Lignin

Wood is composed of many chemical components, primarily extractives, carbohydrates, and lignin, which are distributed nonuniformly as the result of anatomical structure. Lignin is derived from the Latin term lignum, which means wood.[1] Anselme Payen (1838) was the first to recognize the composite nature of wood and referred to a carbon-rich substance as the "encrusting material" which embedded cellulose in the wood. Schulze (1865) later defined this encrusting material as lignin. Lignin has been described as a random, three-dimensional network polymer comprised of variously linked phenylpropane units.[2] Lignin is the second most abundant biological material on the planet, exceeded only by cellulose and hemicellulose, and comprises 15-25% of the dry weight of woody plants. This macromolecule plays a vital role in providing mechanical support to bind plant fibers together. Lignin also decreases the permeation of water through the cell walls of the xylem, thereby playing an intricate role in the transport of water and nutrients. Finally, lignin plays an important function in a plant's natural defense against degradation by impeding penetration of destructive enzymes through the cell wall. Although lignin is necessary to trees, it is undesirable in most chemical papermaking fibers and is removed by pulping and bleaching processes.

1.1.1 *Biosynthesis*

Plant lignins can be broadly divided into three classes: softwood (gymnosperm), hardwood (angiosperm) and grass or annual plant (graminaceous) lignin.[3] Three different phenylpropane units, or monolignols, are responsible for lignin biosynthesis.[4] Guaiacyl lignin is composed principally of coniferyl alcohol units, while guaiacyl-syringyl lignin contains monomeric units from coniferyl and sinapyl alcohol. In general, guaiacyl lignin is found in softwoods while guaiacyl-syringyl lignin is present in hardwoods. Graminaceous lignin is composed mainly of *p*-coumaryl alcohol units. These three lignin precursors are shown in Figure 1. The principles employed in Figure 1 to denote carbon atoms in the side chain will hold throughout this paper.
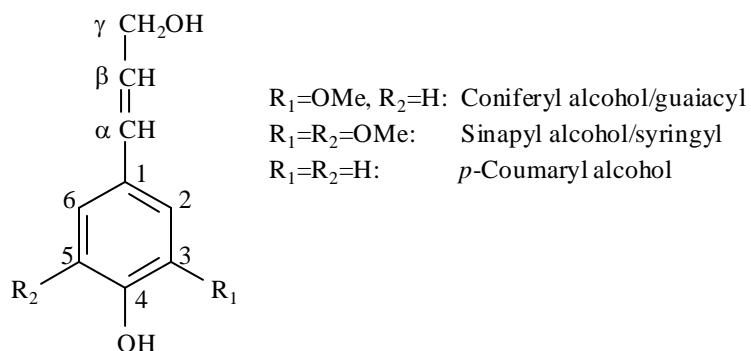
Figure 1. The three building blocks of lignin.

Lignin polymerization is initiated by oxidation of the phenylpropane phenolic hydroxyl groups. Freudenberg has shown that lignin precursors undergo dimerization through enzymatic dehydrogenation, which is initiated by an electron transfer and yields resonance-stabilized phenoxy radicals. Figure 2 shows an example of a phenoxy radical formed from coniferyl alcohol and its resonance forms. Stabilization of the radical occurs by coupling to another radical in any of the positions of the unpaired electron.
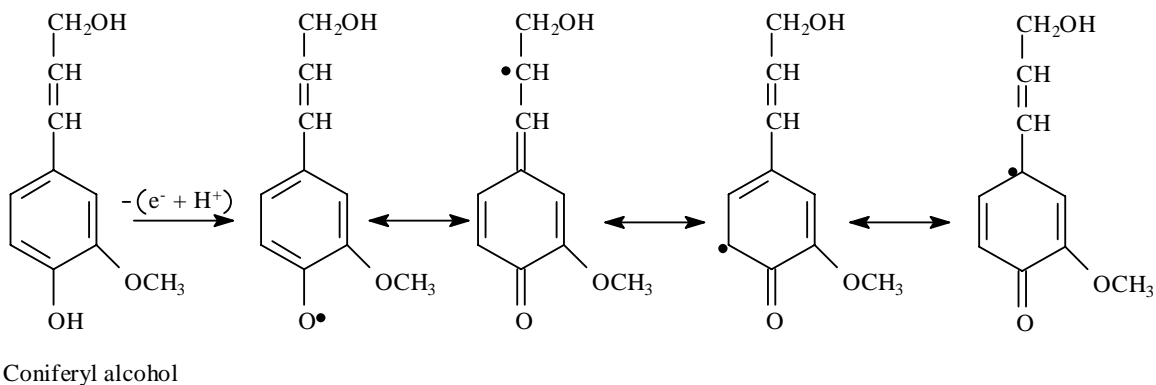

Figure 2. Formation of resonance-stabilized phenoxyl radicals by enzymatic dehydrogenation of coniferyl alcohol.

