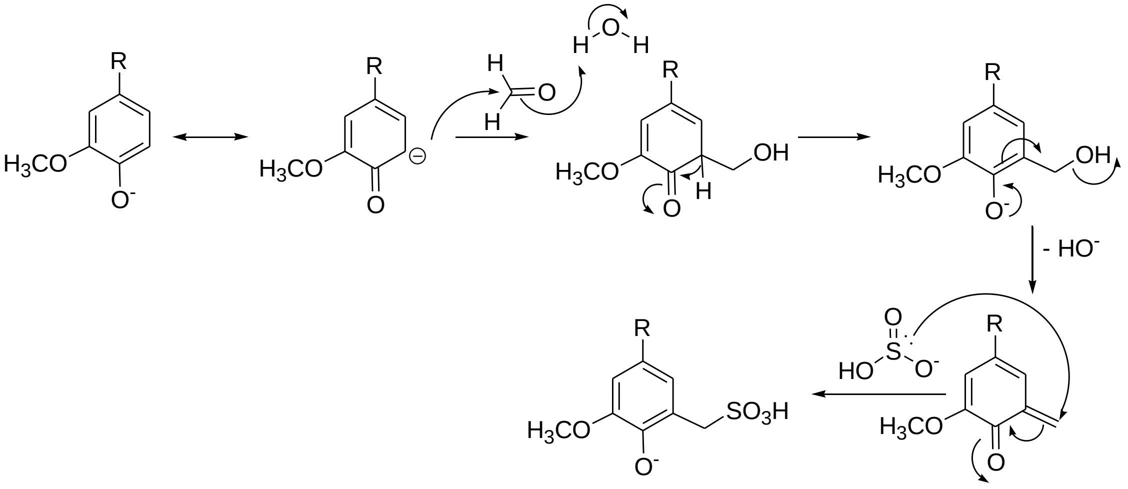

Fig. 13. Proposed mechanism for sulfomethylation of kraft lignin with formaldehyde and sodium sulfite

The preparation of water-soluble sulfonated lignin can be performed with both wood and non-wood lignins. Sulfomethylated lignin from sugarcane bagasse, esparto grass, and a mixture of hardwood were used as dispersant and cement additives (Kamoun *et al.* 2003; Li and Ge 2011; Konduri and Fatehi 2015). An increase in the degree of sulfonation through the sulfomethylation of kraft lignin will increase the charge density. This provides a lower viscosity to the cement paste in comparison to commercial lignosulfonates and acid sulfonation. The sulfur content of sulfonated lignin is essential for its solubility and dispersion (Aro and Fatehi 2017).

In a study by Inwood (2014) with softwood kraft lignin, the acid sulfonation and sulfomethylation were evaluated, in addition to the application of the products as dispersants and flocculants. In the sulfuric acid treatment, adding charged groups to lignin at an α-position occurs on the aliphatic chain. However, lignin condensation (*i.e.*, the polymerization of lignin) can occur on the same site (Yasuda *et al.* 1999). Due to the balance of these possible reactions, some conditions may negatively influence sulfonation (*e.g.*, temperature). An increase in temperature decreased the charge density because the condensation reaction required less energy than lignin modification (Zoumpoulakis and Simitzis 2001). After optimizing the conditions, a sulfonated lignin with a charge density of 0.75 mEq/g and a solubility of 8% was produced.

However, Gao *et al.* (2019) showed that during acid sulfonation the -SO_3H groups may also be linked on the aromatic chain, evidencing that this treatment can be effective in sulfonation of kraft lignin.

Sulfomethylation of softwood kraft lignin was performed on previously hydroxymethylated lignin (H-lignin) with formaldehyde (Inwood 2014). The sulfonation with sodium sulfite of this pretreated lignin yielded material having a charge density of 1.2 mEq/g and solubility of 100%, evidencing better results when compared with acid sulfonation. The molecular weight (MW) of kraft lignin increased from 25,100 g/mol to 37,161 g/mol, which indicates a slight condensation of lignin. The MW of hydroxymethylated lignin (prior to sulfonation) was 45,420 g/mol, with the decrease being attributed to hydrolysis, which occurs at a high pH (Mao *et al.* 2012). The hydrolysis of H-lignin is the dominant reaction, though in addition, condensation in alkaline conditions can occur (Gierer and Petterson 1977). According to Matsushita and Yasuda (2005), the increase in the molecular weight helps promote effective dispersion processes due to the application of a larger steric force, thus increasing the efficiency of the products as dispersants.

