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Strategies for Lignin Pretreatment, Decomposition and Modification: A Review

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Abstract

The dependency of chemical industry on nonrenewable sources of energy such as petroleum based carbon feedstock is rising dramatically day to day. Nonetheless, global warming caused by greenhouse gas emissions threatens the environment balance and the climate stability. Accordingly, it is necessary to find a renewable resource to decrease the environmental concern, specifically gaseous emissions from fossil fuels and to provide the energy stock. Outstanding to the significance of lignocellulosic biomass as most remedy to the current environmental issues and substituent of nonrenewable source of energy, this review affords understandings about the role of lignin as polymer and raw material for large molecules. In this review article, types of lignin with their extraction methods, fractionation technology to valuable chemicals, modification of the macromolecules to other polymers with tunable properties, and an extensive range of applications are discussed widely. The major valuable chemicals produced from lignin via chemical depolymerization are also summarized and illustrated with their molecular structures.

INTRODUCTION

The majority of chemicals used in chemical industry are derived from the relatively rational economically and readily available petroleum based carbon feedstock. The production of value added chemicals and materials from renewable resources (including waste) will be a major role in the future chemical industry (Appels & Dewil, 2012; Ahuja et al., 2017). The application of coal-based chemicals for energy production has the largest reserves compared with oil, gas and other fossil energy sources (Boumanchar et al., 2017; Zhang et al., 2016). Nevertheless, global warming caused by greenhouse gas emissions from fossil fuels threatens the environment balance and the climate stability. Therefore, it is mandatory to find a renewable resource for decreasing the environmental concern, specifically gaseous emissions from fossil fuels and providing the energy stock (Hu et al., 2017). Biomass, which is derived from distinct energy sources like wood, agricultural residues, food waste and industrial waste, is receiving worldwide attentions contributing to moderate amount of total energy consumption of the world and is considered as an alternative source of energy stock (Hrnčič et al., 2016). Moreover, due to low amount of gaseous molecules emission such as NO_x and SO_x, it is green and ecofriendly as it reduces the emission of greenhouse gases to the atmosphere. Therefore, biomass is the most sound carbon-based material obtained from living organisms such as plants, animals, and microorganisms (Chen et al., 2017; Shen et al., 2015). Conversion of biomass to valuable chemicals for chemical industry is an imperative development direction for biomass

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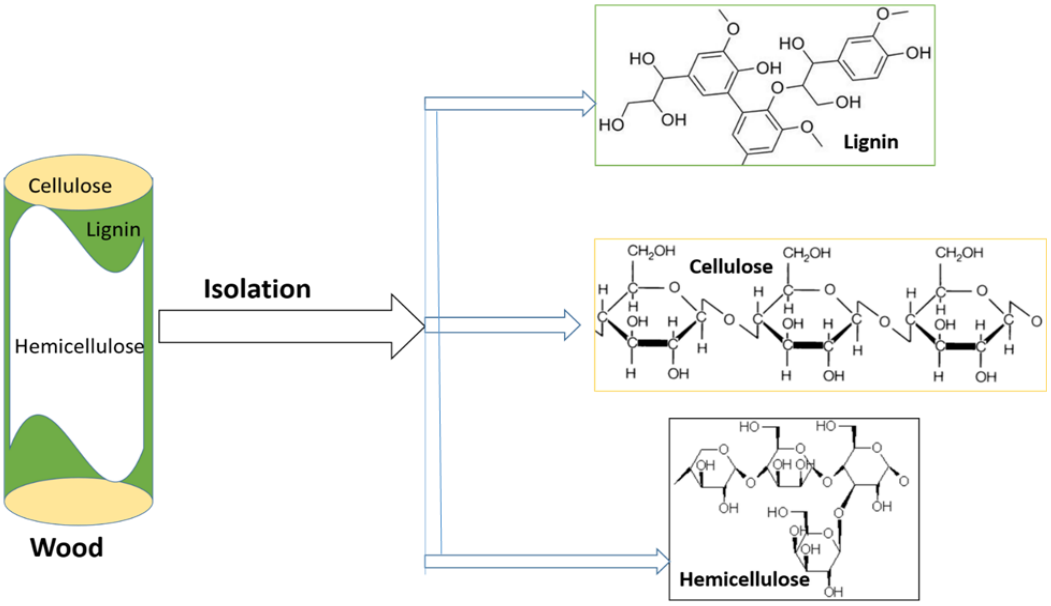


Figure 1. Schematic representation of the subcomponents in lignocellulosic material.

utilization, which has been attracting more attention of researchers (Uzun et al., 2017; Chen et al., 2016) .

Among biomasses, lignocellulose is the most common, which is principally obtained from plant sources and is composed of three major constituents: cellulose, hemicelluloses and lignin (Morgan, Jr et al., 2017). The transformation of these compounds to other chemicals relies on their structural characteristics. Structurally, lignocellulosic biomass is complex and requires advanced process to isolate and convert the polymer to other valuable chemicals (Yan et al., 2015). Lignin is a polymer of phenylpropanoid units connected via C-C or C-O linkages like β-O-4', 4-O-5', β-β', β-1', β-5', and 5-5' (Kang et al., 2012). Numerous extraction methods have been reported to separate lignin from cellulose and hemicellulose (Anugwom et al., 2017). Depending on the technique applied the properties and types of lignin obtained varies. The isolation processes can be catalyzed by enzymatic (Mayer & Staples, 2002), base (Jiang et al., 2016; Kassaye et al., 2017; Yang et al., 2017), acid (Si et al., 2015; Watkins et al., 2015), ionic liquids (Ma et al., 2016; Reis et al., 2017; Dong et al., 2015; Moghaddam et al., 2014; Tan et al., 2009), or processed in hydrothermal (Hrnčič et al., 2016) or supercritical solvents (Daza Serna et al., 2016). The availability of various linkages in lignin made it irregular in structure and resistant to microbial attack. The complexity and the strength of this biopolymer mark challenging the process of production of valuable chemicals (Kim et al., 2017). However, due to the fabulous applicability of chemicals obtained from lignin for medical, industrial and intermediates for other polymers like resins and pesticides, this area is attracting the attention of researchers (Kim et al., 2015). In this context, isolation techniques, chemical depolymerization and modification of lignin to other biodegradable polymers are briefly reviewed in this paper.

THE CHEMICAL COMPOSITION OF WOOD

Lignocellulose is a composite material synthesized by plant cells, consisting mainly of polymeric compounds cellulose and hemicelluloses (the carbohydrates) and lignin (the aromatic polymer) (Brandt et al., 2013). These polymers are the major components of the plant cell wall and commonly known to be adaptable starting materials for chemical modifications for further application (Mohtar et al., 2017). In addition to the carbohydrates and the aromatic polymer lignin, it is also contains smaller amounts of inorganic and organic compounds such as pectin, proteins, waxes and lipids, which also have potential value in biological and chemical industry. The chemical structures of the biopolymers is depicted in Figure 1.

Cellulose

Cellulose is the most plentiful renewable polymeric material in this planet (Taflick et al., 2017), and can be utilized in various applications such as paper, thin film, packaging, textile, sorbent, adhesive, building material, consumable and energy (Sobhana et al., 2017). Cellulose in lignocellulose is highly crystalline and made up of very long unbranched fibrils composed exclusively of glucose. Structurally the glucose is held together by hydrogen bonding and this property protects it from chemical and biological degradation (Fu et al., 2010). Hemicellulose such as xylan, xyloglucan and glucomannan, and pectin are very essential in synthesizing plant cellulose to control its structure (Basu et al., 2017). Pectin is described as an independent network, embedded in a load-bearing cellulose-hemicellulose network, with some structural proteins (Lopez-Sanchez et al., 2017). Cellulose is a high molecular weight linear polymer composed of D-anhydroglucopyranose units linked by β-(1-4)-glycosidic bonds (Xu et al., 2017).

