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Depolymerization and Activation of Lignin: Current State of Knowledge and Perspectives

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Abstract

A very important topic in present-day research is the depolymerization of lignin, meaning the multi-parametric decomposition of the biopolymer into low-molecular-weight products (monomers) by breaking of the intermolecular bonds. Depolymerization can occur under many different factors, such as high temperature or catalysts, which determine the mechanism of disintegration. In the case of lignin, this process is carried out in order to obtain many valuable low-molecular-weight compounds. It is becoming more and more popular as a result of the use of ionic liquids, but methods using alkaline, acidic, and metallic catalysts, as well as pyrolysis and supercritical fluids, are also known. All of these methods will be described in detail in this chapter.

Keywords: biopolymers, lignin, depolymerization, ionic liquids, modification

1. Introduction

Pro-ecological technologies for the production of activated, functional products with unique properties are being vigorously developed in the field known as green chemistry. Of particular significance is the production of novel materials based on polymers of natural origin, such as lignin and its derivatives.

Lignin is a byproduct in the paper and pulp industry and has been mostly used as a fuel to provide energy for technological processes. This biopolymer is a main source for the production of biofillers. It can also be used as an effective sorbent of organic compounds and hazardous metal ions, as a polymer filler, in the synthesis of polyethers, polyurethanes and epoxy

resins, and as a component of abrasive tools. Lignin can be applied in its untreated state. However, to fully exploit its properties, its natural conformation has to be improved through certain structural modifications, which will be described in this chapter.

Activation of lignin is carried out to modify functional groups while leaving the aromatic base of the polymer intact. Originally, lignin was subjected to oxidation to better understand its structure and to identify its bonds. At present, it is known that the use of strong oxidants breaks up the aromatic ring of the polymer, whereas using milder ones changes only its functional groups. The lignin surface contains many hydroxyl groups, which can be oxidized to carbonyl groups. These functional groups are more reactive than the hydroxyl groups and hence the resulting compound can offer more potential applications, including in electrochemistry.

2. Lignin – an overview

There is an ever increasing importance to polymers of natural origin. They are widely used in many branches of science and industry, chiefly because of their distinctive or unique properties and their renewability. Of particular interest are materials obtained from biomass, broadly defined. These include lignin and its derivatives.

Lignin is a biopolymer that occurs in the cell walls of plants. It enables plants to retain rigidity, mechanical strength and integrity between the other natural polymers contained in the basic plant cell: cellulose and hemicellulose [1]. Depending on the species of tree, lignin may account for between 20 and 30% of the total mass of wood (lower values in tropical and subtropical hardwoods, and higher in softwood from conifers) [1]. It is estimated that lignin is the source of approximately 30% of the organic carbon occurring in nature [2].

Lignin has a complex structure, which is still not completely understood, and is thus currently the subject of intense research efforts among a large group of scientists. It is known that the basic monomers making up the structure of the biopolymer include *p*-coumaryl, coniferyl, and sinapyl alcohols, generally called monolignols (see **Figure 1**), which link together in an unsystematic manner [1–3]. The content of particular monolignols varies depending on the type of wood.

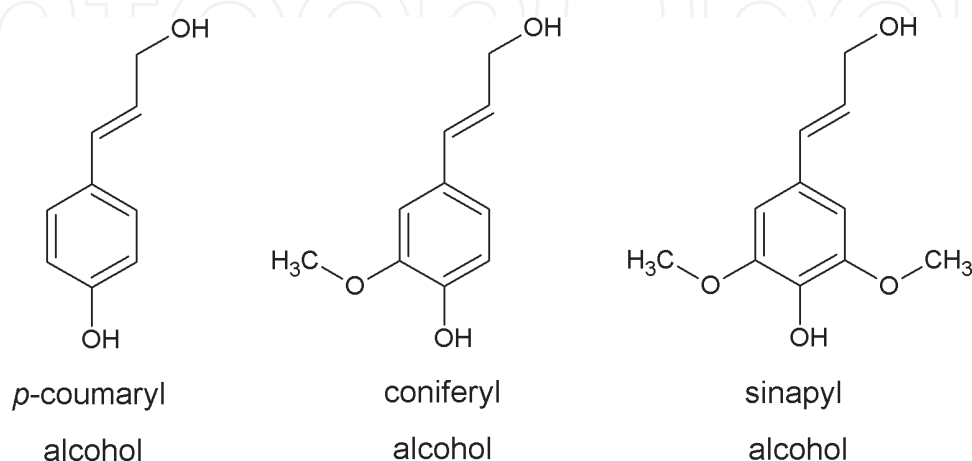


Figure 1. Basic monomers making up the structure of the biopolymer, based on [1–3].

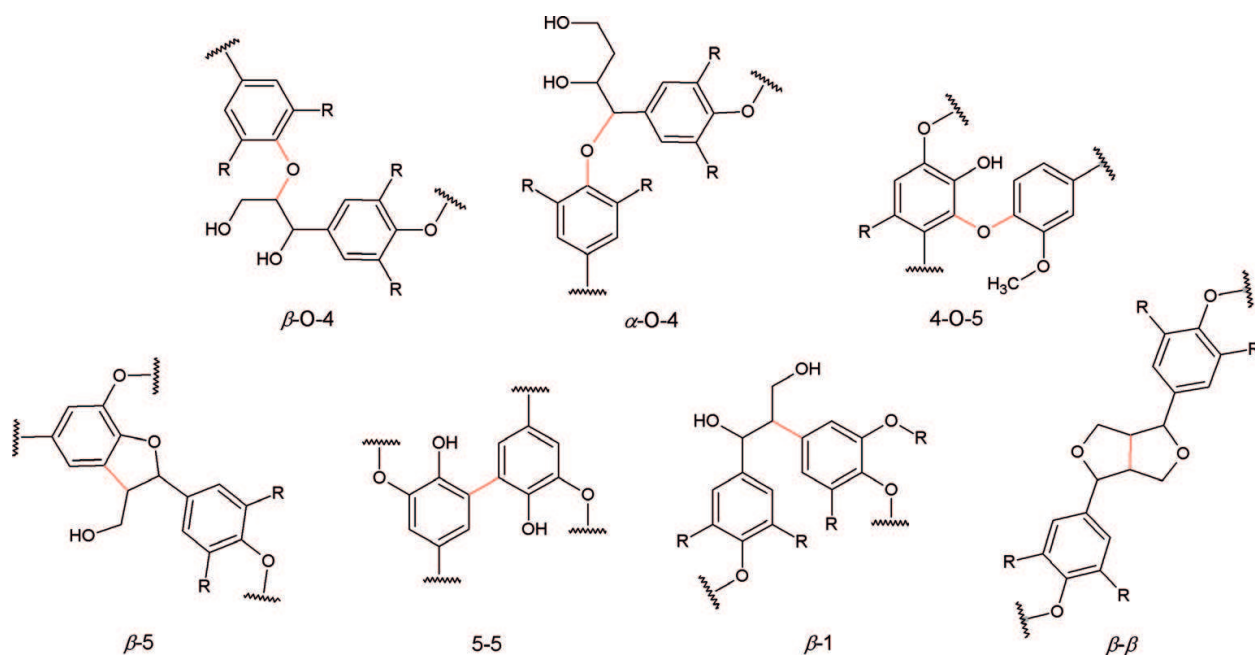


Figure 2. Characteristic bonds occurring in the structure of lignin, based on [2–4].

Characteristic bonds occurring in the lignin structure include carbon–oxygen bonds (β -O-4, α -O-4, 4-O-5), which account for almost two-thirds of all of the bonds present, as well as carbon–carbon bonds (β -5, 5-5, β -1, β - β)—see **Figure 2** [2–4]. Of the linkages occurring in the structure, the most easily decomposed are the β -O-4 bonds [5]. It should also be noted that the lignin macromolecules contain various functional groups that affect its reactivity. These are mostly methoxy and hydroxyl groups, as well as carbonyls and carboxyls. Only some of the hydroxyl groups are free to react, since most form bonds with neighboring structural units.

3. Application of lignin and its derivatives

Lignin, which is being produced in greater and greater quantities each year, not only as a byproduct of the paper industry but also as a valuable raw material obtained from biofuel production, is becoming the object of increasing interest in many branches of science and industry.

Approximately, 98% of the lignin produced by the paper industry is burnt for energy recovery, with only 2% being used for commercial purposes. At present, this market consists mainly of low-value products, such as binders and emulsifiers, low-quality fuel, carbon fibers, and phenolic resins. The complex structure of lignin and the fact that methods for its modification and depolymerization are relatively expensive and hard to carry out on an industrial scale, limit possibilities of its wider use [6]. Nonetheless, lignin is constantly finding new potential fields of application.

In recent years, lignin has come to be commonly used in the preparation of multifunctional hybrid systems. There are reports in the literature concerning silica–lignin materials, which may be used as effective and relatively cheap sorbents of environmentally hazardous metal

ions [7], polymer fillers [8–11], innovative systems with antibacterial properties [12], components in abrasive products [13, 14], and substances used in the catalytic reduction of synthetic dyes, in sensors, and in surface-enhanced Raman spectroscopy [15, 16]. There are also reports of systems in which lignin is combined with titanium dioxide [17], magnetite [18], and the oxide systems $\text{MgO}\cdot\text{SiO}_2$ [19, 20] or $\text{TiO}_2\cdot\text{SiO}_2$ [17], as well as chitin, another natural polymer occurring as a waste product [21, 22]. All of these systems have been used as effective sorbents of environmentally hazardous metal ions, and the chitin-lignin system can also be used as an enzyme carrier.