Sulfomethylated hardwood kraft lignin was successfully prepared by using sodium sulfite and formaldehyde (Konduri and Fatehi 2015). The conditions were optimized, and the unmodified lignin had a negligible charge density and 0.03 mmol/g of the sulfonate group, while the sulfomethylated lignin presented -1.6 mEq/g charge density and 1.48 mmol/g of the sulfonate group. The molecular weight increased *via* sulfomethylation from 22,746 g/mol to 53,360 g/mol, and the solubility analysis confirmed the high solubility (40 g/L) of sulfomethylated hardwood kraft lignin at a neutral pH. In contrast, the unmodified lignin was insoluble at pH 7.

In addition to the benefits of increasing the charge density and sulfonic groups in kraft lignin for the various applications, Huang *et al.* (2018) observed a high lignosulfonate yield (94.9%) through the sulfomethylation of the bamboo kraft lignin with sodium sulfite and formaldehyde, evidencing that the process may be industrially viable.

Lignin as Technical Carbons

The structure and composition of lignin, which is the largest biomass source with aromatic properties and a carbon content above 60%, make it an ideal precursor to produce advanced carbon materials (Chatterjee and Saito 2015). Carbon fibers, activated carbons, and carbon black are some of the products that can be obtained by thermochemical conversion of kraft lignin (KL) (Rosas *et al.* 2014).

Carbon fiber is a material with excellent mechanical properties and low density. It is widely used in structures that need to be lightweight but strong, such as sports equipment and in the automotive and aerospace industries (Li *et al.* 2017a). Carbon fiber production from kraft lignin represents one of its highest value-added products and is discussed in the next topic.

Activated carbon (AC) usually exhibits properties suitable for use as adsorbents, and accordingly it is applied in gas and fluid streams, gas separation, catalyst supports, filtration systems, and electrochemical applications (Bansal and Goyal 2005; Puziy *et al.* 2018). Activated carbon has thermal and chemical stability in both acidic and alkaline media, easy modification of its chemical surface, well-developed porous structure (with a large internal surface area ranging from 500 m^2/g to 2000 m^2/g), and good adsorption capacities (Suhas *et al.* 2007; Rosas *et al.* 2010).

Non-renewable coal-based resources are used to produce approximately 80% to 85% of the total production of activated carbon (Ragan and Megonnell 2011). Kraft lignin can partially substitute these non-renewable resources in AC production, due to its high carbon content and high yield of carbon, which is beneficial for the manufacture of AC. In addition, the use of renewable resources reduces carbon emissions during the production process (Puziy *et al.* 2018). However, the low reactivity of lignin is a challenge for obtaining a quality technical carbon, with high yield and suitable textural properties (Li *et al.* 2014). Besides that, adjustments in the production process may be necessary.

The manufacture of activated carbon is a two-stage process: (1) carbonization and (2) physical or chemical activation (Ragan and Megonnell 2011). In physical activation, the carbonization process is carried out to form a char (normally nonporous) *via* pyrolysis, in an inert atmosphere. The char is then activated through contact with an oxidizing gas, resulting in the formation of a well-developed micropore structure (Suhas *et al.* 2007; Rosas *et al.* 2014).

Preparation of activated carbons from eucalyptus kraft lignin through physical activation with CO_2 at 800 °C to 850 °C has been reported as a viable method (Rodríguez-Mirasol *et al.* 1993a,b; Bedia *et al.* 2007; Cotoruelo *et al.* 2012a, 2012b). The maximum specific surface area is found to range from 700 m^2/g to 1900 m^2/g. According to Suhas *et al.* (2007), although they observed high surface areas, the activation times were considerably long, which confirms the low reactivity of lignin due to its cross-linked nature. Fu *et al.* (2013) used black liquor to prepare AC through physical activation with steam and found the maximum specific surface area to be 310 m^2/g. In this case, the specific surface area was negatively influenced by the higher periods and higher temperatures required for activation.

Impregnation with chemicals such as H_3PO_4, KOH, NaOH, Na_2CO_3, K_2CO_3, H_2SO_4, and $ZnCl_2$ was followed by heating under a nitrogen flow simultaneously with carbonization. Compared with the physical method, this method produces an activated carbon with higher micropore volumes and wider micropore sizes (Suhas *et al.* 2007; Supanchaiyamat *et al.* 2019). Among these activation agents, H_3PO_4 and KOH are preferred to produce AC from the kraft lignin in the range of 450 °C to 900 °C (Hayashi *et al.* 2000; Fierro *et al.* 2007; Li and Luo 2013). The textural properties and yield of ACs from kraft lignin are dependent on the lignin pretreatment methods, the activation methods, and the activation conditions (Li *et al.* 2014).