Hemicellulose

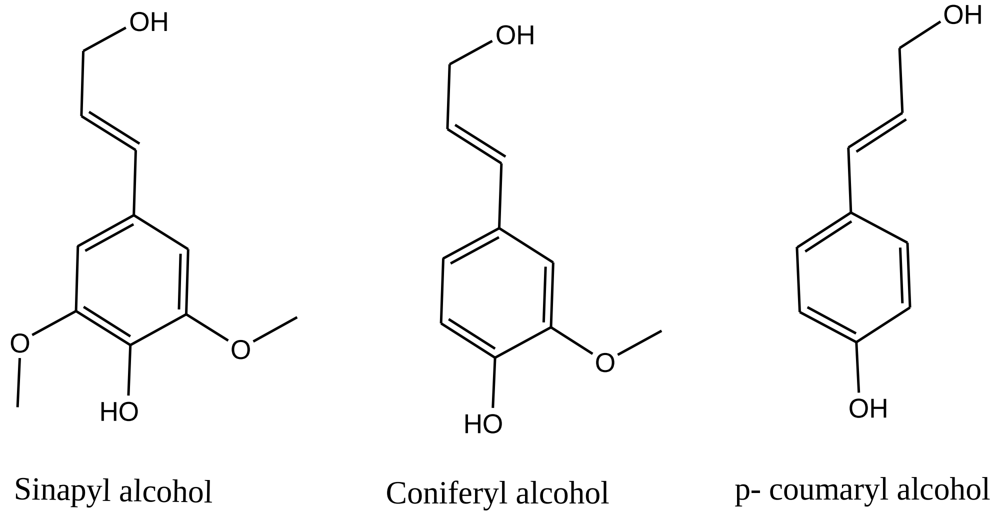
Hemicelluloses is the second abundant plant material following cellulose (Lin et al., 2017), representing about 30% of lignocellulosic biomass (Guan et al., 2016). It consists of short branched mono-saccharides of pentose (xylose, rhamnose and arabinose) and hexose (glucose, mannose, and galactose), and emerged as an immense renewable resource of biopolymers (Jung et al., 2015). Besides the monosaccharides, hemicellulose is a complex group of polysaccharides, such as xylan, glucuronoxylan, arabinoxylan, mannan, glucomannan and galactoglucomannan, which are hydrolysis products and have promising applications in the fields of chemical, food and pharmaceutical industries (Lin et al., 2017). These macromolecules were made up more than a quarter of the dry mass of cell walls in dicot plants (Zhao et al., 2017). In order to use hemicelluloses as novel biopolymers for functional biomaterials, chemical modification is necessary (Guan et al., 2016). Hemicellulose is a source of simple polysaccharides like xylan, the highly corrosion resistant material to oxidation and high temperatures and highly relevant in industrial coatings (Goldmann et al., 2017). Its modification also yields xylooligosaccharides that have various applications, especially in food industries as ingredients for functional foods (Palamae et al., 2017). Due to the compositional complexity of hemicellulose, the hydrolysis reaction is constituted of parallel paths that lead to a complex mixture of sugars (xylose, glucose, arabinose, and mannose) and organic acids, such as formic acid, acetic acid and levulinic acid (Li et al., 2016).

Lignin

Lignin is a complex, amorphous, branched polyphenolic macromolecule with aromatic polymeric structure (Ahuja et al., 2017; Ma et al., 2016; Chen et al., 2017), comprises roughly 20% of the total mass of the planet's biosphere (De Gregorio et al., 2016). In plants, the functions of lignin is to provide structural strength, closing the water-conducting system that links roots with leaves and shelter the plants against degradation (Behling et al., 2016). The protection against abiotic and biotic strains, especially pathogens and insects and conferring stability to xylem vessels for efficient water transport is also by lignin (Frei, 2013). Structurally, lignin is a polymer of heterogeneous phenyl-propanoid units (Feng et al., 2016) in vascular plants that is built arbitrarily by oxidative coupling between hydroxyphenyl (H), guaiacyl (G), and syringyl (S), which are derived from three corresponding monolignols: p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol as structurally depicted in Figure 2. Profiting from its unique polyphenolic structure in nature, lignin holds a significant potential to be transformed into lower molecular weight compounds such as phenols, aromatic acids, esters and some other compounds, which possesses high potential to replace the fossil resources (Chen et al., 2017). The phenolic compounds obtained from lignin are also used as key precursors in chemical industry for plastics, cosmetics, and pharmaceutics (Liu et al., 2016).

TYPES OF LIGNIN AND THEIR EXTRACTION METHODS

Numerous pretreatment processes have been proposed to separate each individual component from lignocellulosic materials (Angelini et al., 2017). Pulping is the major process to isolate lignin from cellulose and hemicellulose for producing pulp that is suitable to be used for pulp manufacturing (Zhao et al., 2013). The pulp and paper industry is the major manufacturer of commercial-grade lignin as a by-product of cellulose-rich material production. Depending on the process employed, the



Sinapyl alcohol Coniferyl alcohol p- coumaryl alcohol

Figure 2. Three phenylpropanoid units formed the bases of lignin structure.