A monolignol free radical can then undergo radical coupling reactions, producing a variety of dimers, termed dilignols. The combination of monomeric radicals through only β-O-4 and β-5 coupling would lead to a linear polymer. However, branching of the

polymer may take place through subsequent nucleophilic attack by water, alcohols or phenolic hydroxyl groups on the benzyl carbon of the quinone methide intermediate. The dilignols then undergo further endwise polymerization, instead of combining with one another.. Figure 3 shows an example of endwise polymerization during lignin biosynthesis.
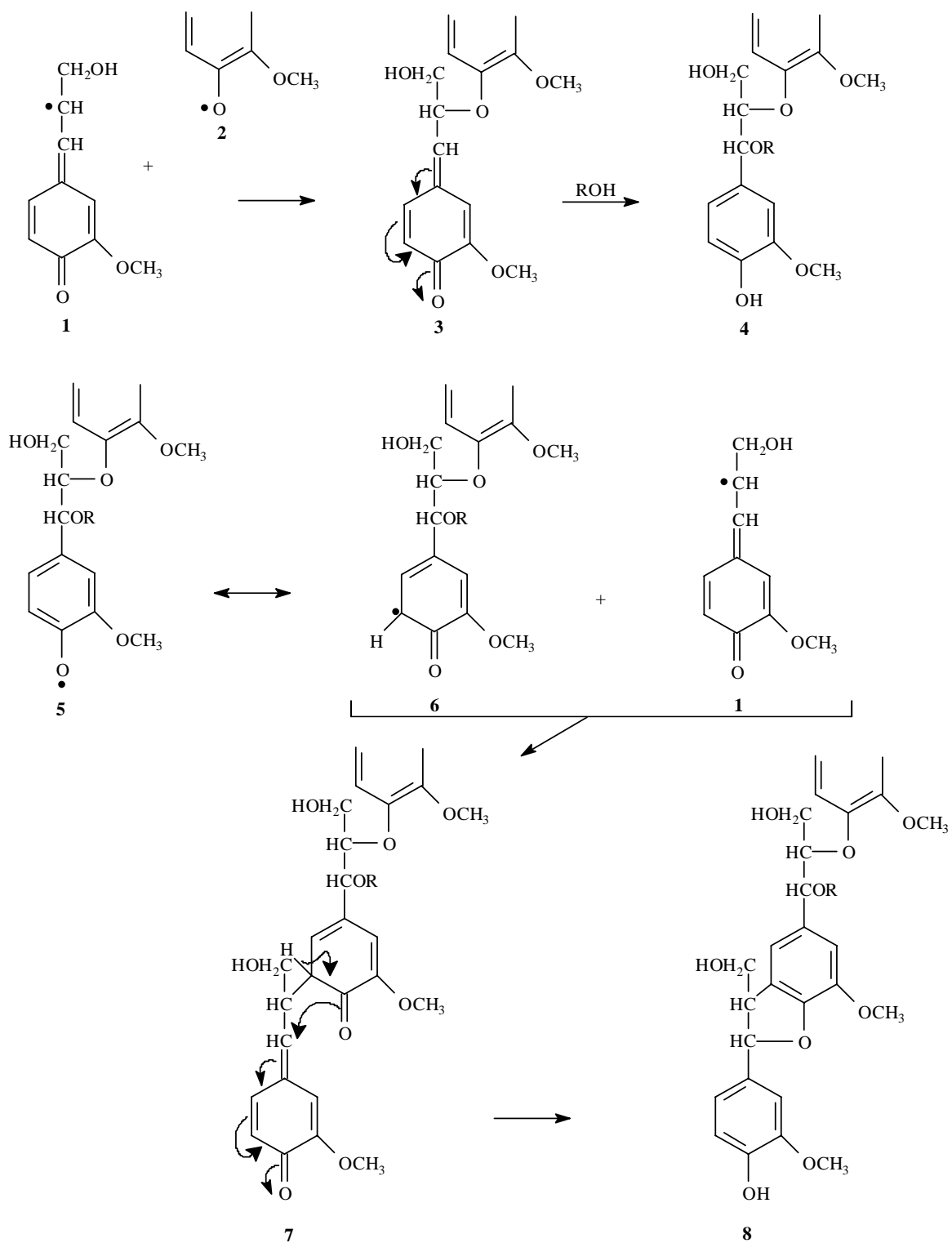
Figure 3.   Endwise polymerization during lignin biosynthesis.