In a study performed by Gustafsson *et al.* (2017), AC derived from kraft lignin is produced as a potential sorbent for sediment remediation. Chemical activation *via* combination was performed with potassium hydroxide (KOH) (lignin/KOH, 1:3 by dry weight) at 700 °C. The sorption tests in water revealed that the softwood kraft lignin presented a similar value to other commercial activated carbons.

Carbon black (CB) is the trade name for a black powder used as a reinforcement filler in rubber products exposed to high wear and tear and plastics products. In addition, CB is used to make conductive polymer composites (Zhang *et al.* 2007). Several types of CBs are differentiated by particle size, surface area, and conductivity (Snowdon *et al.* 2014).

Currently, the raw material that is most used to produce carbon black is heavy fractions of oil. Replacing this compound with a renewable resource, such as kraft lignin, is a great opportunity for the pulp and paper industries. According to Chatterjee and Saito (2015), lignin-based CB is a potential substitute for ordinary CB in ink, paint, reinforcing fillers, and other applications.

A new alternative that meets the specifications for several grades of CB is the high temperature carbonization process, which converts kraft lignin into CB of renewable resource and is used by the SunCoal Company. Snowdon *et al.* (2014) show that the surface area of lignin 654 m^2/g was obtained with a high carbonization temperature (900 °C). Carbon black has a high surface area, but activated carbon has a higher surface area.

Lignin as Carbon Fibers

Carbon fiber is defined as a fiber containing at least 92 wt% carbon and generally has excellent mechanical properties, low weight, high thermal, chemical stabilities in the absence of oxidizing agents, and it conducts both heat and electricity well (Puziy *et al.* 2018). It has been used in composites, sporting goods, the automotive and aerospace industries, and in wind turbine blades (Mainka *et al.* 2015; Titirici *et al.* 2015; Li *et al.* 2017a).

The principal processing steps for the manufacture of carbon fiber (CF) are shown in Fig. 14. Different methods of fiber spinning are used, depending on the raw material's properties, with the melt-spinning method being the most common and preferred method used (Baker and Rials 2013; Meek *et al.* 2016). Generally, the precursor fibers are first stabilized *via* oxidation at approximately 200 °C to 400 °C in air. After that, the carbonization process is performed at a high temperature (approximately 1,000 °C) in an inert atmosphere to remove hydrogen, oxygen, nitrogen, and other non-carbon elements. After carbonization, the fiber can be further graphitized at an even higher temperature (up to approximately 3,000 °C) to achieve a higher carbon content (Huang 2009). The surface treatment is performed to improve the interaction between the CFs and the resin matrix, which is when CFs are used as the strength bearing component in composites (Norberg 2012).

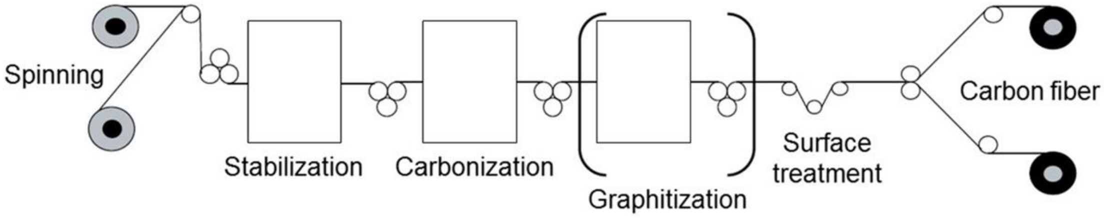

Fig. 14. The principal processing steps for the manufacture of carbon fiber. Figure adapted from Norberg (2012).

Lignin is an attractive precursor to replace polyacrylonitrile (PAN) because of its low cost as a waste from pulp manufacturing facilities. Polyacrylonitrile is a petroleum-based synthetic polymer used to produce approximately 90% of commercial carbon fibers. Due to the high cost of PAN, production costs accounting for more than half the price tag, there is a cost-limitation for its CF applications (Baker and Rials 2013; Frank *et al.* 2014; Mainka *et al.* 2015). Petroleum pitch and regenerated cellulose (rayon) are alternative sources to produce CF. Of these two, lignin is the closest in properties of precursors to petroleum pitch (Norberg 2012).

Lignin as a precursor can promote a broader utilization of carbon fibers. The major advantages of using lignin are its availability, low cost, and high carbon content and high carbon yield during carbonization. In addition, using lignin helps to avoid elimination products such as HCN or nitrous gases released during PAN carbonization (Huang 2009). However, unlike the homogeneous PAN, lignin is a heterogeneous polymer, with different molecular weights, various functional groups, and various chemical linkages. This intrinsic heterogeneity is responsible for the lower mechanical performance of current lignin-based carbon fibers in comparison with petroleum-based carbon fibers (Li *et al.* 2017a).