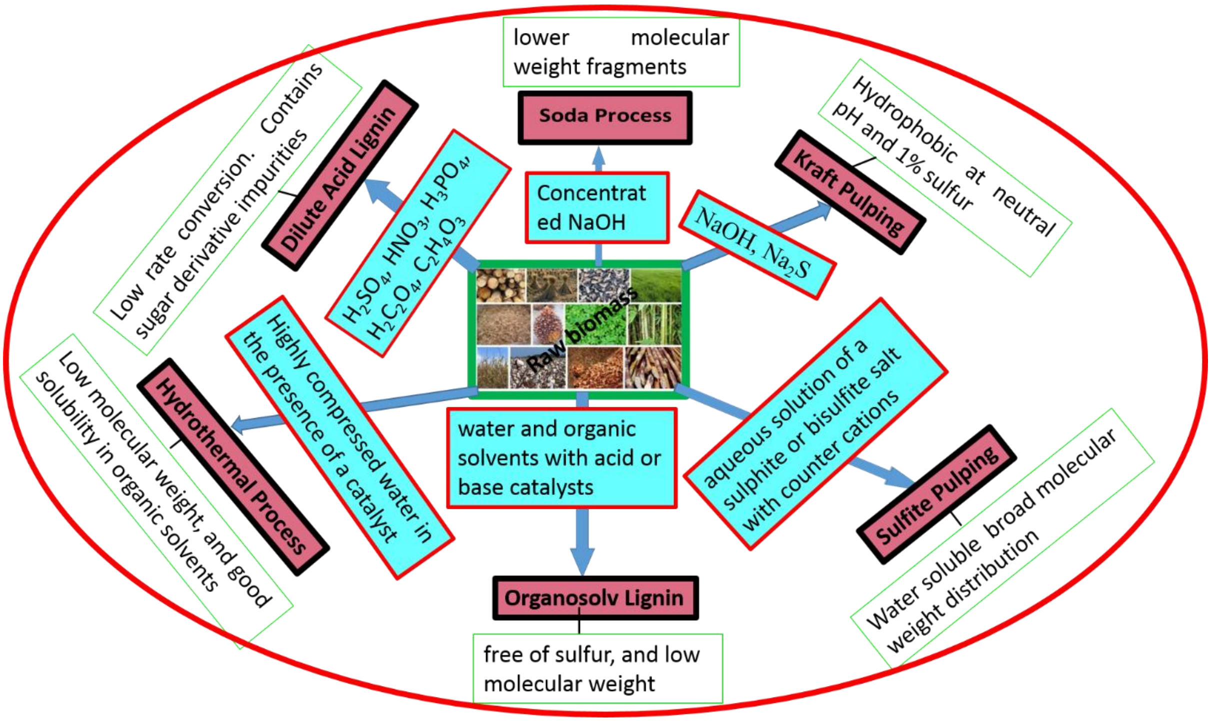


Figure 3. Chemical pretreatment and types of lignin

properties of the resulting isolated lignin differ. The chemistry and properties of lignin and materials derived from it also changed depending on the processing method. A number of methods have been developed for lignocellulose pretreatment. Some of them are under intensive investigation. Those methods can be classified as biological, chemical, physical, and thermal processes. Biological pretreatment, like use of fungi, offers the benefit of low chemical and energy use, but time taking process. Part of lignin could be removed from other biomass by producing digestible cellulose via passing hot water. But, the process is energy intensive and not suitable in sustainability aspects. As a result, chemical pretreatment is the most promising option and most of the techniques are summarized in Figure 3. Some of them are used at industry scale. It is reported that pretreatment process is mandatory for the disruption of lignocellulosic biomass to allow the reduction of the cellulose crystallinity, the increase of surface area, and the modification of lignin and hemicellulose structures during the process (Carneiro et al., 2017).

Sulfite Process

The sulfite process is the most popularly used and the process that produces high-grade cellulose pulp from wood chips by removing lignin and hemicellulose (Guo & Olsson, 2014). The process uses a heated aqueous solution of a sulphite or bisulfite salt with counter cations such as sodium, ammonium, magnesium, or calcium. To isolate lignin from this aqueous mixture, separation techniques like precipitation, ultrafiltration, chemical destruction of sugars, or alcohol fermentation of sugars followed by distillation of fermentation product could be carried out. Tarasov et al. (2017) stated that the amount of solvent used and the type of solvent have impact on the heating value of the precipitates.

Kraft Process

Kraft pulping process is one of the industrially applicable and that produces value for commercial purpose. The process is carried out by neutral sulfite semi-chemical pulping and pre-hydrolysis of pulping process of lignin (Fatehi et al., 2016). According to their study, the acidification of the process assists the formation of large particles in the spent liquors and to isolate lignosulfonate/lignin (with large molecular weights) and hemicelluloses from the spent liquors. The process is facilitated by addition of sodium hydroxide and sodium sulfide to the feedstock and the mixture is heated in a temperature range of 150 °C to 180 °C. Fernandez-Rodríguez et al. (2017b) reported that there is an environmental problem due to its non-uniform structure or the presence of organic and inorganic impurities obtained from this method. They also explained the difficulty of the valorization of the lignin extracted by kraft process (Fernandez-Rodríguez et al., 2017b).

Soda Process

Soda (alkaline) treatment is typically taken for non-wood-based biomass sources which is promising pretreatment technology to fractionate the lignocellulose and to rise the sugars availability. In this process, the fiber is added to an aqueous solution of sodium hydroxide, and is heated to approximately 160 °C. Some of the environmental problems caused by the sulfur used in the Kraft and sulfite process can be alleviated by this treatment (Fernández-Rodríguez et al., 2017b). To identify problematic stages in the production chain and to reduce their environmental impacts study of non-wood high quality specialty paper pulp manufacture was conducted by soda-anthraquinone cooking process (González-García et al., 2010). They concluded that chemical and electricity production are considerably the main factors for the environmental issue and the presence of anthraquinone improves the mechanical strength properties of the materials (Nasser et al., 2015).

Organosolv Process

Organosolv process is one of the most relevant methods, which is based on the solubilization of lignin using a mixture of different organic solvents and water as cooking liquor. It is also helpful in extracting highly homogeneous lignin, which enables its further valorization into value-added products. As a result, high lignin enriched liquor is obtained. In addition, this process enables the solvent recovery by distillation, allowing its reutilization as fresh liquor (Fernandez-Rodríguez et al., 2017b). This method utilizes an aqueous–organic solvent mixture, such as ethanol, acetone, methanol, or organic acids to isolate the biomass components. Relative to others pulping techniques, this process is ecofriendly, because no toxic sulfur chemical is used (Fernández-Rodríguez et al., 2017a). The steam explosion process involves highly compressed water, high pressure steam (100–400 psi) at temperatures from (130 to 300) °C, for (1 to 10) min, resulting significant removal of lignin from the biomass substrate (Chandra et al., 2016). Acid treatment of biomass feedstock is also a potential method for efficient hydrolysis of lignocellulose, in which dilute-acid such as sulfuric acid, nitric acid, hydrochloric acid, phosphoric acid, oxalic acid, peracetic acid was employed to produce sugars and others organic compounds (Miazek et al., 2017).

In addition to the methods discussed above, ionic liquids (ILs)-based processes for lignocellulosic materials treatment have been reported in many literatures (Zhang et al., 2016), but not yet scaled-up to industrial capacity and only utilized in the lab or in pilot plant reactor (Xu et al., 2014). Since ILs can dissolve lignocellulose, many investigations have been conducted using ILs for dissolution, fractionation, and pretreatment of biomass, with the major aim to achieve delignification of biomass. The ability of ILs to dissolve lignocellulose makes it possible to obtain the direct conversion of raw biomass under mild conditions without further processing. The ILs comprising of 1-butyl-3-methylimidazolium [Bmim], 1-ethyl-3-methylimidazolium [Emim], and 1-allyl-3-methylimidazolium [Amim] cations are generally categorized as distinct for extraction of lignin (Mohtar et al., 2017). The candidacy of these ionic liquids for dissolution of biomass to cellulose, hemicellulose and lignin depends on their ability to deform the linkages between components and the intermolecular interactions such as hydrogen bonding, dipole-dipole, and van der Waals interactions.

Li and co-workers (Li et al., 2015) reported that acid pretreatment of the raw wood species in IL [Amim][Cl] resulted in the complete hydrolysis of cellulose and hemicellulose. Other researchers (Moghaddam et al., 2014) also confirmed that lignin obtained from poplar wood and sugarcane bagasse by [Emim][Ac] and [Bmim][Cl] ionic liquids, respectively, had similar structural features to milled wood lignin. An et al. (2017) also proved that cholinium ILs are effective solvents to eliminate selectively lignin and xylan from lignocellulosic biomass. 1-Butyl-3-methylimidazolium chloride ([Bmim][Cl]) has the potentiality to dissolve cellulose capably without degradation of other component (Li et al., 2016). Beside the imidazolium-based ionic liquids, pyrrolidonium-based ionic liquids were used for pretreatment of corn stalk (Ma et al., 2016). The output depicted that, these ionic liquids provided conducive environment for lignin extraction and enzymatic hydrolysis for corn stalk.