4. Depolymerization of lignin

Lignin, which has a complex chemical structure, is often subjected to a process of depolymerization. This has the aim of decomposing the biopolymer into low-molecular-weight products (monomers) by breaking the intermolecular bonds. Depolymerization of lignin may be carried out under a number of factors, including catalysts or high temperatures, which determine the mechanism of decomposition. The depolymerization process may lead to numerous useful low-molecular-weight compounds—see **Figure 3** [23, 24].

Due to depolymerization of lignin, the following fractions are obtained: waste carbon, residual lignin, an aqueous phase, and oil, which consists of a mixture of phenolic monomers (such as 2-hydroxy-1,3-dimethoxybenzene and guaiacol) and oligomers. This last is the most desired fraction, as it contains the greatest quantity of valuable chemical compounds which can be used in industry. The residual lignin consists of particles which have repolymerized or which have not undergone decomposition. The waste carbon fraction contains unwanted products of the depolymerization reaction. Any gaseous products will chiefly be a mixture of oxides of carbon and hydrocarbons. There may also be an aqueous phase, which may contain alcohols, as well as hydrophilic aromatic compounds which cannot be isolated. The quantity and composition of each fraction depends on the process conditions [24–26].

Numerous research projects have helped determine the most effective methods of depolymerization, which lead to large quantities of phenolic monomers. The most important of these methods includes (i) depolymerization in supercritical fluids, (ii) pyrolysis, (iii) the use of metallic catalysts, (iv) acidic catalysts, (v) alkaline catalysts, and (vi) the use of ionic liquids.

4.1. Depolymerization in supercritical liquids

It is becoming increasingly common for the depolymerization of lignin to be carried out with the use of supercritical liquids [27–30]. The thermochemical depolymerization of lignin in supercritical methanol with various catalysts was studied by Singh et al. [27]. Zeolites, sodium hydroxide, and iron filings were used in the process. Analysis of the results led to suggested mechanisms of the decomposition reaction. Depolymerization and demethoxylation of lignin result from the donation of a proton to ether bonds. The proton donor is the solvent, which as a result forms a formaldehyde capable of further reaction, particularly with ring compounds. The presence of NaOH in the reaction system not only accelerates the reaction but also enables

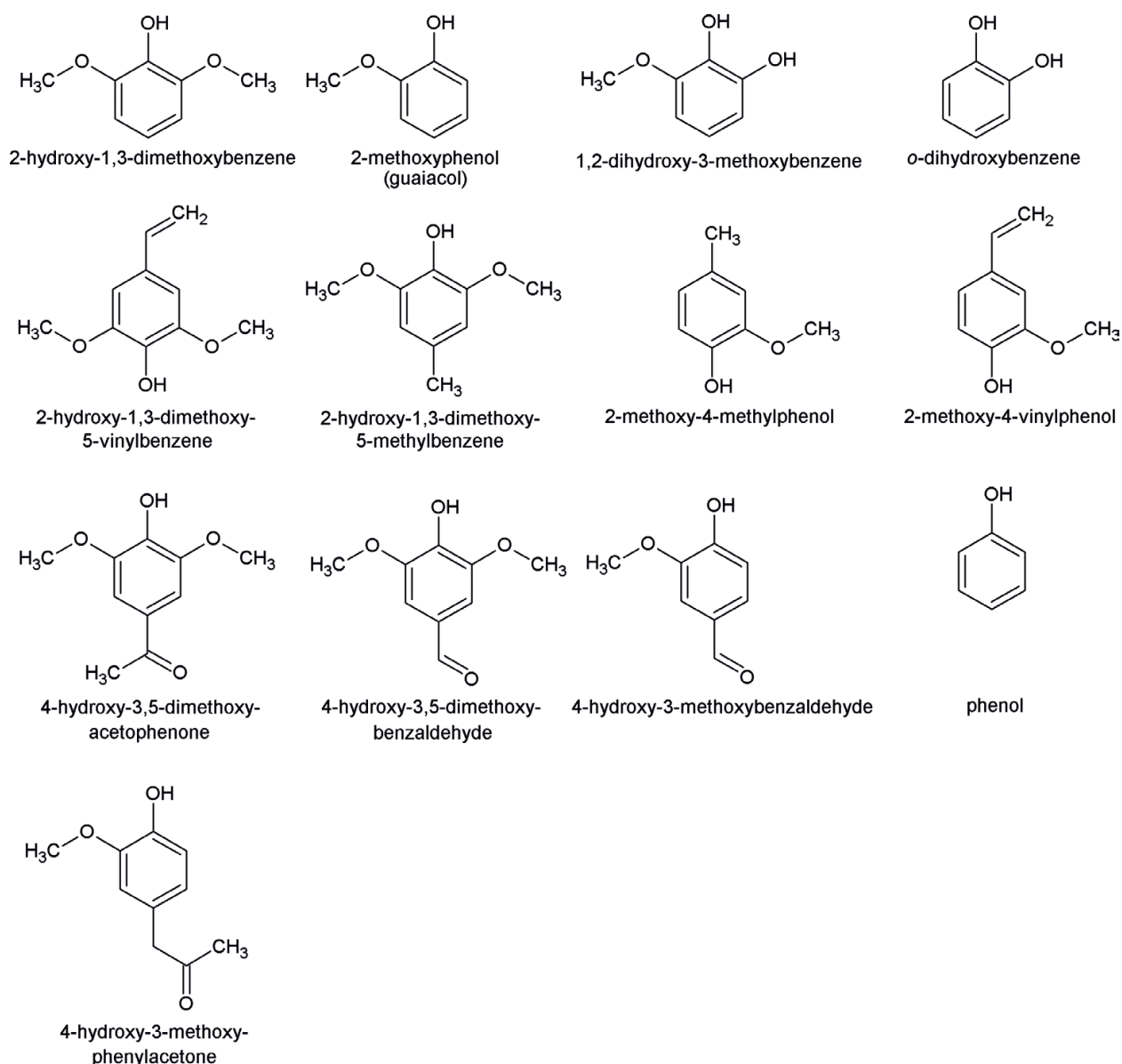


Figure 3. The most important low-molecular-weight compounds obtained from the depolymerization of lignin, based on [24–26].

the initiation of a demethylation reaction. The intermediate products undergo a condensation reaction, leading to a final product which is rich in solid carbon residues. This phenomenon is not observed in the case of zeolites, due to the presence of acid centers capable of catalyzing the direct methylation of the aromatic ring, which retard or prevent any potential condensation reactions [27].

In another study, Erdocia et al. used as the supercritical phase a triple system of methanol, ethanol, and acetone, determining their impact on the decomposition of lignin [28]. The largest content of monomeric phenol derivatives was found in the product obtained in an acetone environment. Detailed analysis confirmed the high degree of degradation of lignin, leading to a high content of solid carbon residues and catechol and cresol in the sample, which resulted from a reaction involving the detachment of alkyl and methoxy groups.

Depolymerization of the biopolymer in supercritical fluids was also studied by Kim et al. [29]. The process was conducted at 350°C in the presence of gaseous hydrogen and at a pressure of 13–19 MPa, using systems consisting of various alcohols in supercritical state—methanol, ethanol, and propan-2-ol—and metallic catalysts deposited on active carbon. The best-performing system proved to be Pd/C/ethanol, with which a very large quantity of oil and the lowest quantity of byproducts were obtained. This can be explained by the catalyst's high surface area and the fact that ethanol is the most effective hydrogen donor among the alcohols used.

Gosselink et al. used a system of carbon dioxide, acetone, and water as the supercritical phase, carrying out depolymerization of lignin in an organic solvent using formic acid as catalyst [30]. The process was carried out at the temperatures of 300 and 370°C under a pressure of 10 MPa. The quantity of products obtained was found to be affected by the depolymerization reactions taking place, which led to the formation of byproducts.

4.2. High-temperature depolymerization of lignin

Depolymerization of lignin also takes place at very high temperatures without the presence of oxygen, in a process known as pyrolysis. The high temperature causes cracking of the ether and carbon–carbon bonds, and the absence of oxygen prevents oxidation of the products. The process leads to, among others, liquid products containing monomeric phenolic compounds, gaseous products consisting mainly of hydrocarbons and oxides of carbon, and solid carbon residues. The proportions of individual compounds depend on the process conditions, including the temperature. Above 500°C, bonds are broken in the aromatic ring and hydrogen is formed. The process carried out at such high temperatures is called gasification, and gases account for more than 80% of the products in that case. There are two ways in which pyrolysis may be carried out—slow (conventional) and fast. In conventional pyrolysis, the lignin is heated more slowly, and the products consist of approximately 40% gases, 30% carbon, and only 10% oil containing monomeric compounds. Fast pyrolysis leads to as much as 60% oil, with only about 10% carbon and 15% gases, and the time of the process is shortened from 5–30 min to 2 s. A disadvantage is the presence of a large number of oxygen compounds in the resulting oil, which means that it cannot be used as a fuel. Research is being done, however, with the aim of improving the pyrolysis process by reducing the number of organic oxide compounds (pyrolysis with the addition of polyolefin) and increasing the content of phenolic compounds in the oil (pyrolysis with the addition of substances whose chain contains compounds of phenol, such as polystyrene) [25, 31].