1.1.2 Structure

After many years of study, the structure of native lignin still remains unclear. However, the dominant structures in lignin have been elucidated as the methods for identification of the degradation products and for the synthesis of model compounds have improved. The results from these numerous studies have yielded what is believed to be an accurate representation of the structure of lignin. Examples of the elucidated structural features of lignin include the dominant linkages between the phenylpropane units and their abundance, as well as the abundance and frequency of some functional groups. Linkages between the phenylpropane units and the various functional groups on these units give lignin a unique and very complex structure.

Figure 4 shows some of the common linkages found in softwood lignin. The dominant linkage is the β-O-4 linkage. In 1995, Karhunen *et al*. discovered a new 8-membered ring linkage in softwood lignin called dibenzodioxocin.[5] This linkage was found through advanced 2-D NMR techniques and is now proposed to be the main branching point in softwood ligniN. The percent abundance of this and other linkages found in softwood lignin has been determined and is shown in Table 1.

The lignin macromolecule also contains a variety of functional groups that have an impact on its reactivity. Lignin mostly contains methoxyl groups, phenolic hydroxyl groups, and few terminal aldehyde groups. Only a small proportion of the phenolic hydroxyl groups are free since most are occupied in linkages to neighboring phenylpropane linkages. Carbonyl and alcoholic hydroxyl groups are incorporated into the lignin structure during enzymatic dehydrogenation. Table 2 illustrates the frequency of some common functional groups found in lignin.
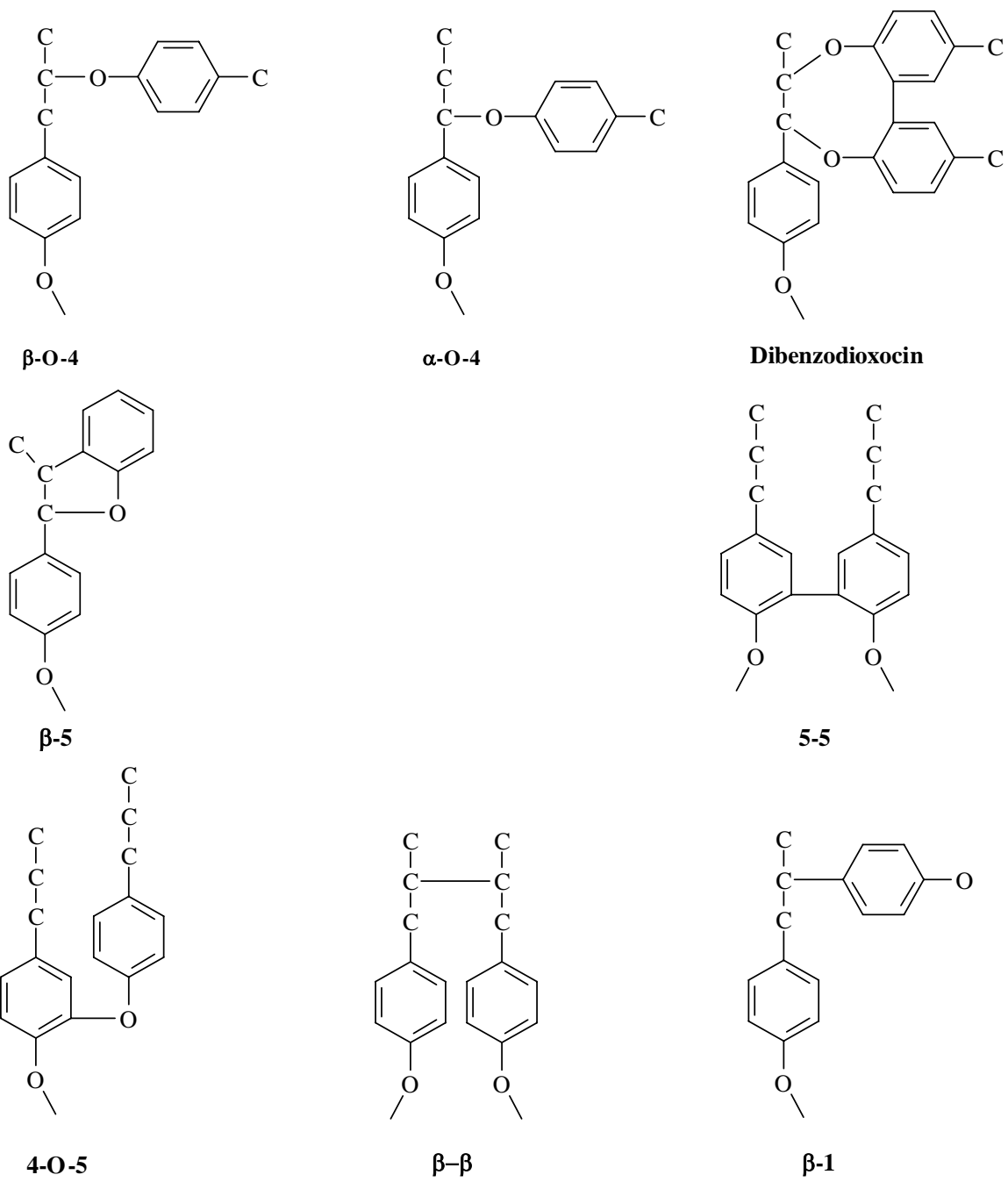
β-O-4 **α-O-4** **Dibenzodioxocin**

β-5 **5-5**

4-O-5 **β–β** **β-1**

Figure 4. **Common phenylpropane linkages in lignin.**

Table 1.   Linkages found in softwood lignin.