Although numerous researchers (Weerachanchai & Lee, 2017; Badgujar & Bhanage, 2015) are focusing on the dissolution of woody and non woody biomass and converting to lignin, cellulose and hemicellulose by using ionic liquids as solvent and/or catalyst, this technology is still not applied to industrial scale due to some inherent limitations. The difficulties of the application of ionic liquids to lignocellulosic materials are: high cost of ionic liquids, high viscosity, and tedious recovery of ionic liquids from product mixtures. To overcome the cost and the viscosity concerns, ionic liquids are used by mixing with water or organic solvents. In economic point of view, the recyclability of ionic liquid is also an important issue. The studies on the recovery of ionic liquid from lignin solutions have been made by several research groups. Xu et al. (2017) have conducted research on pretreatment of eucalyptus with recycled ionic liquids for low-cost bio-refinery and finding that [Amim][Cl] and [Bmim][OAc] ionic liquids are better for the pretreatment and hydrolysis of eucalyptus. The hydrolysis yields of eucalyptus were still remained by recycled ILs pretreatment and no structural change was observed by using the recycled [Amim][Cl] ionic liquid, rather cellulose digestibility slightly decreased with increasing the recycle number of ILs. But the anionic structure of [Bmim][OAc] ionic liquid was destroyed after the 4th recycle. A flowchart for lignin extraction by ionic liquids from wood was proposed by the research groups of Kim et al. (2011) and Sun et al. (2009). Unfortunately, the precipitation of lignin from component by acids, bases, and/or organic compounds for the separation of lignin from ionic liquid is tedious and energy intensive. Therefore, to overcome the restrictions for processing biomass by ionic liquid, simplified and cost effective method should be designed and well-studied to make the method ready for industrial applications.

DEPOLYMERIZATION OF LIGNIN

Structurally lignin is comprised of phenylpropane monomers with a complex and recalcitrant chemical bonds. The irregularity of the structure makes it to resist microbial attack and assists the polysaccharide–protein matrix of plant cells to be safe from external disasters. The complexity and the strength of this biopolymer is emanated from the chemical bonds that linked the units together. Of the many, *β-O-4*-aryl ether bond is the most common one that links the monomers. Nonetheless, the chemical composition varies from species to species depending on the method of pretreatment applied during the process (Xu et al., 2014; Calvo-Flores & Dobado 2010; Pandey & Kim, 2011). Pandey& Kim (2011) reported that the amount of lignin and methoxyl group differs depending on the types of wood: hardwood to softwood or grasses. The proportion of major linkages in lignin present in hardwood and softwood is shown in Table1 and can be varied depending on the sources. The structures of the linkages are also presented in Figure 4.

Very recently, for the replacement of nonrenewable source energies by renewable one, the lignin degradation is receiving great attention. Due to the presence of various chemical bonds and

Table 1 Proportion of major linkages in lignin.

Linkages	Softwood (%)	Hardwood (%)
β-O-4-Aryl ether	43-50	50-65
α-O-4-Aryl ether	6-8	6-8
*4-O-5-Di*aryl ether	3.5-4	6.5
β-5-Phenylcoumaran	9-12	4-6
5-5-Biphenyl	10-25	4-6
*β-1-(1,2-Di*arylpropane)	3-7	5-7
β-β-Aryl ether	2-4	3-7
Others	13	5

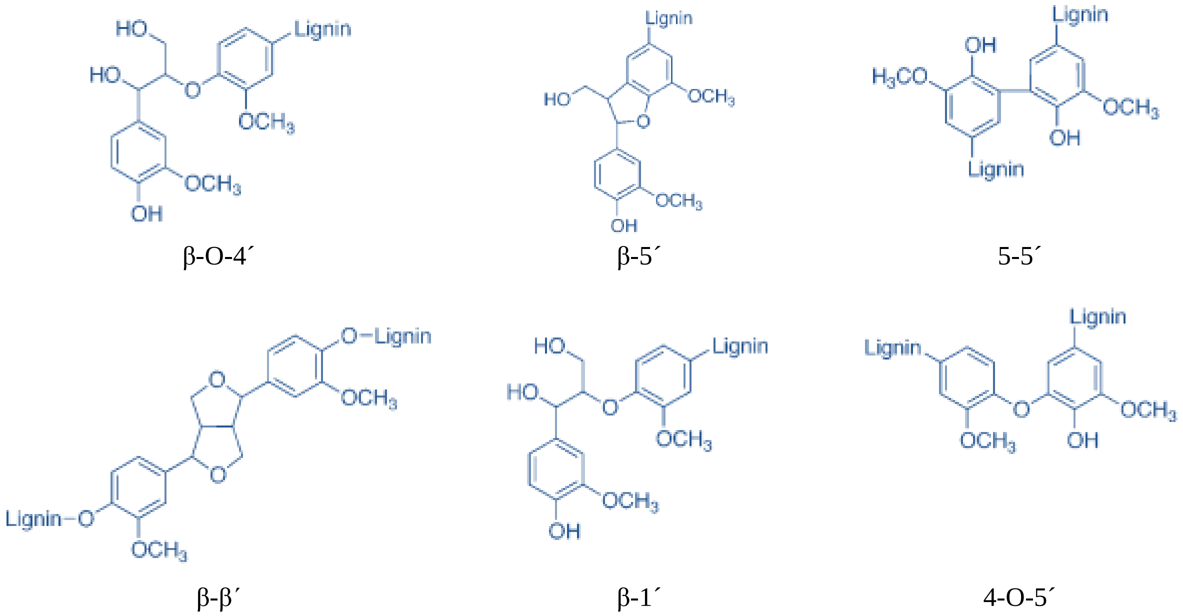


Figure 4. Structure of common linkages found in lignin.

the complexity of their arrangements, chemical or biological techniques may have subjected to convert it into other valuable chemicals.

Base-Catalyzed Lignin Depolymerization

Several studies have been conducted on base-catalyzed depolymerization (BCD) of lignin to valuable chemicals. It is believed that the most powerful factor facilitating lignin degradation is the concentration of the base (Erdocia et al., 2014). The role of the base is to polarize the ether bond that linked the monomers together followed by the cleavage (Fernández-Rodríguez et al., 2017a; Hidajat et al., 2017). Katahira et al. (2016) reported that BCD of lignin using basic media is effective when the process is practiced in relevant to the pulp and paper industry from pretreated lignin. In their study, sodium hydroxide at temperatures of 270, 300, and 330 °C for 40 min was applied to five lignin-rich substrates and 45–78% of the original lignin was depolymerized to value-added water-soluble species. They concluded that BCD is the best way to obtain a higher content of phenolic monomers. It is blamed that using alkali metal hydroxides, such as KOH, CsOH and LiOH, alone showed formation of char and tar (Long et al., 2015). To decrease the formation of char during the BCD, they suggested that hydrogenolysis of phenolic oligomer to more stable aliphatic alcohol could be a favorable technique. As an option, they introduced aliphatic alcohols like CH_3OH as a hydrogen donator with Ru/C as a catalyst and obtained valuable chemicals with a low residual solid. The role of using alcohols as a hydrogen donor is attributed to their low dielectric constant and can easily soften polymers specially lignin to yield oily products (Mahmood et al., 2015). Applying hydrolytic depolymerization of hydrolysis lignin (HL) in water–ethanol, ethanol as a co-solvent yield of 70.5% was achieved at 250 °C for 1 h in the presence of NaOH. Studying the effect of solvent on hydrothermal production of monophenolic compounds from lignin substantiated that the proportions of the co-solvent to water suppresses the demethoxylation monomers (Ouyang et al., 2016). In addition to the char and/or tar formation as by-product during the BCD of lignin, repolymerization reactions also noticed. To suppress the repolymerization, addition of various capping agents were reported (Toledano et al., 2014). To sum up, even though base mediated depolymerization of lignin is rapid, simple and produce valuable aromatic monomers, the repolymerization of the units, the formation of tar, char and harshness of the process have decreased its applicability.