4.3. Depolymerization of lignin using metallic catalysts

The depolymerization of lignin is often carried out at a high temperature in the presence of hydrogen (hydrogenolysis) with the use of metallic catalysts. Catalysts used include palladium, platinum, rhodium, nickel, ruthenium, and copper with the addition of carbon or aluminum oxide. At temperatures as high as 450°C, in the presence of hydrogen gas and under pressures of 2–35 MPa, various substances are obtained, including cyclohexanols, phenolic decomposition products, and cyclic alkanes.

Kloekhorst and Heeres carried out depolymerization in the presence of hydrogen on various different metal catalyst systems, without the use of a solvent. Analysis of the resulting products showed a Ru/TiO₂ system to be the most promising, in view of the variety of monomeric phenolic products obtained. Gaseous products, including methane, were also formed during depolymerization [32].

Depolymerization of lignin without the addition of a solvent was also investigated by Kumar et al. [26]. As catalysts, they used NiMo and CoMo deposited on various basic and acidic media. Apart from lignin and the catalyst, the reaction mixture also contained dimethyldisulfide, which served to create the system S-NiMo/medium or S-CoMo/medium. The introduction of sulfur into the catalyst causes the formation of new active sites with catalytic ability. It was found that the depolymerization was influenced by the type of medium, as well as by other factors. Acid media led to the largest quantities of repolymerization products. The best medium for the catalyst proved to be MgO-La₂O₃, which makes it possible to obtain a large number of monomers (particularly alkylphenols), while reducing the content of residual lignin in the post-reaction mixture [26]. Based on the results of the study, a mechanism for the process was proposed (see **Figure 4**).

Wang and Rinaldi investigated the ability of nickel catalysts to decompose a model lignin molecule—diphenyl ether, having a strong ether bond [33]. Various media were used for the metallic catalyst, and their impact on the hydrodeoxygenation of the compound was studied. A high degree of transformation of the ether was found to be linked to the acidity of the medium and its surface area.

Das et al. carried out depolymerization using niobium(V) oxide as catalyst and hydrogen peroxide and potassium permanganate as oxidizing agents [34]. The main decomposition products

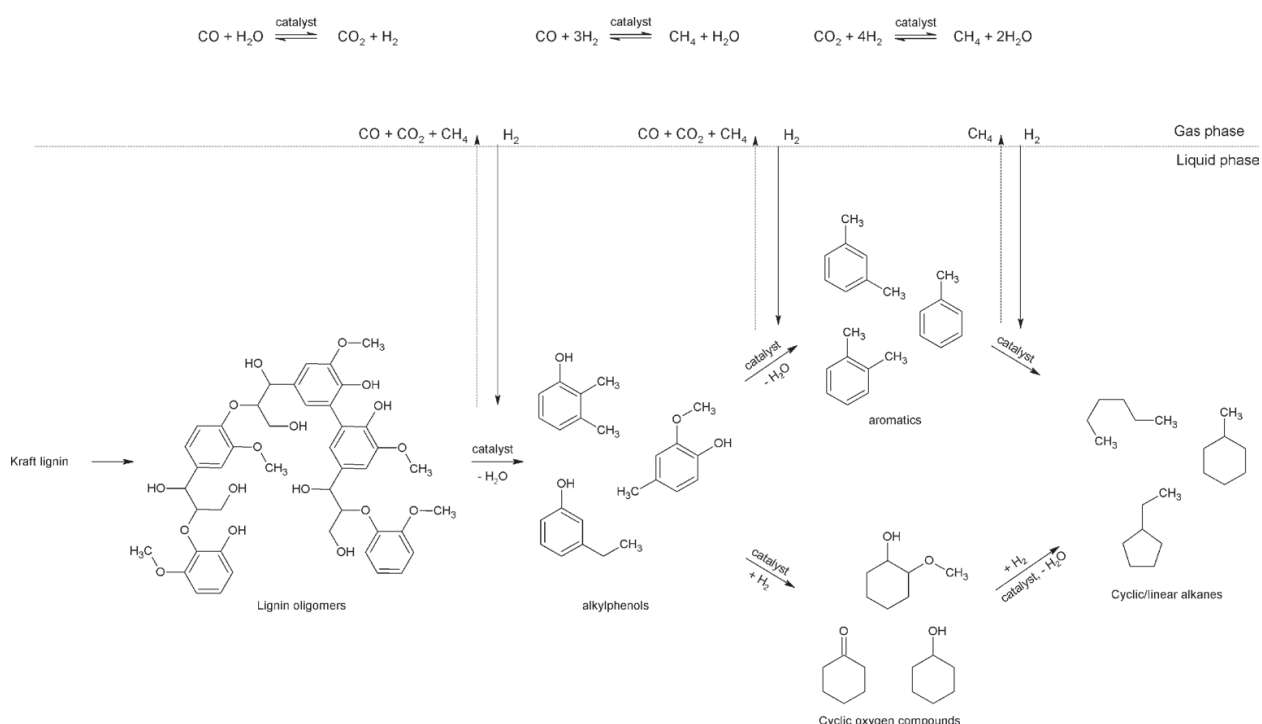


Figure 4. Mechanism of the process of depolymerization of lignin, adapted from Kumar et al. [26].

were vanillin and its derivatives. Due to the presence of trace quantities of acids in the post-reaction mixture, the possibility was suggested that the lignin is adsorbed by the catalyst and aldehydes are formed as a result of reactions taking place on the catalyst's surface.

4.4. Depolymerization of lignin using acidic catalysts

Valuable low-molecular-weight products can also be obtained from lignin with the use of catalysts of acid origin.

Sturgeon et al. investigated the mechanism of decomposition of the β -O-4 bond, adding the following model molecules to a 0.2 M solution of H_2SO_4 at 150°C : 2-phenoxy-1-phenylethanol (PE), 2-phenoxy-1-phenylpropan-1,3-diol (PD), 1-(4-hydroxyphenyl)-2-phenoxypropan-1,3-diol (HH), and 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy) propan-1,3-diol (GG), which represent the phenolic (HH and GG) and non-phenolic (PE and PD) groups [35]. Depolymerization was shown to take place by way of an ionic mechanism, via protonation of the hydroxide group on the α -carbon, followed by the separation of a water molecule and the formation of a carbocation as an intermediate stage (see **Figure 5**). It was also observed that the presence of a phenolic hydroxyl group accelerates the decomposition of the β -O-4 bond.

Deepa and Dhepe carried out depolymerization of lignin using a solid acid catalyst [36]. Several types of lignin were selected to undergo depolymerization in a mixture of water and methanol in a nitrogen atmosphere, at a temperature below 250°C , using various types of zeolites, aluminosilicates, and metal oxides as catalysts. It was found that a very large quantity of monomers could be obtained, particularly when zeolites were used (the yield in that case reached 60%). However, the susceptibility of zeolites to poisoning with metal ions (such as sodium) led to their deactivation and also caused instability during the reaction. It was therefore decided to focus further attention on the possible use of the amorphous $\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyst. Following optimization of the process, a method was proposed for obtaining a large quantity of monomers and for recovering the catalyst for reuse [36].

There also exists the possibility of using organic acids as catalysts in the decomposition of lignin. Rahimiet al. used formic acid and sodium formate for this purpose, carrying out depolymerization on previously oxidized lignin extracted from aspen [37]. Desirable properties of this system include the relatively low process temperature (110°C) and the very large quantity of low-molecular-weight aromatic compounds produced (approximately 61% of the initial mass of lignin).

Güvenatam et al. investigated the possibility of carrying out depolymerization of lignin and its model compounds using trifluoromethane sulfonates of various metals [38]. These

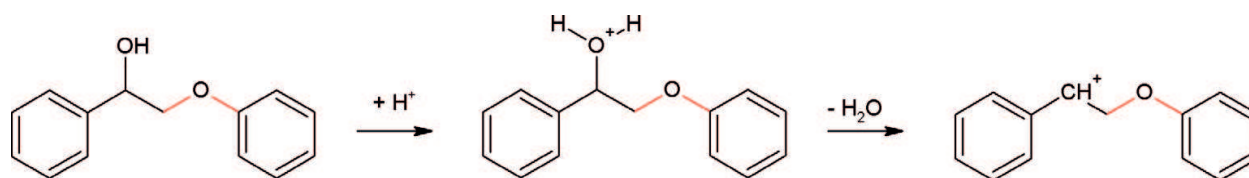


Figure 5. Mechanism of the depolymerization of lignin as established by Sturgeon et al. [35].

compounds are known for their high acidity. The process took place in a mixture of water and ethanol in a supercritical state. It was found that a significant quantity of ether bonds in the model lignin molecules was broken. It was also discovered that ethanol not only served as a solvent but also played an active part in the reaction, attaching itself to the aromatic ring and to the alkyl chain of the molecules. Further investigation confirmed the ability of liquids with a trifluoromethane sulfonate anion to catalyze the decomposition of lignin, proving the significant role played by that anion in the depolymerization process. In the proposed mechanism, the catalyst is capable of interacting with various oxygen functional groups in lignin, causing them to regroup and forming a carbocation, which can react further with nucleophiles, and also with the solvent. There exists a possibility of further dehydration and hydrogenation of the resulting compound (see **Figure 6**). The chief products of the reaction were hydrocarbons, both aromatic and non-aromatic, accompanied by a small quantity of monomeric phenolic derivatives. The absence of residual lignin in the post-reaction mixture was explained by the interaction of ethanol with the carbocation, which prevented repolymerization reactions [38].