The differences in structure between hardwood lignins and softwood lignins can affect the cross-linking ability of lignin and the spinning properties in the CF production process. The difficulties of spinning and thermal mobility of softwood kraft lignin are well-studied (Kadla *et al.* 2002; Norberg *et al.* 2013; Hosseinaei *et al.* 2016). In contrast, a condensed structure (C-C linkages) and unoccupied C5 sites in lignins with a high G content (grasses and softwood) result in faster thermostabilization and a reduction of CF production time (Norberg *et al.* 2013; Hosseinaei *et al.* 2016).

The main processing steps to produce carbon fiber include spinning, stabilization, carbonization, and sometimes graphitization. However, to use lignin as a precursor to carbon fiber, the lignin must undergo purification to attain less than 250 ppm ash in the final lignin product and pelletizing the lignin powder into pellets prior to the spinning process (Mainka *et al.* 2015).

Different methods of the spinning process have been investigated, focusing on the manufacture of lignin-based CFs, including both wet and dry spinning, melt-spinning, and electrospinning (Dallmeyer *et al.* 2010; Thunga *et al.* 2014; Zhang and Ogale 2014). During the oxidative stabilization, the main reactions in lignin are oxidative, caused by radicals (introduced by homolytic cleavage of the β-O-4' bond during heat treatment) and rearrangement reactions (Braun *et al.* 2005). During the carbonization step, the stabilized fiber is converted into a CF, through the elimination of all elements except carbon. The formation of the graphite structure of the lignin-based CF during this process was established by Mainka *et al.* (2015).

Alternatives have been developed to potentiate the CFs production from lignin, mainly related to the spinning process enhancement, *e.g.*, chemical modification through the esterification of lignin phenolic groups, hydrogenation, and phenolation, plasticizing lignin through blending with synthetic polymers, such as polyethylene oxide (PEO), polyethylene terephthalate (PET), PAN, and reinforcement with clay or carbon nanotubes (Sudo and Shimizu 1992; Sudo *et al.* 1993; Uraki *et al.* 2001; Kadla and Kubo 2004; Kubo and Kadla 2005; Sevastyanova *et al.* 2010; Thunga *et al.* 2014; Ding *et al.* 2016; Liu *et al.* 2016; Wang *et al.* 2016; Youe *et al.* 2016). Additionally, purification and fractionation are used to obtain lignin with high thermal mobility and improved melt-spinning performance.

To improve the homogeneity and reduce the complexity of lignin, fractionation techniques by an eluotropic series of organic solvents and precipitation by the pH effect are potential options; also, the use of membranes has been thoroughly studied (Brodin *et al.* 2009; Baker *et al.* 2012; Nordström *et al.* 2013; Wang and Chen 2013; Li and McDonald 2014; Duval *et al.* 2015; Kleinhans and Salmén 2016). These techniques allow lignin to be produced with more uniform molecular weights, thus improving the CF spinning ability and performance (Li and McDonald 2014; Duval *et al.* 2015).

Li *et al.* (2017) studied a new approach to fractionate and modify kraft lignin using an oxidation process to treat kraft lignin with laccase and a mediator. The process resulted in lignin fractions with different molecular weights, functional groups, and interunitary linkages. The insoluble fraction of the treated lignin was used with PAN (1:1 ratio) as the starting material for carbon fiber production. The results suggest that the spinnability was improved due to the better miscibility. The elastic modulus of lignin-PAN carbon fiber was similar to those of several commercial carbon fibers (PAN-CF).

Lignin as a Source of Fuels and Chemicals

Concepts of sustainability and a cleaner environment have encouraged research on replacing fossil fuels with renewable fuels. The development of the lignin-polymer platform in the pulp industry makes it a promising alternative to partially replace oil in the future (Laurichesse and Avérous 2014). Yet, the large-scale production of low-molecular-weight chemicals from lignin is still hindered by technological and economic challenges in relation to petrochemicals (Soile and Owoyokun 2014).

Due to the high molecular mass, complex structure, and heterogeneity of kraft lignin, its fragmentation is necessary to obtain renewable biofuels and chemicals (Aysu and Küsük 2014; Ragauskas *et al.* 2014). The main technologies used are thermochemical processes and biological processes (Gordobil Goñi 2018). Compared to thermochemical fragmentation routes, microbial degradation is expensive and requires an extended reaction period (Berlin and Balakshin 2014).