Acid-Catalyzed Lignin Depolymerization

Alternatively, many studies have considered acids as catalysts for the fractionation of lignin to low molecular weight chemicals. Throughout the depolymerization of the macromolecule, more attention has been paid on cleavage of β-O-4 bond. The role of acids in the process was found to be a source of hydrogen for the formation of H_3O^+ on the ether bond or the aromatic ring that could make the bond weaker and easier for breakdown. Like the BCD of lignin, mineral acids mediated process is also a promising technique for high yields of phenolic monomers from lignin (Hidajat et al., 2017). Of mineral acids, concentrated sulfuric acid hydrolysis is popular for production of bio-fuels from biomass and applicable in large scale production. In Biofine process, dilute sulfuric acid is used at high temperature and yields a Biofine char having very high heating value (Davis et al., 2016). Mineral acids are strong enough to break the β-O-4 bond at high temperature, but, selectivity issue makes the process doubtful. For better selectivity Lewis acids, such as $NiCl_2$ and $FeCl_3$, was reported to initiate lignin depolymerization and then to produce catechols, guiacols, and syringols (Deepa & Dhepe, 2015).

Metal-Catalyzed Lignin Depolymerization

From selectivity point of view, Noble or transition metal catalysts, are getting more attention for fractionation of lignin. Kim et al. (2017) studied catalytic depolymerization of empty fruit bunch (EFB)-derived organosolv lignin on Hβ-supported Ru, and decided that relatively the use of acidic zeolites as supports of the metal catalysts improves the production of lower molecular weight aromatic compounds from lignin. As remedy to char formation during acid-catalyzed depolymerization of lignin, the role of mesoporous SBA-15 and its modified forms like Al-SBA-15 and Ni/Al-SBA-15 were reported. The porosity of these catalysts enables to decrease the possibility of repolymerization reaction which is supposed to occur during the process. The addition of metals like Al and Ni in mesoporous SBA-15 initiates the depolymerization process and improves the cleavage of β-O-4 bond (Chen et al., 2017). Ni-based catalyst shows a powerful hydrogenation process due to hydrogen-added activity and affordable price (Long et al., 2015). It is reported that during the heterogeneous acid-catalysts for cleavage of the ether bonds, the acidity and pore size are the main factors to influence the efficiency of the process. Wu et al. (2016) stated that besides the acidity and pore size of the catalyst, the nature of the co-solvent also determines the quality and quantity of the result. To verify the effect of co-solvents on the efficiency of depolymerization of organosolv lignin over silica-alumina catalysts, study was conducted in the presence of methanol, ethanol and isopropanol over the catalyst. The least result was observed in the process carried out in isopropanol due to bulkiness of the solvent that hinders the fractionation process sterically. High yields of lower molecular weight aromatic compounds were obtained in the cases of using methanol and ethanol. As a result, they concluded that the generation of proton from the co-solvent alone could not be the guarantee for the success of the depolymerization. To prevent the char formation or repolymerization of the oligomers or monomers, the use of additives like boric acid and phenol has been widely considered (Güvenatam et al., 2016). It is described that the presence of phenol makes the reaction homogeneous and as a result the char formation is stuck at the reaction conditions and prevents the repolymerization reactions, which leads to char being formed.

Supercritical Fluid Assisted Lignin Depolymerization

In addition to depolymerization by single method: acid-catalyzed or base-catalyzed alone, the application of one of the methods in near or supercritical solvent is widely investigated. Hidajat et al. (2017) studied on the fractionation of lignin in subcritical water and supercritical methanol at 330 °C with a low concentration of NaOH, KOH, and Na_2CO_3. The results revealed that solvents effect showed grand variation in efficiency of the product. Water is by far better than methanol for the base-catalyzed reaction. In the case of methanol mediated depolymerization, considerable solid formation was observed. The roles of metal oxides in supercritical solvents to degrade the ether bonds of lignin are also examined. Specifically, the study of Cu−Mg−Al mixed oxide catalyst for lignin depolymerization process indicates that the Lewis acid sites enhance the process due to the existence of the metals catalyze C- and O-alkylation reactions (Huang et al., 2015). The alkylation reaction depresses the repolymerization of the phenolic fragments and favors the formation of substantial products. Compared with the other depolymerization techniques, solid-acid or supercritical solvents assisted process is fabulous in producing low molecular weight aromatic chemicals. Nonetheless, the process requires very high temperature and undesired by-products like coke, char, and gases are formed leading to the process harsh and challenging in the separation of products (Ma et al., 2017).

Ionic Liquid Assisted Lignin Depolymerization

To improve the constraints in acid-base catalyzed depolymerization, the use of greener solvents, such as ionic liquids, are under consideration for the treatment of lignocellulosic biomass (Anugwom et al., 2017; Liu et al., 2016; Badgujar & Bhanage 2015; Cox & Ekerdt 2012; Hart et al., 2015; Vancov et al., 2012; Singh & Dhepe, 2016). Due to structural complexing of lignin, the role of ionic liquids on hydrolyzing the C-O linkages, model compounds were designated (Cox et al., 2011). They have examined the effect of nature of ionic liquids on the degradation of guaiacylglycerol-β-guaiacyl ether and veratrylglycerol-β-guaiacyl ether as lignin model compounds. The results show that the acidity of the ILs are the determinant factor for the efficiency of the process. The breaking of the β-O-4 ether bond of lignin model compounds have been done successful in ionic liquids having high acidic property. Scale-upping from lignin model compound to lignin, Cox and Ekerdt (2012) found that effective degradation of alkyl–aryl ether linkages was achieved by using acidic [Hmim][Cl]. The authors reported that the temperature of the experimental condition played an important role in kinetics of the reaction. Moreover, before lignin degradation, the solubility of the polymer in the media should also be considered. The effect of structure of ionic liquid on lignin dissolution was studied (Hart et al., 2015), they suggested that the interactions of the solute with the cation and the anion of ionic liquids determined the progress of the process. Usually, it is reported that the cations such as ammonium, phosphonium and pyrrolidinium of ILs have strong interactions with lignin and suitable for its dissolution (Glas et al., 2015). In addition to the cations of ionic liquids, the anions seemed to play a vital role in a liquefying the biomass (To et al., 2017). Specially, chloride, carboxylates, phosphates, phosphonates and amino acid are the favorable anions of ionic liquid for lignin dissolution. The ability of these anions emanated from their interactions with the biomass, specifically the hydrogen bonding between the molecules (Badgujar & Bhanage, 2015).

Nevertheless, ILs are unaffordable and high in viscosity relative to conventional organic solvents. Using an IL–solvent mixture is a potential technology to overcome this drawback (Wang et al., 2014). Sun et al. (2013) examined the fractionation of lignin in an aqueous solution of the ionic liquid 1-ethyl-3-methylimidazolium acetate [C_2mim][OAc] and they obtained lower molecular weight aromatic compounds at milder reaction conditions. Other researchers also studied the role of aqueous IL solutions of [C_2mim][OAc] in solubilizing and fractionating lignin to valuable monomers (Shi et al., 2017). The study showed that aqueous IL solutions of [C_2mim] [OAc] assisted process provided approximately the same result as that achieved in pure IL. Furthermore, lignin has π bond in its aromatic moiety and ILs show π-π interaction with lignin. The interaction increases the difficulty of recycling or separating the constituent components. Consequently, further investigation must be addressed to scale-up this technology to industrial stage. A summary of various techniques applicable for degradation of lignin to valuable chemicals is given in Table 2. The experimental conditions and catalyst to be used are also tabulated. The chemical structures of the major low-molecular weight aromatic compounds obtained from chemical depolymerization of lignin are also depicted in Figure 5.