Linkage Type	Dimer Structure	Percent of Total Linkages (%)
β-O-4	Phenylpropane β–aryl ether	45-50
5-5	Biphenyl and Dibenzodioxocin	18-25
β -5	Phenylcoumaran	9-12
β-1	1,2-Diaryl propane	7-10
α-O-4	Phenylpropane α–aryl ether	6-8
4-O-5	Diaryl ether	4-8
β - β	β-β-linked structures	3

Table 2.   Functional groups in softwood lignin per 100 phenyl propane units.

Functional Group	Abundance per 100 C9 units
Carbonyl	10-15
Benzyl alcohol	15-20
Phenolic hydroxyl (free)	15-30
Methoxyl	92-96

The nature of the lignin polymerization reactions results in the formation of a three-dimensional, highly-branched, interlocking network of essentially infinite molecular weight. Figure 5 is a schematic representation of a softwood lignin proposed by Adler[6] and later modified by Karhunen *et al*. This model was constructed based on the analysis of various linkages and functional groups. The phenylpropane (C_9 or C_6C_3) units in lignin are connected by C-C and ether (C-O-C) linkages. The frequency of such linkages is believed to have significant consequences on the lignin's overall reactivity toward the delignification process. It is important to note that the model proposed by Adler and Karhunen *et al*. does not depict the actual structure of lignin. Instead, it serves as a tool to visualize the linkages and functional groups believed to occur in lignin.
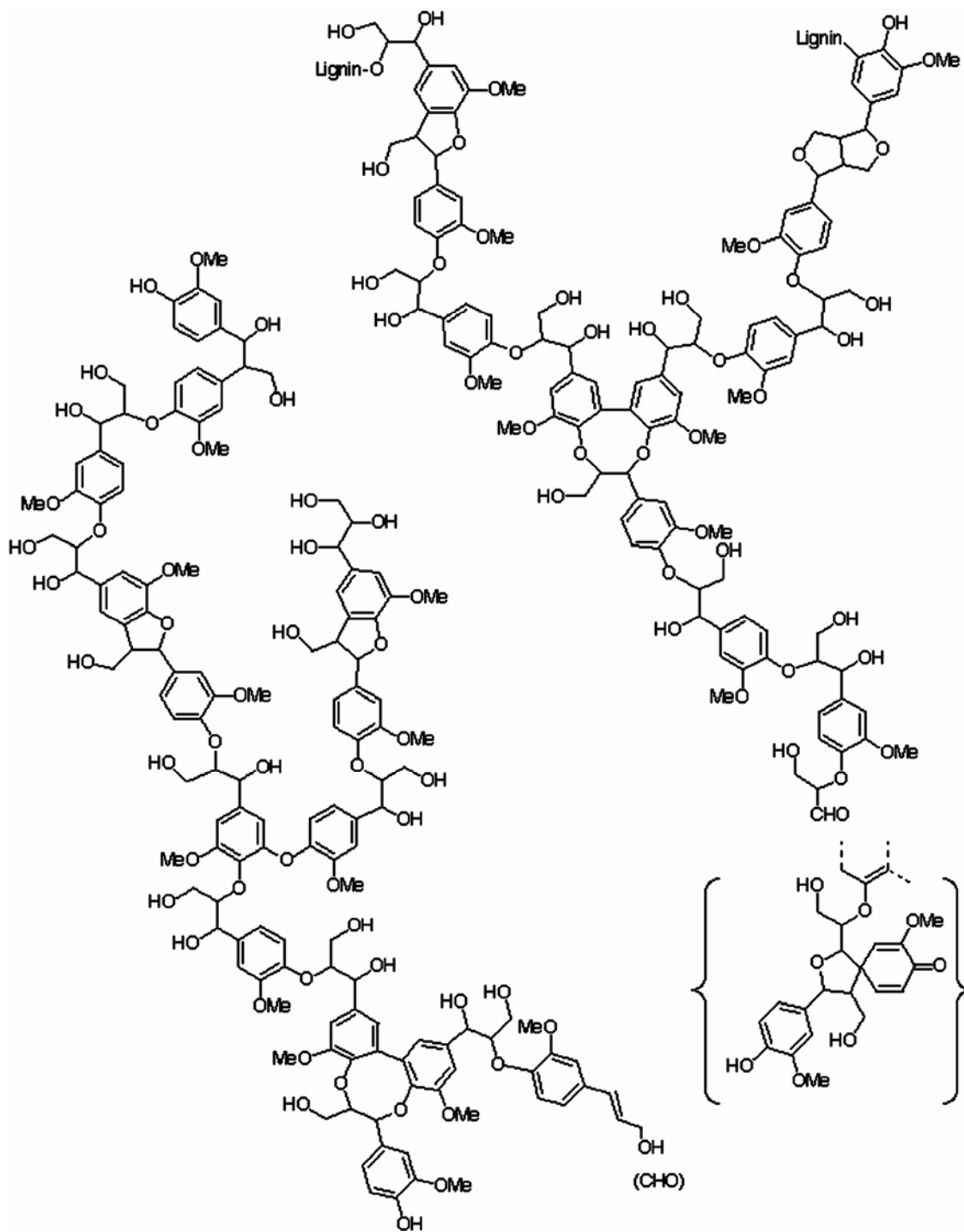
Figure 5. **Structural model of softwood lignin.**