There are two different thermochemical approaches for the conversion of lignin into combustible fuels valorization of lignins: gasification for generating syngas followed by the subsequent conversion of syngas to Fischer-Tropsch synthetic fuels, synthetic alcohols, and hydrogen; and depolymerization to yield aromatics and hydrocarbons with molecular weights ranging from about 100 to 300 Da (Azadi *et al.* 2013).

The gasification process converts kraft lignin into a gas called syngas consisting of CO_2, CO, CH_4, H_2, and H_2S within a temperature range of 700 °C to 1000 °C (Gordobil Goñi 2018). Syngas is used to generate electricity, pure hydrogen, and synthetic liquid fuels and chemicals (Azadi *et al.* 2013). According to Huber *et al.* (2006), the Fischer-Tropsch (FT) method is used to convert syngas components (CO and H_2) to liquid transportation fuels by a chemical catalyst such as a metal (*e.g.,* Fe) in the reactor (Fig. 15). Conventional diesel, kerosene, and gasoline can be produced from hydrocarbons of different lengths formed during the FT process (Verma *et al.* 2016).

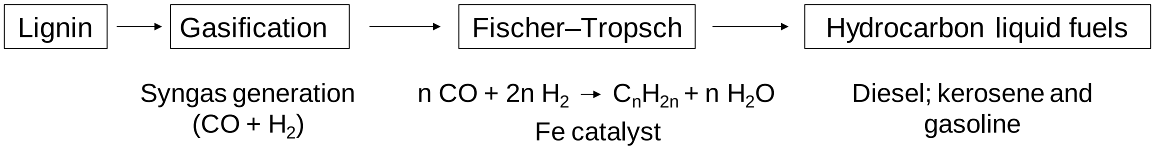

Fig. 15. Process to produce liquid fuels from lignin

A major challenge of using syngas is sulfur contamination by hydrogen sulfide (H_2S). These gases must be removed by means of intensive purification steps, adding to the cost of production. In addition, FT synthesis requires expensive catalysts, a fixed H_2/CO ratio, and extreme temperature and pressure conditions in the reactor (Verma *et al.* 2016).

The depolymerization process is used to convert the complex lignin compound into small molecules with low molecular weight, such as vanillin, unsubstituted and hydroxylated aromatics, aldehydes, aliphatic acids, *etc*. (Kim *et al.* 2015). Pyrolysis, catalytic hydrogenolysis, alkaline hydrolysis, solvent depolymerization, supercritical water, and alkaline oxidation are well-known depolymerization techniques (Pandey and Kim 2011; Azadi *et al.* 2013). According to Ponnusamy *et al.* (2019), the viability of lignin depolymerization depends on the depolymerization technique and the chemical composition of the technical lignin.

Among the depolymerization techniques can be mentioned the degradation by fungi and bacteria (microbial degradation), thermochemical depolymerization (base-catalyzed, acid catalyzed, metal catalyzed and, conventional pyrolysis of lignin) and electrochemical depolymerization of kraft lignin. All lignin degradation approaches are either expensive, consume more energy, or even produce toxic by-products, except for biological degradation. Then, it is a challenging process the controlled degradation of lignin into desired chemical compounds (Agarwal *et al.* 2018).

None of these processes will provide a high yield of monomers or high selectivity of the reaction products. However, lignin can be depolymerized into its aromatic monomer constituents (Azadi *et al.* 2013). These products can be blended into transportation fuels, given that aromatic hydrocarbons constitute approximately 35% to 50% of gasoline and 26% to 30% of diesel (Merker *et al.* 2011).

Regarding the use of kraft lignin for renewable chemicals, aromatic aldehydes such as vanillin (4-hydroxy-3-methoxybenzaldehyde) and syringaldehyde (4-hydroxy-3,5-dimethoxybenzaldehyde) are used as additives in foods, beverages, and pharmaceuticals (Pacek *et al.* 2013; Tarabanko and Tarabanko 2017). Currently, most of the vanillin is produced from petrochemical sources, but producing vanillin from kraft lignin is more environment-friendly and potentially economical than from guaiacol (Pinto *et al.* 2012).

Producing vanillin from kraft lignin faces challenges, such as having a low yield. This has been attributed to the difficulty purifying the vanillin products, mainly in hardwood, which contains less G-type lignin than softwood. In addition, lignin depolymerization has a high demand for energy, as well as high requirements for acids and organic solvents during the extraction process (Fache *et al.* 2016; Wongtanyawat *et al.* 2018).