Table 2 Summary of catalyst-assisted lignin depolymerization.

Raw material	Catalyst	Conditions	Yield (%)	Reference
Organosolv lignin	HOTf	175 °C, 2 h	10.6	Jastrzebski et al. (2016)
Organosolv lignin	$Yb(OTf)_3$	175 °C, 2 h	11.4	Jastrzebski et al. (2016)
Organosolv lignin	$Sc(OTf)_3$	175 °C, 2 h	9.5	Jastrzebski et al. (2016)
Organosolv lignin	$In(OTf)_3$	175 °C, 2 h	9.7	Jastrzebski et al. (2016)
Organosolv lignin	$Ga(OTf)_3$	175 °C, 2 h	9.4	Jastrzebski et al. (2016)
Hydrolysis lignin	H_2SO_4	250 °C, 1 h	87	Mahmood et al. (2015)
Enzymatic lignin	$AlCl_3$	140–180 °C, 1 h	-	Shen et al. (2016)
Alkali lignin	$Cr(NO_3)_3$	4 MPa H_2, 260 °C, 5 h	1.3	Shu et al. (2015)
Alkali lignin	H_2SO_4	4 MPa H_2, 260 °C, 5 h	0.7	Shu et al. (2015)
Alkali lignin	HCl	4 MPa H_2, 260 °C, 5 h	0.9	Shu et al. (2015)
Alkali lignin	$CrCl_3$	4 MPa H_2, 260 °C, 5 h	3.2	Shu et al. (2015)
Organosolv lignin	H-Y Zeolite	250 °C, 1 h	92.58	Wanmolee et al. (2016)
Organosolv lignin	Ni/Al-SBA-15	300 °C for 4 h	21.90	Chen et al. (2017)
Organosolv lignin	5 wt% Ru/Al_2O_3	225 °C, 40 bar, 6 h	3.4	Kim et al. (2017)
Organosolv lignin	5 wt% Pt/HZSM-5	225 °C, 40 bar, 6 h	13.0	Kim et al. (2017)
Organosolv lignin	20 wt% Cu/HZSM-5	225 °C, 40 bar, 6 h	7.1	Kim et al. (2017)
Organosolv lignin	NaOH	300 °C, 80 min	18.48	Erdocia et al. (2014)
Kraft lignin	NaOH	270 - 330 °C, 40 min	45−78	Katahira et al. (2016)
Organosolv lignin	NaOH, Ru/C	260 °C, 4 MPa, 4 h	92.5	Long et al. (2015)
Alkali lignin	$CuO/Fe_2(SO_4)_3/NaOH$	150 °C, 60 min	17.92	Ouyang et al. (2016)
Organosolv	NaOH, H_3BO_3	300 °C for 40 min	-	Toledano et al. (2014)
Oak wood lignin	HMIMCl	110–150 °C,	-	Cox and Ekerdt (2012)
Organosolv lignin	[Emim][ABS]	180 °C, 6 h	-	Nanayakkara et al. (2014)
Klason lignin	[Bmim][$MeSO_4$]	180 °C, 6 h	-	Nanayakkara et al. (2014)
Organosolv lignin	[Bmim][$MeSO_4$]	180 °C, 6 h	-	Nanayakkara et al. (2014)
Klason lignin	[Emim][ABS]	180 °C, 6 h	-	Nanayakkara et al. (2014)
Alkali lignin	[C2mim][OAc]	110–170 °C, 1–16 h	-	Wen et al.. (2014)
Enzymatic lignin	[C4mim]Cl	150 °C, 3 h	-	Yan et al. (2015)
Soda lignin	Ethanol, $Al(OTf)_3$	400 °C, 4 h	11	Güvenatam et al. (2016)
Kraft lignin	$SubH_2O$-NaOH	330 °C, 30 min	21.5	Hidajat et al. (2017)
Organosolv lignin	Supercritical ethanol	350 °C, 3 MPa, H_2, 40 min		Kim et al. (2013)
Organosolv lignin	Supercritical t-BuOH, 5 wt.% Pd/C	350 °C, 3 MPa, H_2		Kim et al. (2015)
Organosolv lignin	Supercritical ethanol	350 °C for 40 min, 3 MPa, H_2	73	Park et al. (2016)
Kraft lignin	Subcritical methanol, HZSM-5	220 °C, 15 h	39.3	Singh et al. (2016)
Alkali lignin	Supercritical water	400 °C, 240 min		Wahyudiono et al. (2008)

CHEMICAL MODIFICATION OF LIGNIN

At the present time, the majority of materials to be used in our daily life are polymers. Specifically, most of plastic resources are derived from nonrenewable sources (Gordobil et al., 2016). For the continuity of the resource to fulfil our demand, it is mandatory to develop new bio-based materials. The materials to be designed need to have lower weight, heat and water resistance, durability and toughness (Graichen et al., 2017). Beside the properties of the polymer, the raw materials should be environmentally friendly, locally available, affordable and renewable. Accordingly, lignocellulosic biomass is a promising candidate for the required polymer as raw material. Of the lignocellulosic biomass, lignin is the most abundant biomass on the world next to