Studies have also suggested that covalent linkages between lignin and hemicelluloses exist in native wood.[7] These structures are typically referred to as lignin-carbohydrate complexes or simply LCCs. The lignin is covalently bound to the hemicellulose which, in turn, is bound to cellulose through extensive hydrogen bonding. Lignin-carbohydrate complexes could be very important when considering pulping of wood since lignin is chemically bound to the cellulose.

Kraft Pulping

Brief Overview

Chemical pulping is a means of removing lignin from wood (delignification) by chemically altering it to produce soluble fragments of the polymer. The removal of lignin allows individual fibers to be freed from the wood matrix with mild mechanical treatment. Pulping must be able to remove lignin from fibers through chemical degradation, while minimizing damage to the cellulosic portion of the fibers to maintain strength. In 2001, the world pulp production was over 180 million metric tons. The United States produced 53 million metric tons; 85 percent of this was from chemical pulping. The kraft pulping process was the most commonly used chemical pulping process, accounting for 98 percent of chemical pulp production in the United States and 92 percent of chemical pulp production in the world.[8]

In an effort to help industrialize the modern papermaking process, Hugh and Burgess developed and patented an alkaline pulping process in 1854 that utilized wood as the raw material, since wood was rather inexpensive and was in ample supply. This alkaline pulping process involved treating wood shavings with sodium hydroxide under elevated temperature conditions. Since the source of sodium hydroxide was from caustic soda, this alkaline pulping process was called the soda process. C.F. Dahl, a German chemist, later developed the sulfate or kraft process in 1879 when he replaced the sodium carbonate or soda ash in the recovery cycle with sodium sulfate. The sodium sulfate was reduced by the burning of organic matter to sodium sulfide and was then used in this

form to prepare the pulping liquor. The pulp produced from this alkaline pulping process, although dark in color, made a paper that was far stronger than any paper up to this time. The paper, and the process for making it, was hence given the name "kraft" which means strength or power in Swedish and German.

Although in use since 1879, the kraft pulping process remains the dominant commercial pulping process today. One major reason for its predominance is that the kraft process produces stronger pulps than any other pulping process. In addition, it is insensitive to the presence of bark and high amounts of extractives and has been found to be adaptable to both hardwood and softwood tree species. The kraft process requires shorter cooking times than other chemical pulping processes. Finally, efficient recovery of pulping chemicals and the production of heat and valuable materials from by-products such as tall oil and turpentine from pine species has been a strong asset to the kraft pulping process. However, there are several disadvantages to kraft pulping which include high capital investments, high reaction temperatures, low pulp yields, the foul odor generated by degradation products, and the dark color of the resulting pulps.

During the kraft pulping process, wood chips are treated with a mixture of sodium sulfide (Na_2S) and sodium hydroxide (NaOH), also known as white liquor, at elevated temperatures to produce a pulp suitable for the manufacture of paper and related products. The white liquor and the wood chips are charged to a large pressure vessel called a digester. The temperature in the digester is increased to approximately 170°C for roughly two hours, depending on the degree of delignification desired. The hydroxide and hydrosulfide anions react with lignin during this treatment, causing he polymer to fragment into smaller alkali/water soluble fragments. The sulfide accelerates the pulping process; therefore, the wood chips are exposed to high temperatures and alkaline conditions for a shorter period of time than in other alkaline pulping processes like the soda process, thereby producing a pulp that is much stronger than soda pulp.[9]