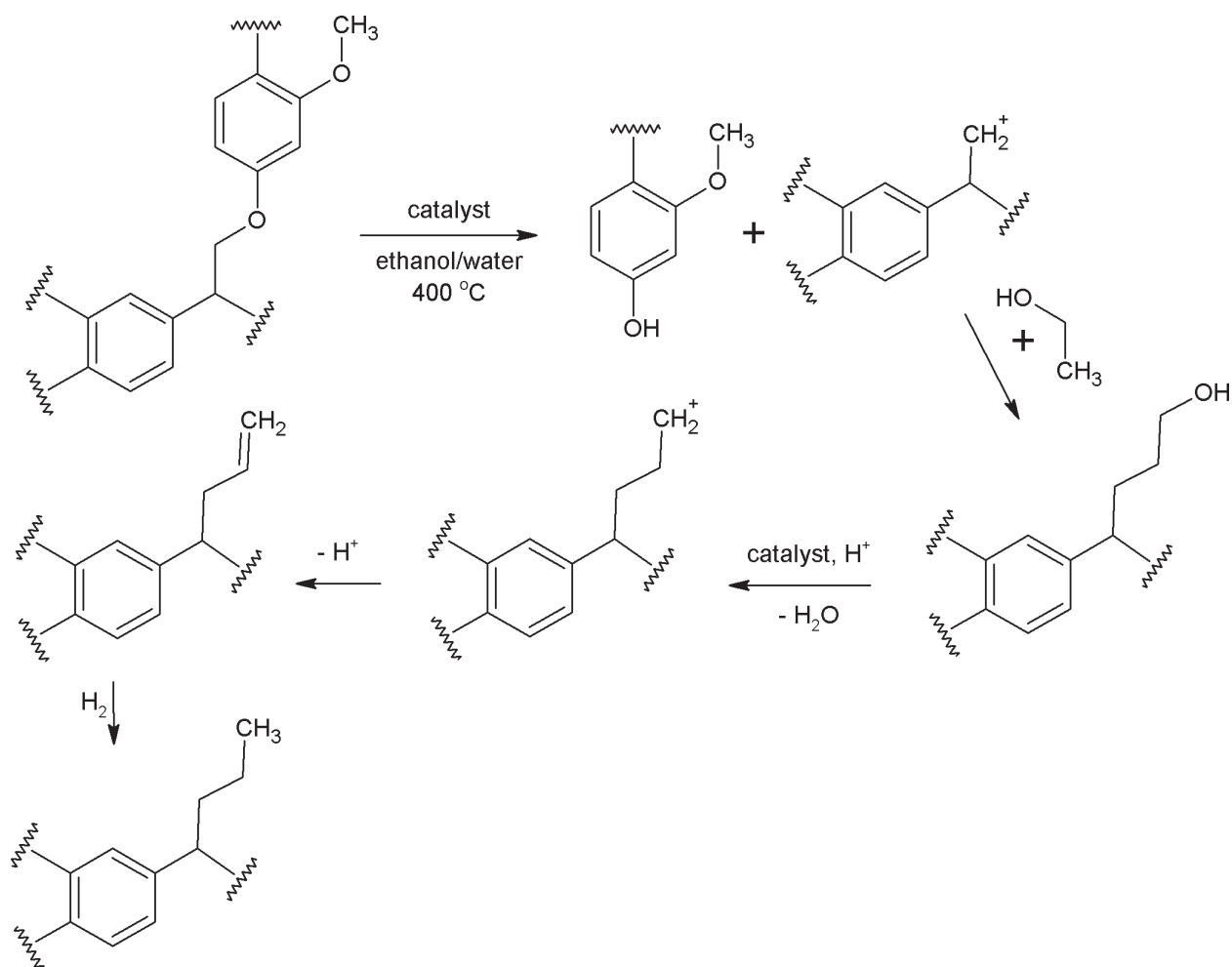


Figure 6. Mechanism of the process of depolymerization of lignin proposed on the basis of studies by Güvenatam et al. [38].

4.5. Depolymerization of lignin using basic catalysts

The reaction of the decomposition of lignin into low-molecular-weight products is also carried out using inorganic basic catalysts such as NaOH [24, 39]. During the process, alkyl-aryl ether bonds are broken under the action of the sodium ion, which polarizes the bond, making it easier to break (see **Figure 7**).

Optimization of the depolymerization process using a basic catalyst was performed by Roberts et al., who investigated the effect of temperature, the quantities of NaOH and lignin, and the pressure and reaction time on the quantities of monomer particles formed [24]. The largest quantity of monomers as a percentage of the original quantity of lignin was obtained using 4% NaOH. The process was most successful when carried out at a temperature of 300°C for 4 min. With increasing reaction pressure, the concentration of monomers decreased, possibly as a result of the stronger intermolecular interactions. The quantity of depolymerized lignin behaved analogously. It was also shown that the process temperature has a strong impact on the quantity of particular monomers occurring in the mixture [24].

A study by Erdocia et al. also investigated how the decomposition products depend on the type of lignin used [28]. Three types of lignin dissolved in organic solvents (acetone, formaldehyde, and a mixture of the two) were subjected to the action of NaOH at a temperature of 300°C and a pressure of 9 MPa. A large quantity of residual lignin (approximately one quarter of the original quantity) was present following the depolymerization process, due to repolymerization of the compounds formed during that process. These recombine with each other or with the original lignin, forming new C–C and C–O bonds, and this process is promoted by the presence of formic acid. The quantity of monomeric phenolic particles formed was found to depend on the average molecular weight of the lignin used—the smaller the molecular weight, the greater the quantity of particles formed during depolymerization [28].

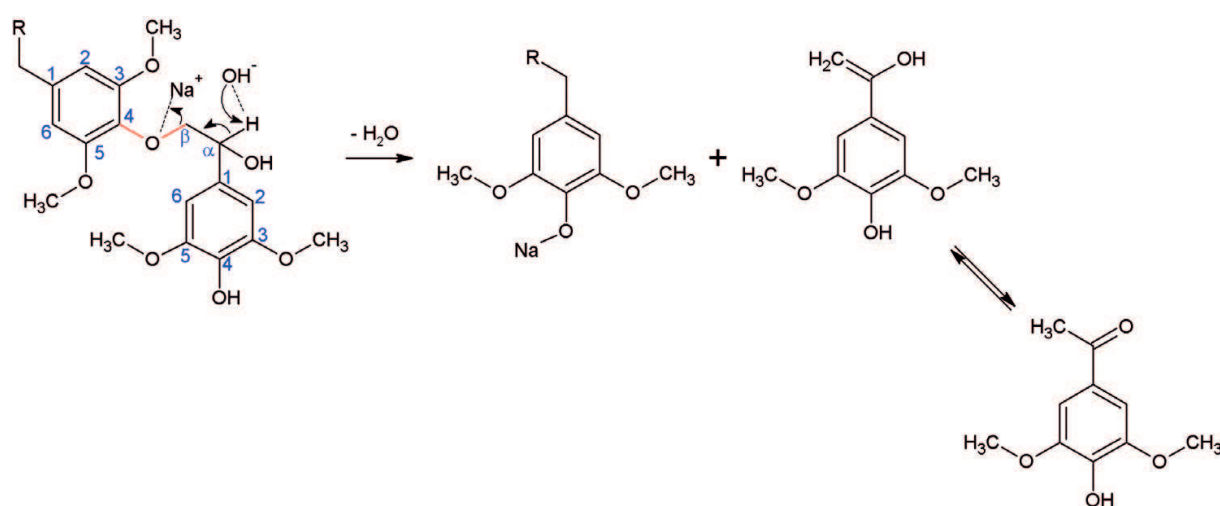


Figure 7. Low-molecular-weight products resulting from the depolymerization of lignin with the use of NaOH, based on [24].

Santos et al. also investigated the depolymerization of the biopolymer using NaOH [40]. Based on the analysis of the oil produced, it was shown that the principal decomposition products were catechol and phenol. Small amounts of cresol, guaiacol, and 2-hydroxy-1,3-dimethoxybenzene were also formed. The authors not only analyzed the product but also suggested a potential application: the antiseptic and insecticidal properties of catechol, in combination with the preserving and disinfecting action of phenol, meaning that the mixture might potentially be used as an antifungal treatment for wood. Preliminary studies showed that the oil indeed increased the resistance of wood panels to fungal action, thus confirming its potential for use as a wood preservative [40].

An investigation of the effect of the catalyst on the depolymerization of lignin was carried out by Toledano et al. [39]. Lignin was dissolved in an organic solvent with the addition of potassium, calcium, lithium and sodium hydroxides and sodium carbonate, and the biopolymer underwent depolymerization at 300°C under a pressure of 90 MPa. The large differences in the quantities of phenolic particles (from around 10% for Ca(OH)₂ to 20% for NaOH) and residual lignin (above 37% for almost all of the catalysts apart from calcium carbonate) show that the catalyst used affects the mechanism of the reactions taking place during depolymerization.

Although metal hydroxides would appear to be the most popular catalysts, they are not the only compounds used in the depolymerization process. Long et al. used magnesium oxide, together with the solvent tetrahydrofuran, which increases the power of the catalyst [41]. The quantity of phenolic monomers produced (more than 13%) and their increased ease of separation from the mixture mean that this is a promising catalyst for the decomposition of lignin.