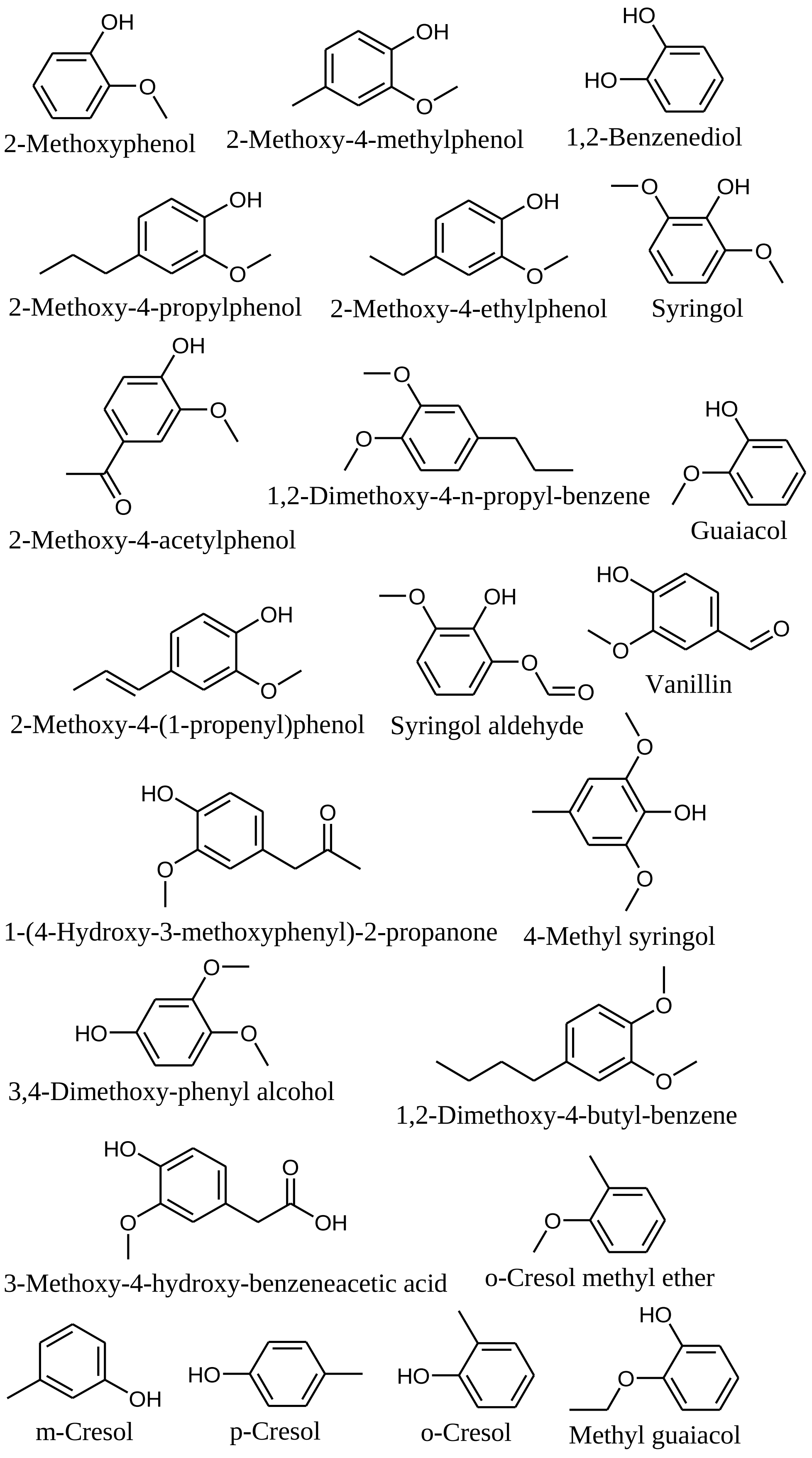
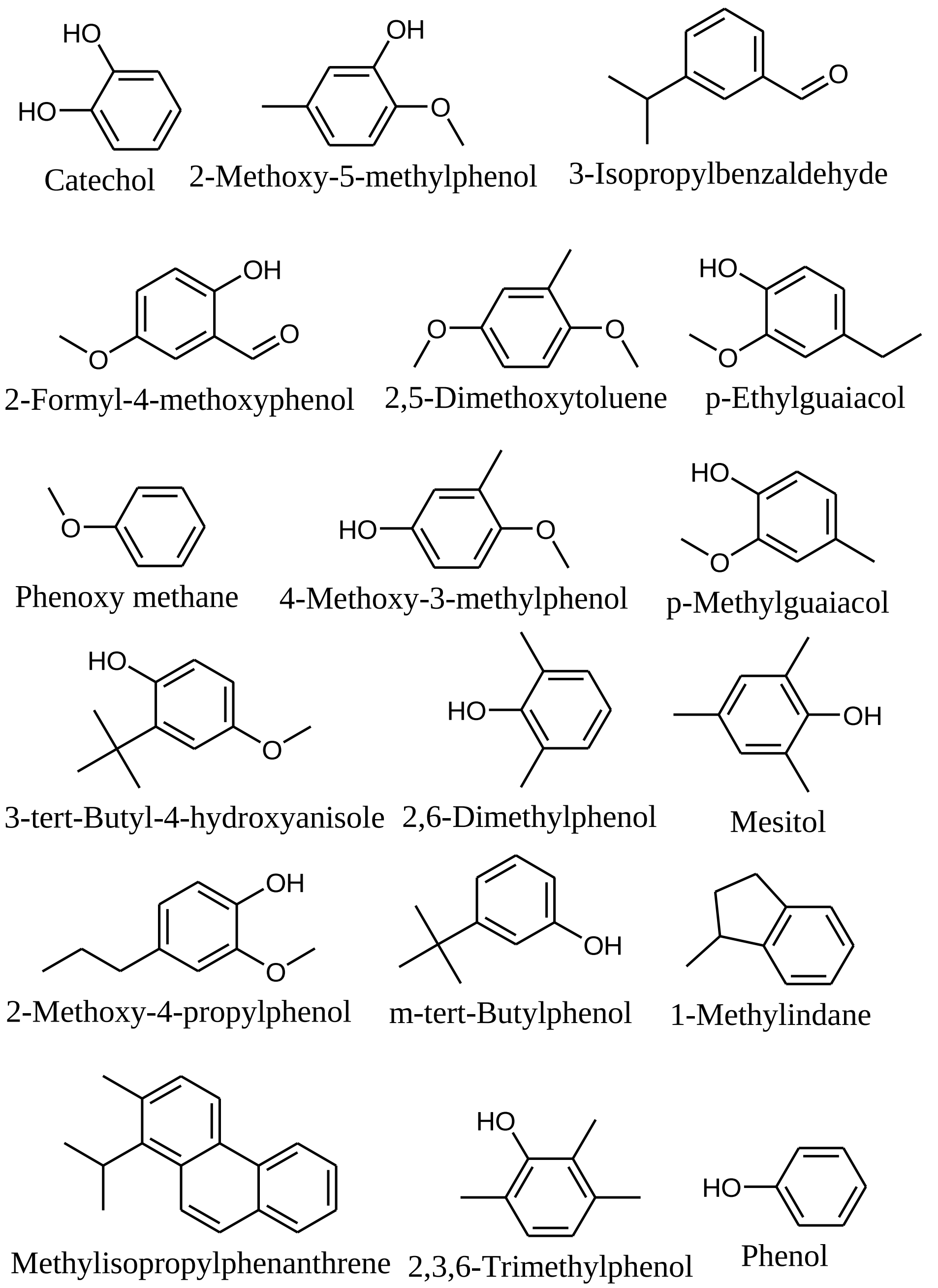


Figure 5. Chemical structures of the major valuable chemicals produced from depolymerization of lignin.



Catechol
2-Methoxy-5-methylphenol
3-Isopropylbenzaldehyde
2-Formyl-4-methoxyphenol
2,5-Dimethoxytoluene
p-Ethylguaiacol
Phenoxy methane
4-Methoxy-3-methylphenol
p-Methylguaiacol
3-tert-Butyl-4-hydroxyanisole
2,6-Dimethylphenol
Mesitol
2-Methoxy-4-propylphenol
m-tert-Butylphenol
1-Methylindane
Methylisopropylphenanthrene
2,3,6-Trimethylphenol
Phenol

Figure 5. Chemical structures of the major valuable chemicals produced from depolymerization of lignin (cont.)

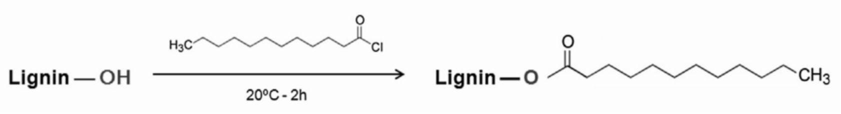


Figure 6. General scheme of esterified lignin synthesis (Gordobil *et al.*, 2017).

cellulose and hemicellulose (Kun & Pukánszky 2017; Mahmood et al., 2016; Naron et al., 2017). Structurally lignin has various functional groups such as hydroxyl, methoxyl, carbonyl, and carboxyl, and can be easily modified to any required polymer (Naseem et al., 2016). Of these functional groups the hydroxyl groups are the utmost typical functional groups in lignin and can act as a nucleophile to react with electrophilic moieties like acidic compounds, acid anhydrides, and acid chlorides to form ester linkages. Esterification of the lignin reduces the number of hydrogen bonding as a result the glass transition of the material could be decreased and its thermoplasticity increased (Gordobil et al., 2017). The general scheme of lignin esterification is presented in Figure 6. Moreover, adding lignin to some polymers like polyolefin assists the material to have a modified properties, including surface properties, thermal resistance, and biodegradability being as filler (Gordobil et al., 2015).