The yield of aldehydes depends on the source of lignin, the condition of its isolation, and the condition of lignin oxidation (Tarabanko and Tarabanko 2017). In a study performed by Wang *et al.* (2018), three technical lignin samples were oxidized by alkaline nitrobenzene to evaluate their feedstock potential for vanillin production. They showed that the β-O-4 linkages in lignin affected its aldehyde yield. Kraft lignin showed a lower vanillin yield when compared to alkali lignin and sodium lignosulfonate.

Yoshikawa *et al.* (2013) performed an optimization of a two-step process to produce phenols from kraft lignin. First, lignin was depolymerized into liquid products with lower molecular weights using a H_2O/BuOH solution. Next, lignin catalytic cracking was carried out in the lignin-derived slurry liquid over ZrO_2-Al_2O_3-FeOX, and there was an increase in the total recovered fraction of phenols.

Lignin as Bioplastics and Coatings

A continuous increase in oil prices and an environmental concern with the use of common petroleum-based plastics has resulted in a growing interest in eco-friendly materials. Kraft lignin can be used as an additive or raw material to produce new plastics (Kun and Pukánszky 2017). Currently, the most common commercial thermoplastics used by the polymer industry for food packaging and bottles are polypropylene (PP), polyethylene (PE), polystyrene (PS), and polyethylene terephtalate (PET) (Gordobil Goñi 2018).

Lignin can be used in polymer-lignin blends (*e.g.*, plastics blends), as an ultraviolet and thermal stabilizer, and to improve the mechanical properties and processability (Stewart 2008; Doherty *et al.* 2011; Laurichesse and Avérous 2014). In addition, the phenolic structure inherent in lignin enables it to function as a free radical scavenging antioxidant in plastics, similar to the commercial phenol-based antioxidants (Egüés *et al.* 2012; Lu *et al.* 2012).

The depolymerization of kraft lignin is required for its use in polymers (*e.g.* polyethylene and polypropylene) because the unmodified lignin exhibits a large molecular mass as well as low reactivity and low compatibility with other polymers. This process has the potential of decreasing the molecular weight, reducing the hydrophilicity, increasing the phenolic content, and decreasing the aliphatic hydroxyl content of lignin (Kabir 2017). These characteristics increase the antioxidant activity of the lignin (Pan *et al.* 2006; Ugartondo *et al.* 2008).

In a study performed by Kabir (2017), the depolymerized kraft lignin presented more thermo-oxidative stability than unmodified species and used a 5% addition of kraft lignin as an antioxidant for polyethylene (PE) and polypropylene (PP). Additionally, the depolymerization improved the compatibility of the lignins with the non-polar polymer matrix by decreasing the aliphatic hydroxyl content and improving the hydrophobicity.

Chemical modification may be performed to achieve a uniform distribution of lignin with non-polar polymers in order to not affect the polymer's mechanical properties.

Esterification is often used as a chemical pre-treatment when manufacturing lignin-based polymers to reduce the polarity (Maldhure *et al.* 2011; Maldhure *et al.* 2012; Gao 2017). However, alkylation can be performed to decrease the number of hydroxyl groups responsible for lignin's polar character (Chen *et al.* 2011; Maldhure *et al.* 2012).

Acetylated softwood kraft lignin (ASKL) was used as filler in synthetic polymers (PE, PP, PS, and PET), and the acetylated lignin was more thermally-stable than the unmodified lignin (Jeong *et al.* 2012). The miscibility between ASKL and the synthetic polymers was favorable, reflecting positively on the tensile properties of ASKL and synthetic polymers. In another study, the properties of lignin-polyethylene blends were evaluated according to the raw material used (Dehne *et al.* 2016). Kraft lignin of hardwood and softwood were esterified and the results did not show any clear influence of the source of the raw material on mechanical properties. Despite this, the esterification of lignin turned out to be beneficial for the blend properties.

The use of kraft lignin is also being studied to improve biodegradable polymers. A known biodegradable thermoplastic is polylactic acid (PLA), which can be manufactured from renewable resources, and processed in conventional equipments by condensation of lactic acid or ring opening polymerization of lactide. It has desirable properties such as high strength and high stiffness, but it is too expensive to be widely used and possesses low thermal resistance and flexibility, which could be overcome by using lignin as an additive (Spiridon *et al.* 2015; Vila *et al.* 2016; Gao 2017). In a study performed by Spiridon *et al.* (2015), new bioplastics were obtained by melt compounding softwood kraft lignin (7%) with PLA. Adding lignin improved the thermal stability and the mechanical properties (elastic modulus and impact strength) of PLA. Gordobil Goñi *et al.* (2015) observed an increase in the thermal stability of PLA when kraft lignin is added; however, they recommend adding no more than 5% of lignin. Performing lignin chemical modification (acetylation) resulted in improving the compatibility with the PLA matrix, which was reflected in the observed mechanical properties.