In turn, Widyay et al. studied the impact of different catalysts (magnesium and calcium oxides, potassium acetate, and potassium hydroxide) on the depolymerization of lignin in ethanol [42]. In spite of the very good results obtained for the potassium catalysts, in view of their high solubility in the reaction medium, further tests were carried out using magnesium oxide. At the next stage, an analysis was made of the effect of the polarity of the solvent on the products obtained. Among the various solvents used, the best results were obtained for ethanol. The post-reaction mixture contained large quantities of hydroxyl (aromatic and non-aromatic) and carboxyl groups, probably due to the oxidation reactions taking place. Also noted was the degradation of some of the carbon-carbon bonds and the structural units of lignin. The authors further drew attention to the possibility of reusing the catalyst without detriment to its activity or structure [42].

4.6. Depolymerization of lignin using ionic liquids

The unique properties of ionic liquids are exploited in a number of new multifunctional applications, including their possible use in the depolymerization of lignin. A number of important studies of such depolymerization processes have been carried out by Jia et al. [43]. Since the most frequently occurring bond in lignin is the β -O-4 bond, the model compounds used were 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)propan-1,3-diol and 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)propan-1,3-diol (VG). Although both of these contain the β -ether bond, in view of the different substitutions, they represent, respectively,

the phenolic and non-phenolic character of the subunits of the biopolymer. One of the experiments was carried out in the presence of the ionic liquid [HMIM][Cl] (acting as both catalyst and solvent) with varying quantities of water. A significant percentage (more than 70%) of the ether bonds was broken, and the product formed most often and in the largest quantities was guaiacol. It was also found that a larger quantity of water favors the decomposition of the β -O-4 bond. Importantly, it was confirmed that the ionic liquid can be reused without loss of activity [43]. Further studies were made to analyze the ability of the N-base-[BDMIM][Cl] system to break β -O-4 bonds. Following heating of the systems to a temperature of 150°C, the principal decomposition product was found to be enol-ether (EE) [44].

The same researchers have also evaluated the effect of the anion on the depolymerization process. Using the aforementioned model substances (VG and GG), they carried out a depolymerization reaction at 150°C for the first substance and at 110, 130, and 150°C for the second, selecting appropriate ionic liquids with the 1-methylimidazole cation and various anions. A determination was also made of the Hammett acidity of particular ionic liquids (with the use of 3-nitroaniline), showing them to be strongly acidic. Although no dependence was found between the acidity of the liquid and the effectiveness of depolymerization, the results indicated a link between the possible formation of anion–molecule hydrogen bonds and hydrolysis of the β -O-4 bond. This was found to be a factor that favored the decomposition of the bond, and thus the depolymerization of the molecule [45].

Yan et al. also studied the depolymerization of lignin using a liquid with the imidazole cation, confirming the dependence between the anion of the ionic liquid used and the resulting depolymerization products [46]. Moreover, factors affecting the process of decomposition of lignin were found to include the pH of the reaction mixture, the quantity of ionic liquid used, and the presence in the system of a cosolvent. In this case, however, the addition of water to the reaction system was found to limit depolymerization. It was concluded that there is a clear need to seek new model lignin molecules which better imitate the structure of the biopolymer.

Liu et al. developed an innovative catalyst containing choline methane sulfonate and palladium deposited on carbon [47]. This produced a system which combined the acidic properties of the ionic liquid with the oxidizing properties of the metal and was at the same time a very good solvent of lignin. Studies carried out using kraft lignin confirmed the selectivity of the hydrogenolysis process, as well as the high content of phenol and its derivatives, particularly 2-hydroxyphenol. In addition, in an experiment using a model lignin molecule, the reaction mechanism was investigated. It was found that the hydrolysis of the substrate leads to breaking of the ether bond and the formation of phenol derivatives. The intermediate products may subsequently undergo hydrogenolysis or a retro-aldol reaction (see **Figure 8**) [47].

Another method used to carry out the depolymerization of lignin used a model lignin molecule in an environment of 1-benzyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide, with phosphoric(V) acid as catalyst [48]. Following thorough analysis of the product, which was rich in phenol and benzoic acid, a possible mechanism of the decomposition was proposed, according to which the ionic liquid not only interacts with the molecule undergoing decomposition but also has the ability to take part in a reaction with atmospheric oxygen leading to the formation of radicals, these being capable of further interaction with the

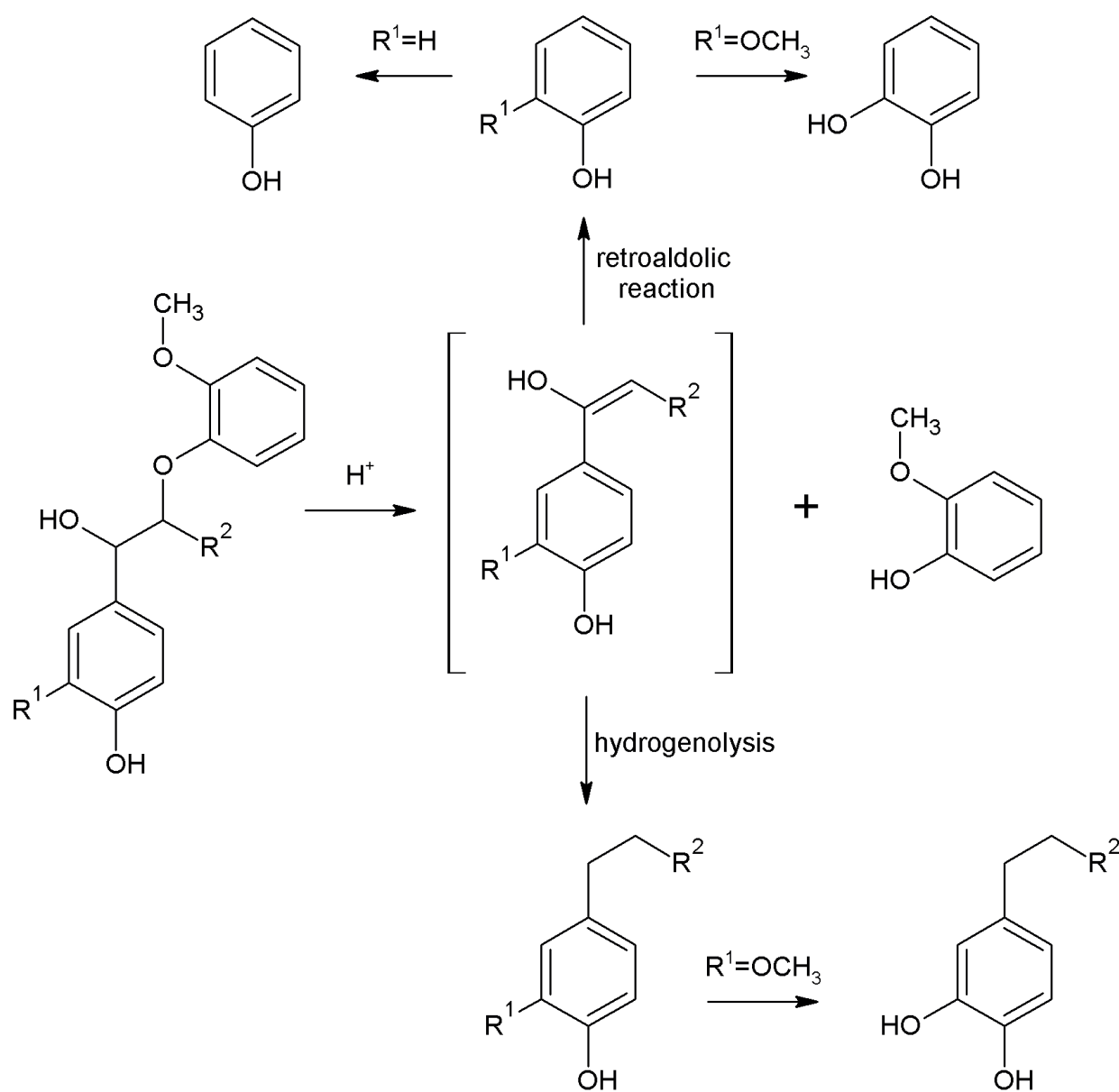


Figure 8. Mechanism of the depolymerization reaction of a model lignin molecule with the use of choline methane sulfonate, adapted from [47].

depolymerized compound. As a result, peroxy acid is formed, which via acidic hydrolysis is transformed into the final decomposition products—phenol and organic acids [48].

In the search for effective solvents, Rashid et al. investigated the ability of protonic ionic liquids to dissolve lignin [49]. Various pyridine ionic liquids with methanoate, ethanoate, and propanoate anions were synthesized. Among the systems obtained, the largest quantity of lignin was dissolved in pyridine methanoate, demonstrating that an increase in the length of the alkyl chain in the anion has an unfavorable effect on the solubility of lignin. In the next stage, the regeneration of lignin was carried out and its properties were analyzed. The regenerated lignin was found to have a significantly smaller average molecular weight, showing that the material underwent defragmentation during dissolution. There was also a decrease

in the quantity of hydroxyl groups linked to the aromatic ring and an increase in the quantity of quinone groups. This meant that the properties of the material were more favorable for further chemical treatment. An effective process of regeneration of the solvent was also carried out, obtaining a liquid suitable for reuse [49].