It is reported that the presence of hydroxyl groups in lignin enables it to form urethane linkage in polyurethane (Gómez-Fernández et al., 2017). The authors stated that lignin acts as an additive in the polymer and can replace the main reactive material required for polyurethane foams. Spiridon et al. (2015) also added lignin to other polymers like poly-(lactic acid) to enhance their thermal and mechanical stability. Duval & Lawoko (2014) claimed that the lignin hydroxyl groups has the tendency to initiate the ring opening polymerization of epoxide, ε-caprolactone, and lactide to synthesize lignin derived copolymers as shown in Figure 7.

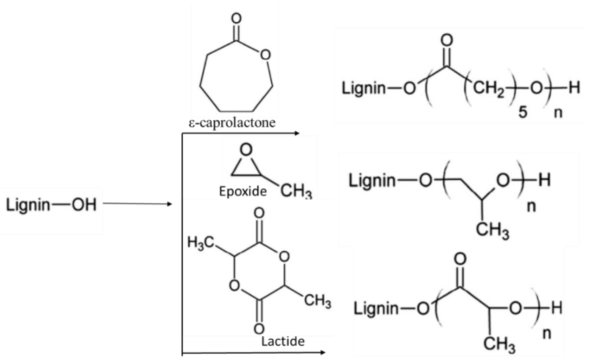


Figure 7. Ring opening polymerization initiated by lignin hydroxyls to synthesize lignin graft copolymers.

In addition to modifying lignin for specific application, it can be adapted to introduce another reactive species. The introduced reactive functional group on lignin will make it ready for further polymerization reaction allowing it to be chemically active. Gordobil and coworkers (Gordobil et al., 2016) synthesized methacrylic derivatives from methacryloyl chloride and lignin as depicted in Figure 8.

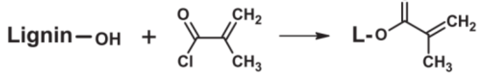


Figure 8. Reaction scheme of introducing vinyl groups in lignin.

The chemically activated lignin is macroinitiators to prepare lignin-based nanocomposites via atom transfer radical polymerization (ATRP) synthetic routes (Hilburg et al., 2014). The authors described that the polymerization process is facilitated by the lignin macroinitiators. The synthetic paths of poly (methyl methacrylate) (PMMA) and polystyrene grafted lignin is presented in Figure 9. From the study of property characterization, they concluded that the synthesized materials have higher thermal and chemical stability relative to homopolymers. The synthesized polymer is a triblock copolymer in nature and which can be used as a compatibilizer for another composites like polyethylene (Sailaja & Deepthi, 2010).

For processing and further characterization of polymer, its solubility in organic solvent is challenging. Studies have identified that the solubility problem appearing in polymers can be improved by converting the material to highly branched polymers. Highly branched polymers will decrease gelation through partial transformation of the functional groups. Sivasankarapillai and McDonald (2011) synthesized a highly branched poly(ester-amine) (HBPEA) from dicarboxylic acid, lignin, and 1,1,1-triethanolamine as shown in Figure 10. The synthesized polymer can be used as an additive to other polymers to increase toughness. After characterization of the highly branched poly(ester-amine), its high functionality and low viscosity properties were confirmed.

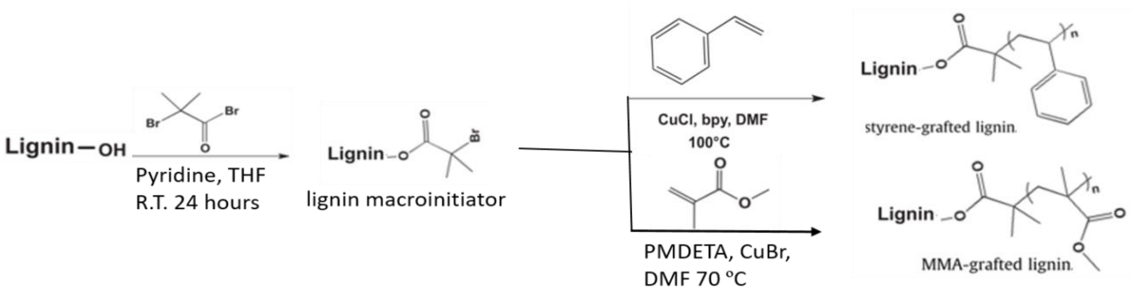


Figure 9. Synthesis of poly (methyl methacrylate) (PMMA) and polystyrene grafted lignin.

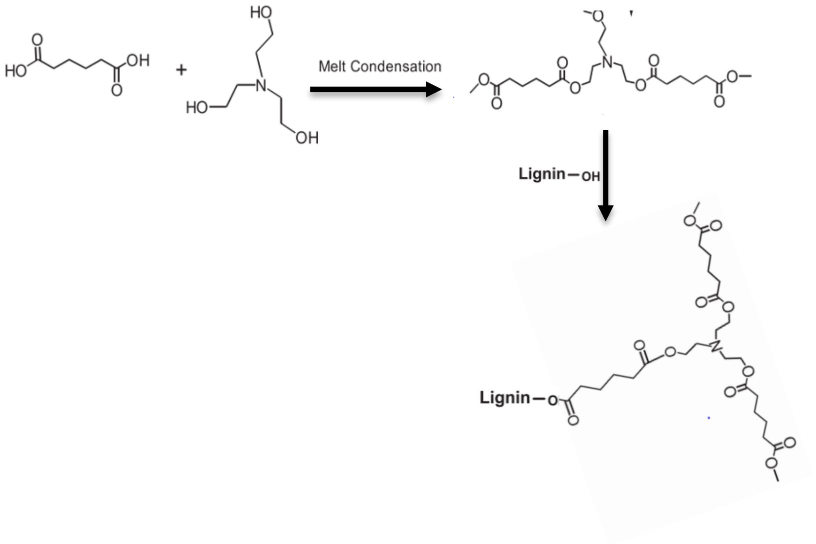


Figure 10. Reaction routes of synthesis of HBPEA

CONCLUDING REMARKS

Currently grand amount of lignin is produced worldwide. However, few amount is applicable for further applications such as additives, dispersants, binders, or surfactants. The remaining part is burn and cause environmental problem. Due to the environmental issues, extraction of lignin from agricultural wastes and other biomass is the main remedy to the problem. The dependency of our energy source on non-renewable chemicals is increasing day to day. Considering lignin as a raw material for aromatic compounds proves a dual functionality of the polymer. As result researchers from various disciplines have been focusing on manufacture of chemicals and bio-based polymers from lignin eco-friendly. Chemical fractionation of the lignin macromolecule yields high value aromatic compounds, which are applicable to medical and material. Plastic resources used for our daily activities are derived from nonrenewable sources. Therefore, the conversion of lignin to lignin-based polymers and composites is a vital technique to increase the access of plastic polymers. The lignin-based materials have higher thermal and chemical stability and shows better surface properties, thermal resistance, and biodegradability relative to homopolymers. This aromatic biopolymer produces versatile materials having tunable properties and an extensive range of applications. Generally, lignin is especial biopolymer for renewable aromatic ingredients and capable from economic and environmental point of views.

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