For use in coating, kraft lignin needs to be depolymerized and/or chemically modified (Mulder *et al.* 2011; Gao 2017). An industrial softwood kraft lignin was used for coating in combination with PLA to improve the slow release of urea. The lignin was esterified for hydrophobicity development, which improved the water barrier property of the coating, thus increasing the efficiency of the nitrogen fertilizer (Li *et al.* 2017b). Additionally, the esterified kraft lignin is a potential material for sustainable coating applied to replace the conventional petroleum-based materials. According to Hult *et al.* (2013), kraft lignin can be used as a barrier in fiber-based packaging materials.

Softwood kraft lignin was used as polyurethane coatings (Griffini *et al.* 2015). Solvent extraction with MeTHF was used to improve the homogeneity of kraft lignin, and the MeTHF-soluble lignin fraction was used to polyurethane synthesis. The results showed that a viable strategy for the development of advanced lignin-based PU thermosetting systems can be obtained with the direct reaction of fractionated lignin with polyisocyanates. Besides that, the authors highlighted the potential of lignin-based thermoset PUs as sustainable bioderived materials for application in the field of high performance coatings and adhesives. Klein *et al.* (2018) considers the kraft lignin as a renewable resource for the production of bio-based polyurethane coatings for application in areas such as construction.

Hajirahimkhan *et al.* (2019) performed a reaction with kraft lignin and methacrylic anhydride in tetrahydrofuran solvent. They demonstrated that the obtained methacrylated lignin (ML) is curable in a UV-cured coating system with positive effects on the hydrophobicity, crosslinking percentage, and thermal stability of the coating system in which it was incorporated. Thus, the ML as an environmentally friendly UV-curable material for UV-cured coatings.

In addition to the necessary changes in kraft lignin, another challenge is the odor found in lignin-based composites, such as bioplastics, coating, binders, or adhesives because the characteristic odor can persist even when using pure lignin (Kalliola *et al.* 2012). The compounds that contribute to the scent are guaiacol and ethyl-guaiacol and not the sulfurous compounds (*i.e.*, dimethyl disulfide, dimethyl trisulfide, and dimethyl tetrasulfide). Softwood kraft lignin is primarily composed of G-type lignin, a potential source for guaiacol production, which is an important aromatic monomer in depolymerized lignin (Barton *et al.* 2018; Feng *et al.* 2019).

Therefore, the guaiacol must be removed from the lignin to be applied in situations that require a totally odorless material. Two pending patents have been developed to accomplish the removal of guaiacol: (1) the guaiacol removal treatment takes place during the lignin precipitation and washing process, removing approximately 60% of the compound, and (2) the washed lignin is treated, *i.e.*, after the lignin extraction and washing treatment; the latter approach is considered efficient due to the removal of approximately 97% of the guaiacol (Valmet 2017).

Lignin as Adhesives and Binders

The adhesives based on phenol-formaldehyde (PF) are used as a binder to produce wood-based composites such as plywood, laminated veneer lumber, glue-laminated timber, fiberboard, and particleboard (Malutan *et al.* 2007; Bertaud *et al.* 2012). Reacting phenol with formaldehyde is conducted in an alkaline medium, and the process conditions (*e.g.*, phenol-formaldehyde ratio, pH, time, and temperature) determine certain physical and chemical properties of the adhesives, such as viscosity and the overall mechanical properties of the final glued product (Xu *et al.* 2012; Ghorbani *et al.* 2016).

Due to the possible future scarcity of fossil resources and global environmental concerns, the consumption of synthetic adhesives needs to be reduced (Solt *et al.* 2018a). Due to its availability and low cost, kraft lignin is a potential source of bio-phenol to substitute as the petroleum-based phenol when manufacturing phenolic resins (Yang *et al.* 2019).

Currently, the use of kraft lignin in PF resins is limited in its commercial application because lignin has a lower reactivity with formaldehyde compared with phenol, and the lignin-phenol-formaldehyde requires higher curing temperatures (Siddiqui 2013). Chemical modifications in the complex structure of lignin to improve its reactivity for use as adhesives have been studied with moderate success, *e.g.*, phenolation and demethoxylation (Hu *et al.* 2011; Laurichesse and Avérous 2014; Ghorbani *et al.* 2018).

In addition, the technique of solvent fractionation to improve the lignin homogeneity was studied and resulted in resins of lower strength values compared with commercial PF resins (Solt *et al.* 2018b). Fractions with lower molecular mass are more reactive due to increased content of phenolic hydroxyl groups from the depolymerization of kraft lignin and reduced steric hindrance (Mahmood *et al.* 2013; Siddiqui 2013). However, fragments with a high molar mass have a better chance of contributing to polymerization (Tejado *et al.* 2007).