An innovative depolymerization solution was proposed by Cai et al., who carried out the process in an emulsion reactor [50]. They used a solution of water and an ionic liquid—1-butyl-3-(butyl-4-sulfone)imidazolium hydrogen sulfate(VI)—as a catalyst and an n-butanol/n-hexane system as the oil phase. Lignin was used as a surfactant, in view of the presence in that material of both hydrophilic and hydrophobic groups. The lipophobic nature of the ether groups in lignin facilitates contact between the compound and the catalyst and thus favors the decomposition process. Detailed analysis of the results confirmed the high effectiveness of the process and the significant increase in the quantity of monomeric phenolic products obtained compared with traditional techniques, thereby confirming the good potential of the method for practical application [50].

The ability of ionic liquids to dissolve lignin is exploited not only in depolymerization processes but also in extraction from lignocellulose materials. Prado et al. combined both processes, carrying out the depolymerization of lignin present in the black liquor formed during one of the stages of delignification. For this purpose, butylimidazolium hydrogen sulfate(VI) and triethylammonium hydrogen sulfate(VI) were used, with hydrogen peroxide as an oxidizing agent. The oils obtained were rich in phenol derivatives, particularly acids, including vanillic and benzoic acids [51]. In a subsequent study, titanium(IV) oxide was used as an oxidizing agent alongside hydrogen peroxide. Analysis of the products showed the inorganic oxide to be an effective catalyst, enabling a large quantity of monomeric phenolic compounds to be obtained. The product also contained no significant quantity of molecules originating from the process of oxidation of carbohydrates, which indicates that titanium(IV) oxide exhibits greater selectivity than hydrogen peroxide in the oxidation of lignin [52].

Stärk et al. investigated the effect of systems of various ionic liquids and salts of iron(III), copper(II), and manganese(II), used as catalysts, on the degree of conversion of lignin in organic solvent [53]. Aerobic depolymerization was carried out for over 10 h at a temperature of 100°C under increased pressure. Among 40 systems investigated, the best parameters were obtained for [EMIM][OTf] combined with manganese(II) nitrate(V) as catalyst; this produced a conversion yield of more than 50%.

Nanayakkara et al. carried out an experiment to determine the effect of adding 4-tert-butyl-2,6-dimethylphenol (TBDMP, blocked in the ortho and para positions to prevent a polymerization reaction) on the products obtained from depolymerization via a redistribution reaction [54]. Using Klason lignin, an organic solvent and a Cu/EDTA complex as catalyst, the depolymerization reaction was carried out at 180°C with the addition of TBDMP in two ionic liquids: [EMIM][ABS] and [BMIM][MeSO₄]. The process produced numerous oligomers which could not be obtained without the addition of the catalyst and TBDMP, which demonstrates that these two components are essential for the depolymerization of the biopolymer in the proposed ionic liquids [54].

Binder et al. investigated the possible depolymerization of lignin in an organic solvent and of its model molecules—eugenol (2-methoxy-4-(2-propenyl)phenol), 1-phenoxy-2-phenylethane, and 4-ethyl-2-methoxyphenol—at temperatures below 200°C [55]. A Brønsted acid catalyst was used, with the ionic liquids [EMIM][OTf] and [EMIM][Cl]. From the first two model compounds, guaiacol and phenol, respectively, were obtained, but in the case of 4-ethyl-2-methoxyphenol and lignin itself, no depolymerization reaction could be achieved. This indicates the need to seek better model substances and to gain a more precise understanding of the mechanism of depolymerization.

The depolymerization of lignin (extracted from oak) was also investigated in a study by Cox and Ekerdt, who used acidic [HMIM][Cl] [56]. It was shown that this ionic liquid may serve both as a solvent and as a catalyst for the depolymerization reaction, and confirmation was obtained for a proposed mechanism of decomposition via hydrolysis of the alkyl-aryl ether bond.

It can therefore be concluded, based on an exhaustive survey of the latest literature, that the catalytic properties of ionic liquids, in combination with their ability to dissolve lignin, give them great potential for practical applications in the conversion of lignin materials. They are also made more attractive in comparison with existing methods by their low toxicity and the ability to create liquids with specified parameters. It is expected that research efforts in this area will lead to further progress in the near future.

5. Modification of the lignin structure

In the preceding chapters, attention has been drawn to the potential for practical applications of lignin and of the products obtained as a result of its depolymerization. Nonetheless, this biopolymer may alternatively be used following preliminary processing or modification of its structure. Such an operation can be used to introduce new functional groups into lignin by way of chemical reactions of many kinds and also to achieve mild oxidation of the surface hydroxyl groups [57]. These groups, which are substituted not only on the aromatic ring but also in aliphatic chains, are of decisive importance for the modification of lignin. Modification of the structure of functional groups serves to increase the chemical reactivity of the biopolymer, improve its solubility in polar or non-polar solvents, facilitate the creation of a network of interactions between lignin and polymers in composites or inorganic compounds in functional materials, and simplify the processing of the final product. These goals may be achieved by creating new active centers. By this means, it is possible to increase the biopolymer's reactivity using, for example, hydroxyl groups (inductive effect) or substituents in the ortho position of the aromatic ring (mesomeric effect) [57]. It is significant that hydroxyl groups occur in lignin both in aliphatic chains in the C α and C γ positions and as substituents on the aromatic ring. In view of their weak acidity, it is phenyl groups that determine the reactivity of the whole lignin molecule [57]. The types of reaction used to obtain new active centers include sulfonation [1, 58], hydroxyalkylation [59], nitration [57], amination [60, 61], halogenation [57], and alkylation/dealkylation [57].

The sulfonation of lignin and of its previously sulfonated equivalents enables improvement of its solubility in aqueous solutions, irrespective of their pH. In the reaction, the biopolymer is acted on by a 95% solution of sulfuric(VI) acid, with intense mixing, at a temperature of 40°C [62]. Lignosulfonates can also be included in the group of modified lignins produced as a result of sulfite pulping [1]. An alternative method of sulfonation was described by Ouyang et al. [58]. The first stage involved hydroxymethylation of alkaline lignin with the use of formaldehyde in a basic environment (see **Figure 9**). Following this substitution, the lignin underwent sulfonation with the use of Na_2SO_3 , where the hydroxymethyl substituent undergoes a reaction. The mechanism of this modification of the lignin structure is shown in **Figure 9** [58]. Compared with the lignosulfonates commonly used in concrete mixtures, lignin prepared in this way exhibits a higher degree of sulfonation, a lower surface tension, and a stronger interaction with the surface of cement particles. It also produces desirable electrostatic repulsion forces among the cement particles, providing further confirmation of its potential for use in concrete mixtures [58].

The hydroxymethylation of lignin was also investigated in a study by Sen et al. [63], where a sample of the biopolymer was dissolved in sodium hydroxide and then subjected to the action

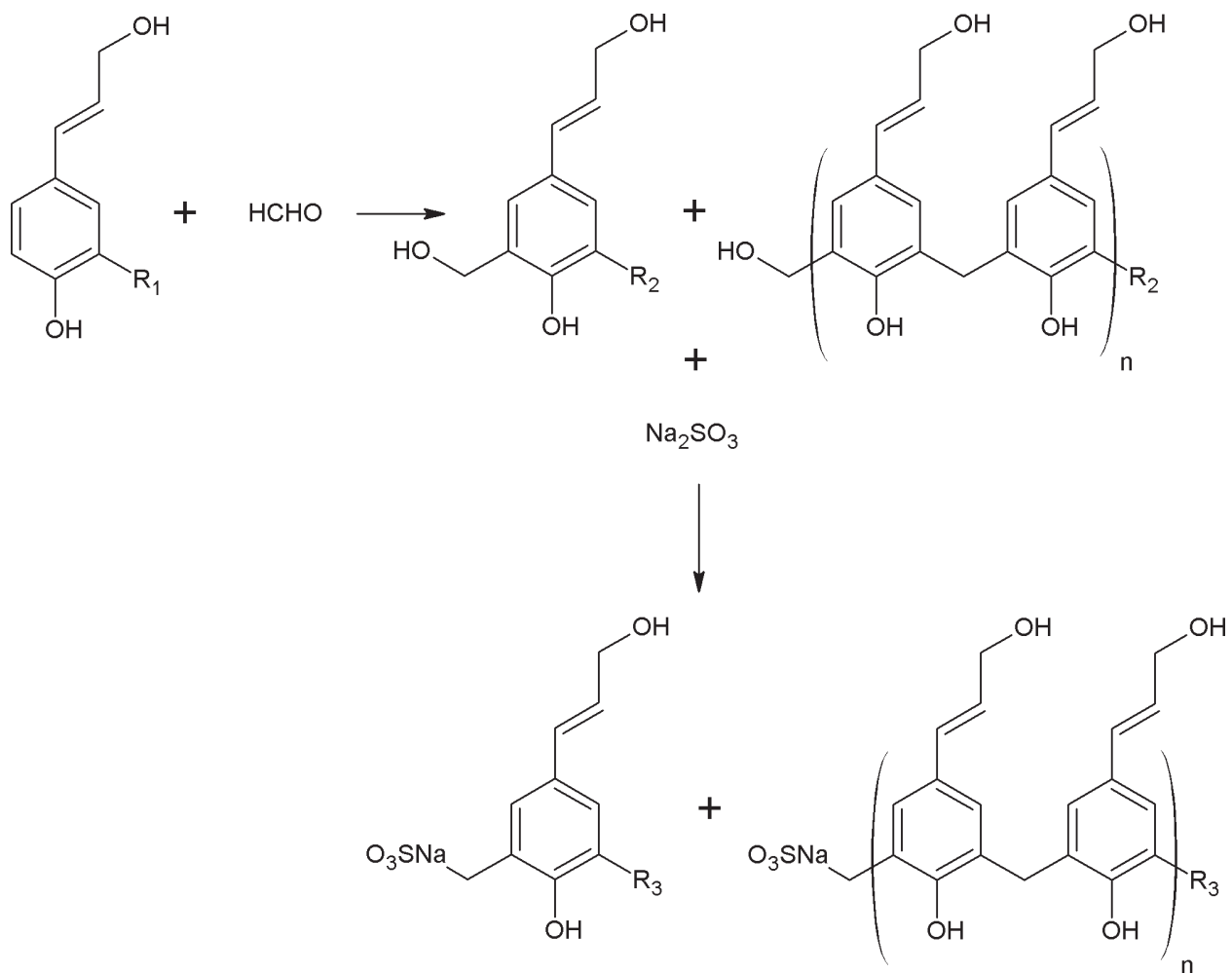


Figure 9. Mechanism of hydroxymethylation and sulfonation of lignin, adapted from [58].