Kraft delignification occurs by modifying the structure of lignin in two different ways to enhance its dissolution. The first is to degrade the lignin into smaller units by cleaving interunit linkages. The second is to introduce hydrophilic groups into the polymer and cleaved fragments, making the lignin more soluble in the cooking liquor. These phenomena occur when linkages holding the phenylpropane units together are cleaved, thereby generating free phenolic hydroxyl groups. The presence of these hydroxyl groups increases the hydrophilicity of the lignin and lignin fragments. Thus, the solubility of the lignin in the cooking liquor is increased. Meanwhile, the carbon-carbon linkages, being more stable, tend to survive the kraft pulping process.[10]

There are three fairly distinct phases of delignification during kraft pulping which include the initial phase, bulk phase, and residual or final phase. The three phases of delignification are shown in Figure 6.[11] The initial phase of delignification, taking place at temperatures below 150°C, has been characterized as a rather unspecific alkaline extraction leading to the dissolution of approximately 15-20% lignin and 20-25% of the carbohydrates present in the wood. The delignification rate during this phase is first order with respect to lignin concentration and independent of the hydroxide and hydrosulfide ion concentrations, provided minimum threshold amounts of these ions are used. The activation energy of the initial delignification (61 kJ/mol) indicates that the rate of the process is diffusion- rather than chemically controlled. As the cook proceeds above 150°C, the bulk phase of delignification begins. The bulk phase includes the heating period from 150°C to 170°C and the cooking treatment at 170°C, and results in the dissolution of the main portion (about 60%) of the lignin present in wood. Bulk delignification is first order with respect to lignin concentration, almost linearly dependent on the hydroxide, but only slightly dependent on the hydrosulfide ion concentration. The activation energy of this phase of lignin degradation was found to be 150 kJ/mol, which is of the magnitude typically encountered in chemical reactions. The residual phase of delignification includes the final treatment at 170°C and leads to dissolution of roughly 10-15% of the lignin originally present in wood. This process is

very slow, the rate being dependent on the temperature and hydroxide ion concentration, but almost independent of the hydrosulfide ion concentration. The activation energy was found to be about 120 kJ/mol. The selectivity for lignin in this phase is poor, as evidenced from an increased degradation of carbohydrates relative to the rate of delignification. The cook should be terminated at this point to prevent significant loss of pulp strength, and the remaining residual lignin should be removed using alternative delignification techniques, such as bleaching.
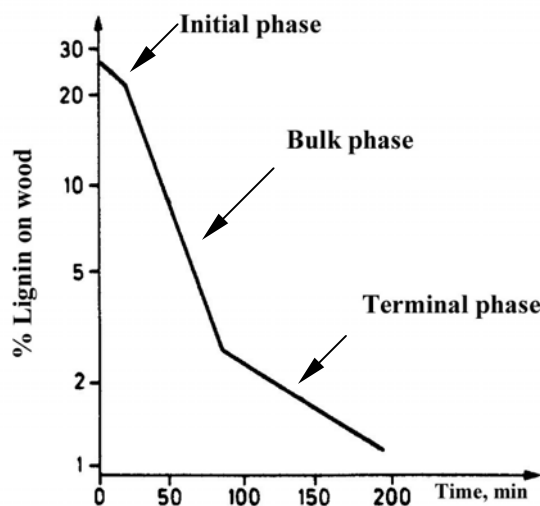

Figure 6.   Lignin content (% on wood) versus reaction time for conventional softwood kraft pulping [45].

The residual or remaining lignin content of a typical conventional softwood kraft cook is in the range of 4-5% or 27-33 kappa number. Pulping to lower lignin content under these conditions causes severe degradation of the carbohydrate fraction, resulting in a pulp with poor papermaking qualities. The low rate of lignin dissolution could possibly be ascribed to the fact that while reactions in the residual phase require high alkalinity, the concentration of alkali at this stage of pulping is considerably lower than during the preceding phases due to neutralization reactions with various degradation products, particularly those arising from carbohydrates. Acids formed during the degradation of carbohydrate degradation consume 60-70% of the charged alkali while 10% of the added

alkali is used to neutralize uronic and acetic acids and 20-30% is consumed in solubilizing the degradation products of lignin. It is also possible that the degree of swelling decreases as a result of alkali shortage. A fiber wall in an unswelled state may resist diffusion. It has also been shown that dissolved lignin is precipitated inside the fibers when the alkalinity is lowered. It is therefore possible that a partially reversible precipitation of degraded but not dissolved lignins occurs when the alkalinity is lowered. Another reason for the poor selectivity of the residual phase of delignification is that the structure of the residual lignin that remains in the fiber at the end of the cook has a low reactivity toward the pulping chemicals, thereby making fragmentation and dissolution difficult [49, 50]. Alternatively, several researchers have proposed that lignin dissolution is hindered by the attachment of the residual lignin to carbohydrates.[12]