Despite the large variety of lignin's molar mass, the functional groups of different lignin raw materials can impair its applicability as a binder in adhesives. Unlike phenol, in which electrophilic aromatic substitution can take place at the *para* and the two *ortho* positions, many reactive sites of lignin’s aromatic ring are methoxylated or occupied by other groups, which impedes the reactions with formaldehyde (Hu *et al.* 2011; Ghorbani *et al.* 2016).

Another chemical property of lignin involved in polymerization reactions is the presence of hydroxyl groups (phenolic and aliphatic). According to Yang *et al.* (2019), because of activation of the aromatic ring in the *ortho* position, phenolic hydroxyl groups increase the reactivity of lignin with formaldehyde.

Hardwood lignin is less reactive than the softwood type because S-type lignin contains both *ortho* positions occupied by methoxyl groups. Ghorbani *et al.* (2016) substituted 20% of phenol with pine kraft lignin and the phenol-formaldehyde adhesive performed similarly. The G-type kraft lignin of pine is superior to the hardwood lignin with respect to phenol replacement due to its high molecular weight and high amount of activated free ring positions (Ghorbani *et al.* 2016).

Presently, a promising method to increase lignin’s applicability is the conversion of the polymer into smaller fragments through depolymerization. These fragments exhibit increased chemical reactivity because they are structurally similar to phenol (Cheng *et al.* 2013; Wang *et al.* 2013; Rößiger *et al.* 2018). Therefore, the depolymerized lignin is an interesting alternative to phenol substitution. In this case, higher substitution levels are achieved due to increased reactivity of the low-molecular-mass lignin fragments (Siddiqui *et al.* 2017; Solt *et al.* 2018a).

Pine kraft lignin was cracked using a base-catalyzed depolymerization process (250 bar, 320 °C, and 10 min) to obtain oligomeric lignin units (Solt *et al.* 2018a). The results demonstrated that the lignin oligomers can successfully replace phenol in PF resins at high substitution levels (up to 70%). No penalties were observed on the final dry or wet tensile shear strength, and the time of bond strength development was fully comparable with that of the PF reference at the 120 °C hot pressing temperature. However, the high viscosity of the lignin-phenol-formaldehyde (LPF) resin still poses a challenge for industrial applications.

In addition to the substitution of phenol to manufacture adhesives, lignin has been studied as binder material for eco-friendly Li-ion batteries. To assemble electrodes in Li-ion batteries, three components are employed: an active material, a conductive material, and a binder (the conventionally-used binding material is polyvinylidene fluoride (PVDF)) (Chen *et al.* 2003). Currently, it is essential to develop alternative binders that are non-fluorinated, less costly, and more environment-friendly (Lu *et al.* 2016; Nirmale *et al.* 2017).

The main study using lignin as a binding material for Li-ion battery electrodes was performed by Lu *et al.* (2016). A lignin pretreatment needs to be performed to remove the soluble, low-molecular-weight fractions of lignin. Electrodes based on pretreated lignin exhibit a relatively high specific capacity and a good stability, evidencing that lignin is a promising binding material for electrodes.

SUMMARY AND OUTLOOK

A steady increase in the interest of producing high value-added products from kraft lignin is evident based on the combination of a growing market, increasing environmental restrictions with the use of non-renewable fuels, and the economic return of the lignin biorefinery.

The potentials and opportunities of providing the pulp and paper industries with the capacity to act as a biorefinery based on lignin are being exhaustively studied. Kraft lignin can be used as lignosulfonates and dispersants, technical carbons (*e.g.,* carbon fibers), transportation fuels, bioplastics, and adhesives. For some end markets, however, specific lignin requirements and/or specifications are needed to reach the conditions set for the final product (*e.g.,* a water-soluble lignin is a prerequisite for producing lignosulfonates from kraft lignin).

In order to exploit different applications, challenges remain, especially in terms of the structure complexity, heterogeneous nature, and low reactivity of lignin. The lignin from different raw materials (hardwood, softwood, and grasses) is different, which may have a direct impact on the final product. In some cases, changes in the extraction process to reach a specific requirement may additionally be necessary to enable current pulp industries to act as lignin biorefineries and expand their commercial potential.

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Article submitted: February 20, 2019; Peer review completed: April 12, 2019; Revised version received: June 7, 2019; Accepted: June 8, 2019; Published: June 20, 2019.
DOI: 10.15376/biores.14.3.Demuner