of formaldehyde. In this way, the content of aliphatic hydroxyl groups and carbonyl groups was increased, as was confirmed by various analytical techniques. Based on the results, it was proposed that the derivative obtained might be used in glues or for wood preservation [63]. A similar modification of the lignin structure was studied by Malutan et al. [64]. They used lignin extracted from annual plants, subjecting it to hydroxymethylation with formaldehyde in an alkaline environment at room temperature. It was found that the reaction took place chiefly in the ortho position of the aromatic ring. At higher temperatures, methylene bonds are formed between the substituted lignin fragments. The desired reaction is the Lederer–Manasse reaction, in which a hydroxymethyl group is substituted on the aromatic ring, increasing the reactivity of the molecule. Based on literature data, it can be stated that the hydroxymethylation reaction is dependent on the type of lignin used (the raw material and the method of isolation) and also on the process conditions.

In a study by Du et al., amination of lignin took place via the Mannich reaction [60]. The authors also investigated the impact of preliminary phenolation of the biopolymer structure on the effectiveness of the amination reaction. For a successful Mannich reaction, it is very important to select a lignin with a free C-5 position in the aromatic ring of the guaiacyl units. This carbon has very high electron density, which promotes the introduction of amino-alkyl groups in the ortho position relative to the hydroxyl group. Irrespective of the pH of the reaction, although it may proceed according to different mechanisms, these lead to the same product, with substitution at C-5. The mechanism of the reaction of amination of lignin is shown in **Figure 10** [60]. The study also showed that preliminary phenolation of the lignin sample increases the content of unsubstituted C-5 carbons, which subsequently improves the yield of the amination reaction. However, in view of the toxicity of this reactant, it must be considered whether such pretreatment is reasonable [60].

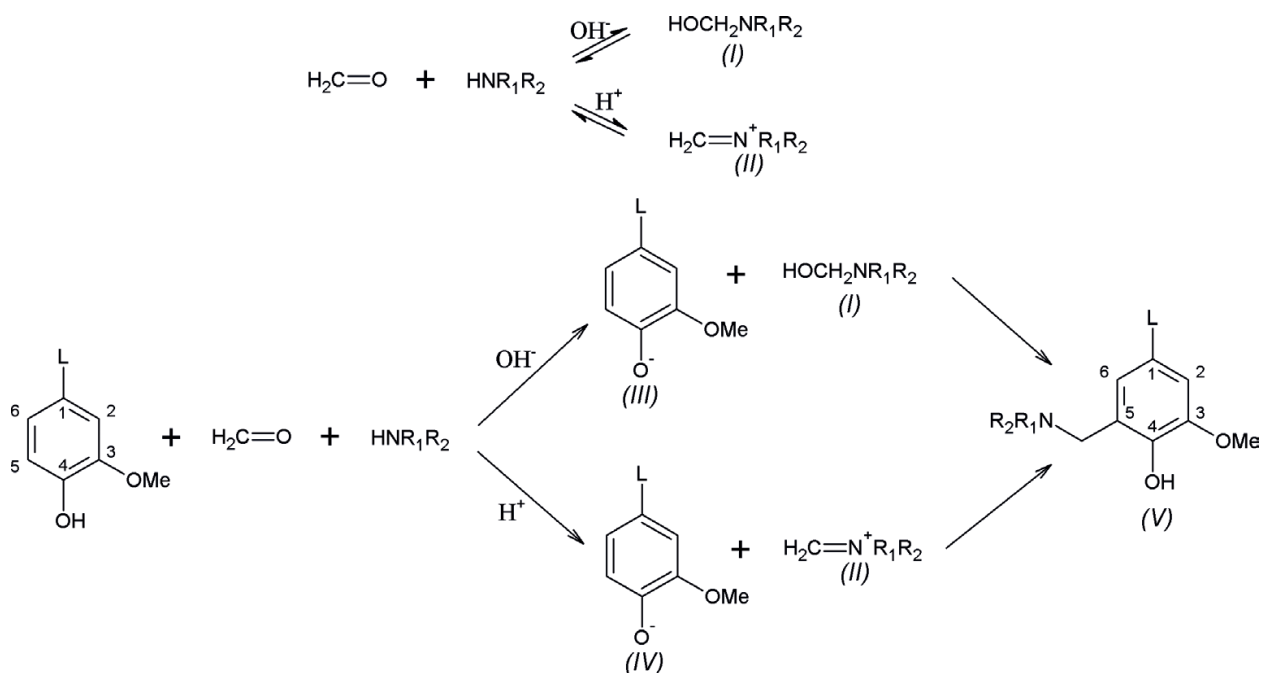


Figure 10. Mechanism of the reaction of amination of lignin in a basic or an acidic environment, adapted from [60].

Corresponding results on the formation of aminated lignin were published by Ge et al. [61]. They used alkaline lignin, which they modified at pH 8–13 with methylamine, adding appropriate doses of formaldehyde to the reactor. The product was evaluated as a possible sorbent of lead ions from aqueous solutions. Aminated lignin may be used successfully as a surfactant, in polycationic materials, in slow-release fertilizers [60], and in the sorption of lead ions from waste water [61].

The aforementioned use of the phenolation of lignin to unblock a greater number of C-5 carbons in the aromatic ring was also investigated by Podschun et al. [65]. The purpose of the study was to determine optimum conditions for the modification of lignin with phenol, to give a product with better solubility in various thermosetting resins. The reaction took place in an acidic environment at an elevated temperature, via the mechanism shown in **Figure 11**. In addition, some of the ether bonds are broken during the process, which leads to a reduction in molecular weight [66]. In the process used by Hu et al., the phenolation of lignin took place in ethanol at 70°C, over a time of several hours [66].

Lignin may also be successfully subjected to alkylation or dealkylation, by which means alkyl groups can be introduced into the biopolymer molecule. Here, the alkylating agent reacts with the nucleophilic centers of the biopolymer (oxygen atoms). In the case of lignin, atoms with an excess of electrons are attacked not only in the aromatic ring but also in the aliphatic chains. Sen et al. carried out methylation of kraft lignin with the use of dimethyl carbonate (DMC) [63]. They confirmed the possibility of controlling the degree of methylation by varying the quantity of DMC used. There was no drop in the thermal stability of the methylated lignins, although the glass transition temperature was reduced. This was achieved by a reduction in the number of sites capable of forming intermolecular hydrogen bonds [63]. It was also shown that the use of DMSO enables the reaction to be carried out at higher temperatures, thus increasing the degree of methylation of lignin. Moreover, the use of a polar aprotic solvent further catalyzed the substitution of the nucleophilic center [63].

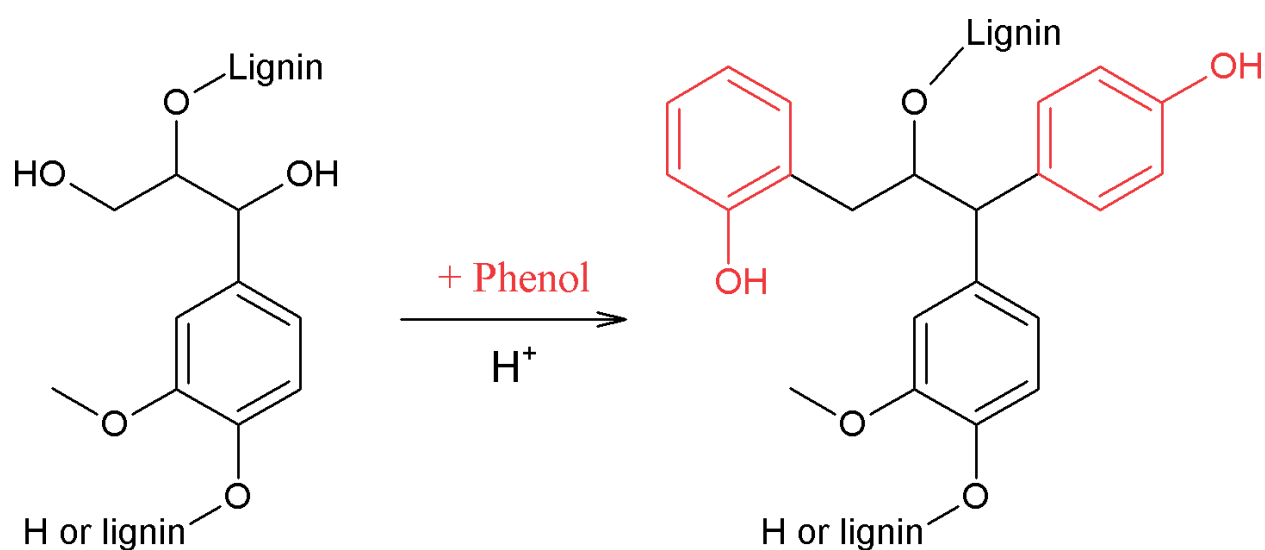


Figure 11. Mechanism of the reaction of phenolation of lignin, adapted from [65].