1.1.3 *Delignification Chemistry*

The primary reactions of lignins during kraft pulping can be divided into two classes, degradation and condensation reactions. Degradation reactions lead to the liberation of lignin fragments and ultimately to their dissolution. These degradation reactions are therefore desirable to kraft pulping. Condensation reactions lead to the formation of alkali-stable linkages, thereby increasing the molecular size of lignin fragments and may result in their precipitation. Although having an opposite effect, these two types of reactions are intimately connected with each other by proceeding via common intermediates. There are other types of reactions occurring during kraft pulping. These reactions do not involve any net fragmentation of the lignin macromolecule, yet yield alkali-stable structures that make additional fragmentation difficult. Carbohydrates undergo similar reactions to lignin during the kraft pulping process. The reactions undergone by lignin and carbohydrates during the kraft pulping process allow both polymers to become partially hydrophilic, thereby enabling solubilization of polymer fragments into the alkaline liquor during kraft pulping. The following is a general overview of the degradation, condensation, and other types of reactions that occur during kraft pulping.

1.1.3.1 Degradation reactions

Degradation or fragmentation reactions are the most important reactions occurring during kraft pulping because these reactions assist in the fragmentation and dissolution of the lignin polymer. The most prevalent degradation reactions occurring during kraft pulping include the cleavage of α-aryl ether and β-aryl ether bonds. However, the reactivity of such linkages is sensitive to the type of moiety (i.e., free or etherified phenolic group) present at the para position relative to the propane side chain. The α-aryl ether linkage is readily cleaved, the reaction involving an alkali-assisted rearrangement of the phenolate structure to the corresponding quinone methide structure with elimination of the α-aroxy substituent. Figure 7 illustrates this type of cleavage. Since no hydrosulfide ions are involved in the cleavage of α-aryl ether bonds, the rate of reaction is also independent of the concentration of these ions.
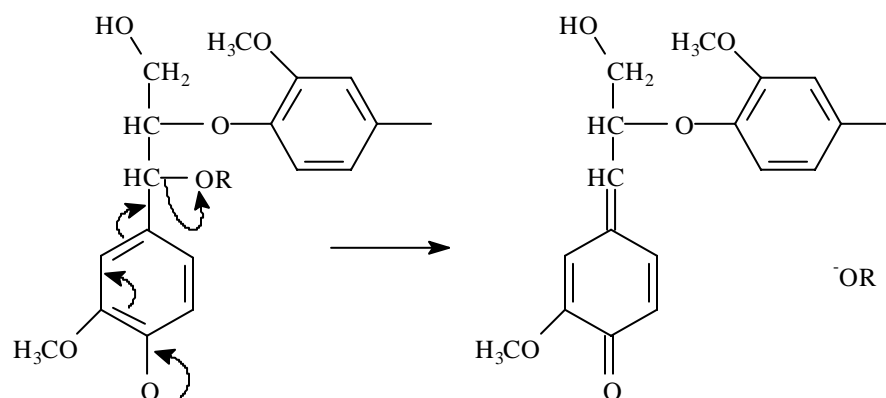

Figure 7.   Alkaline cleavage of α-aryl ether bonds in phenolic phenylpropane units.

As is true for the cleavage of α-aryl ether bonds, the cleavage of β-aryl ether bonds in phenolic units proceeds rapidly, with the initial conversion into the quinone methide constituting the rate determining step in the overall reaction. Phenolic β-aryl ether structures can also undergo an alkali-assisted transformation into a quinone methide, provided a suitable leaving group exists at the α-position of the propane side chain. The

quinone methide intermediate can then react in different ways to restore the aromaticity of the aromatic ring. The quinone methide could be converted into an alkali-stable enol ether structure through the elimination of the terminal hydroxymethyl group as formaldehyde. This reaction is more prominent in the absence of hydrosulfide ions, as is the case during soda pulping. However, enol ether structures have been detected in kraft residual lignin and this reaction pathway is therefore possible.

Under kraft pulping conditions, the hydrosulfide ion, which is a stronger nucleophile than hydroxide ion, readily reacts with the quinone methide intermediate to restore the aromaticity of the aromatic ring. The reversible addition of hydrosulfide ions results in the formation of a benzyl mercaptide structure. This mercaptide anion can then attack the β-carbon, through a neighboring group participation reaction, thereby forming a thiirane intermediate and eliminating the β-aroxy substituent. The intermediary thiirane structure can then lose elemental sulfur, generating a coniferyl alcohol-type structure. Although the presence of hydrosulfide ions is believed to influence the reaction pathway resulting in the fragmentation of the aryl ether linkage, enol structures have been detected in kraft residual lignin, suggesting that both reaction pathways in Figure 8 can occur during kraft pulping. The initial phase of delignification is characterized by diffusion-control and low activation energy (61 kJ/mol). Therefore, any fragmentation reactions that occur during this phase must occur at the same or higher rate than diffusion. This requirement is met by the cleavage of α- and β-aryl ether linkages in phenolic units. Thus, the degradation of lignin during the initial phase, involving only phenolic units, may continue until it reaches units which are not of the α- or β-aryl ether type (peeling of lignin).