Lignin has also been successfully subjected to cationization, which leads to a material that may function as a flocculant of dyes from aqueous solutions. Cationic modification of the lignin structure was performed with the use of glycidyl-trimethylammonium chloride, which in a basic environment (pH=12.6) is joined to the phenol group of the aromatic ring in the biopolymer. The resulting material can be subjected to hydrolysis, with separation of the biopolymer from the quaternary ammonium salt. The mechanism of the modification of the biopolymer and hydrolysis is shown in **Figure 12** [67]. The resulting material may interact with the dye being removed, and in addition, the aromatic part of the lignin may develop hydrophilic/hydrophobic interactions with the pollutant [67].

Another method for modifying the structure of lignin is epoxidation of the phenol groups of the aromatic ring, carried out in an alkaline environment [59, 68–70]. Pan et al. performed such an action using epichlorohydrin, which was mixed with alkaline lignin in an appropriate ratio at 50°C [68]. The solid product was further subjected to amination using propan-diamine. This Lewis base reacts with the ether oxygen, lengthening the chain of the alkyl substituent. The use of diamine makes possible a reaction with a further epoxy substituent, which finally increases the degree of crosslinking of the biopolymer. The epoxy lignin prepared in this way, or aminated crosslinked derivative, can be used as an active bioorganic additive to epoxy resins. This solution is friendly to the environment and can reduce the costs of resin production [68]. In a similar study by Feng and Chen [69], lignin was obtained by pulping of raw material in acetic acid, followed by phenolation of the biopolymer. This pretreatment enables an increase in the content of phenolic hydroxyl groups, which in the next stage are attacked by the epoxidation agent. Moreover, phenolation of lignin enables reduction of the molecular weight and thermal stability, compared with the unmodified biopolymer [66, 69]. It was shown that the addition of epoxidated lignin to an epoxy resin mixture increases its adhesive shear strength and water-absorbing power. Based on the results of the study, it was proposed that lignin might be used in the manufacture of cheap epoxy resins [69]. An oxypropylation reaction can also be used in the case of other biopolymers, such as chitin and chitosan [70]. A general mechanism for this reaction is given schematically in [70], see **Figure 13**.

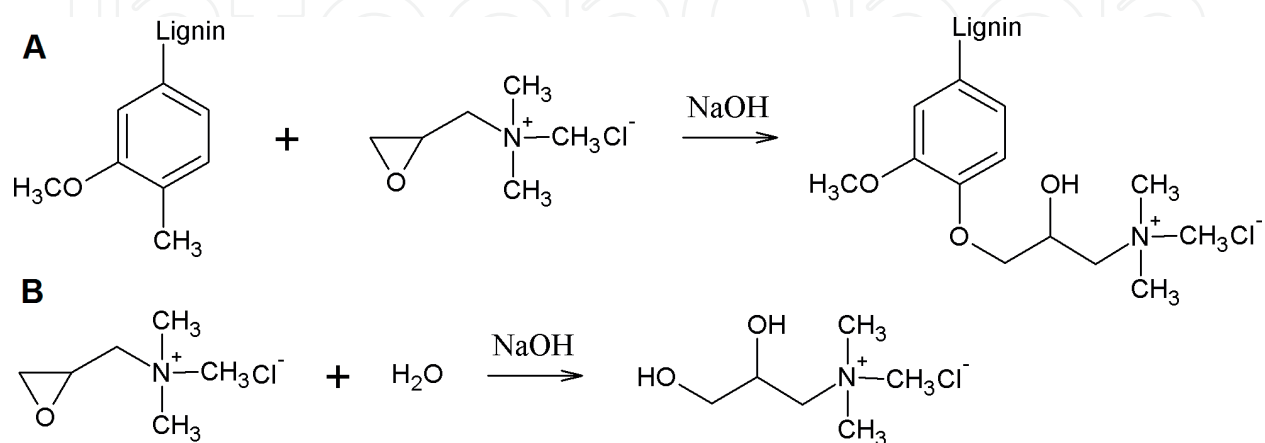


Figure 12. Mechanism of the cationization of lignin (A) and its hydrolysis (B), adapted from [67].

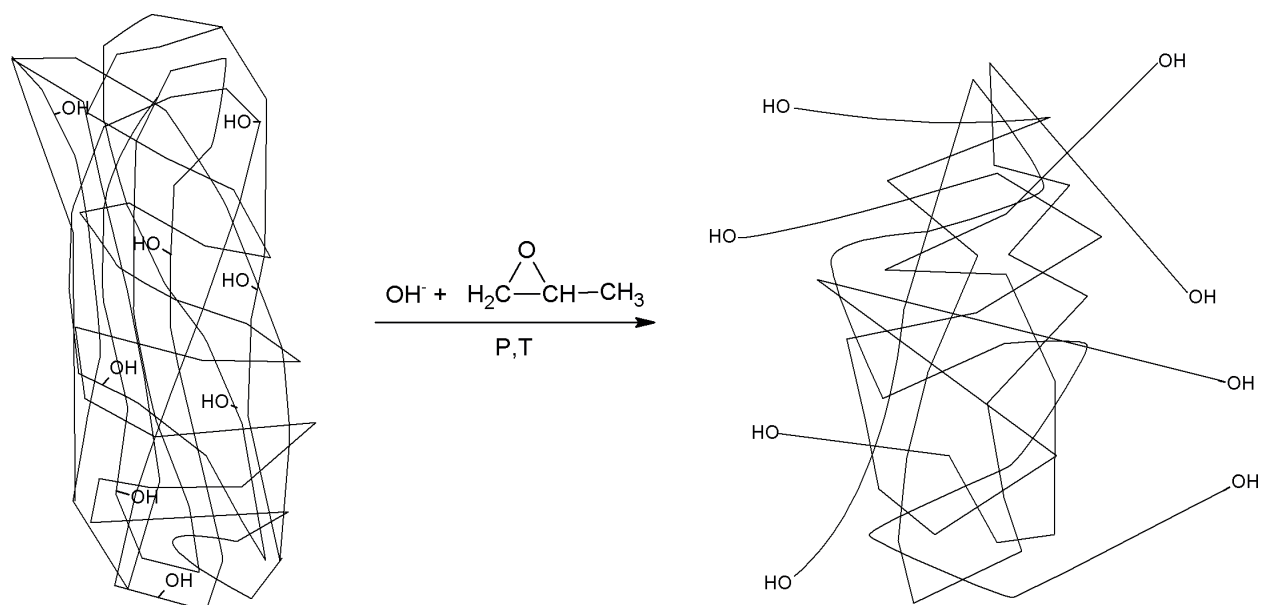


Figure 13. Schema for the oxypropylation (epoxidation) of hydroxyl groups in biopolymers, adapted from [70].

Esterification of lignin was investigated by Thielemans and Wool [71]. This modification was catalyzed using 1-methylimidazole, where acetic anhydride acted on the hydroxyl groups of lignin. At this stage, a cation is formed from N-alkyl-N'-methyl imidazolium, which acts on the hydroxyl group (aliphatic or aromatic). This leads to a protonated catalyst and acetylated lignin. The study showed that phenyl hydroxyl groups undergo acetylation significantly more easily. It was also found that the modification improves the solubility of lignin in styrene and butanoic acid, confirming its potential for use in the processing of thermosets [71].

An alternative focus of research is the optimization of the structure and degree of polymerization of the lignin molecule. For example, Duong et al. carried out polycondensation from sebacoyl chloride catalyzed with triethylamine [72]. The resulting material offered better thermal stability than kraft lignin, giving it potential for use in environmentally friendly composites [72].

Interest in the use of lignin in many areas of chemistry and everyday life is motivated by the high potential for its reproduction by plant organisms. The annual production of the biopolymer is certainly large enough not only to meet some of the demands for low-molecular-weight organic compounds obtained in refineries but also to serve as a functional material. This would also enable a reduction in atmospheric CO₂, which is taken up by plants and transformed into more complex compounds via photosynthesis. In addition, the use of lignin would appear to be favorable not only in terms of the trend toward policies focused on protecting the natural environment but also for economic reasons. Fluctuations in the prices of petroleum-based products therefore make lignin and other renewable biopolymers into attractive alternatives to the products currently in common use [70].

6. Summary and a look at the future

In recent years, many techniques and methods have been developed for the depolymerization and modification of lignin, making use of a variety of substances offering catalytic properties or the ability to dissolve the biopolymer. Nonetheless, their use in technological processes on a wider scale remains very limited. This is primarily a result of the lack of sufficient fundamental information on the structure of lignin itself, which makes it harder to gain a precise understanding of the mechanism of depolymerization and thus to propose appropriate means to enable its degradation, in addition to further optimization of the process. It is therefore important that wide-ranging research into lignin be continued, enabling its detailed physicochemical properties to be determined and consequently the most effective and efficient techniques to be developed for converting it into valuable products.

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