Enol Ether

-CH$_2$O
-H$^+$

-($^-$OR)

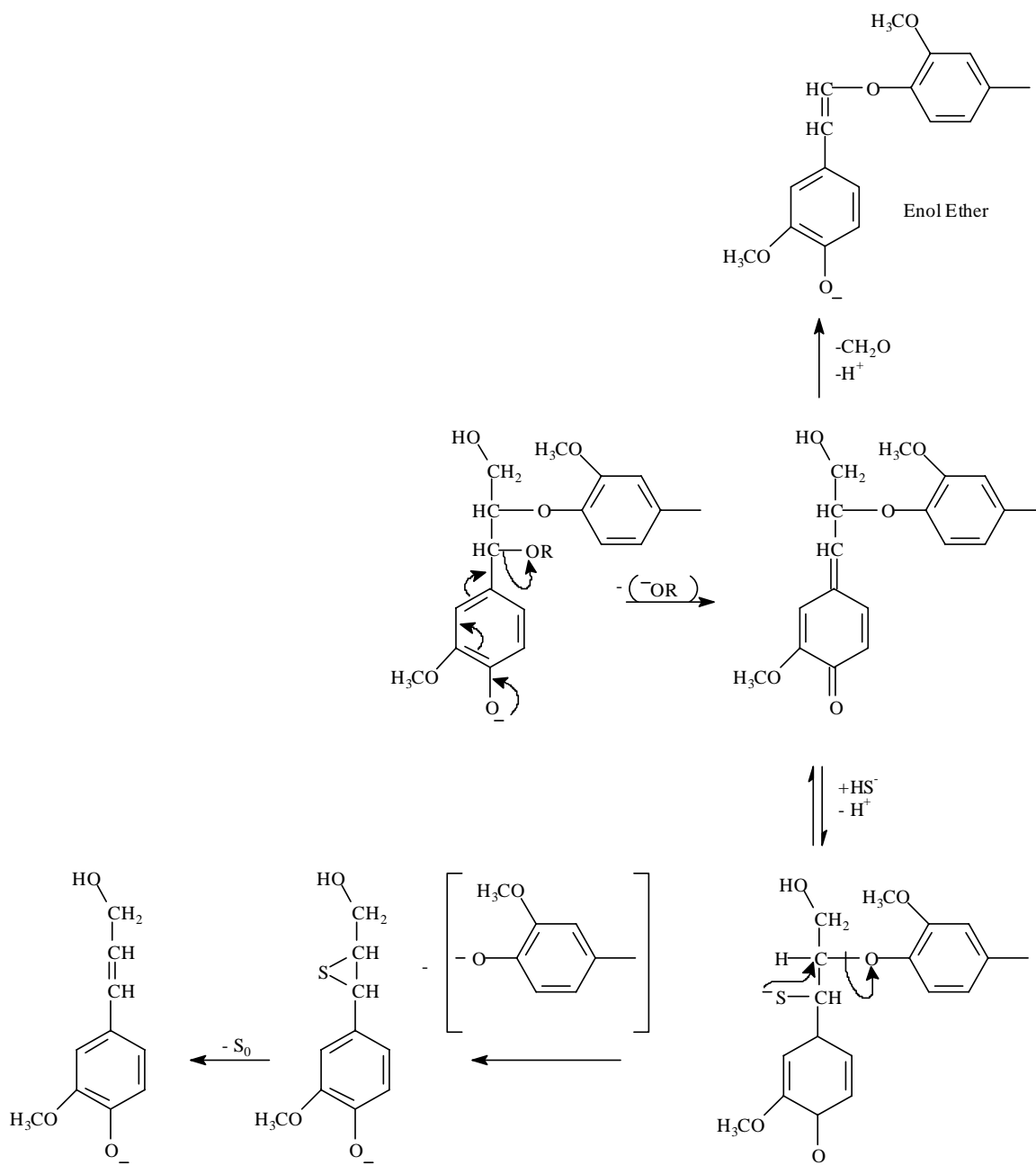+HS$^-$
- H$^+$

- S$_0$

-

Figure 8. **Sulfidolytic cleavage of β-aryl ether bonds in phenolic phenylpropane units and conversion into enol-ether units.**

When all phenolic units of the α- and β−aryl ether types, both those originally present and those liberated during the initial phase, have reacted, further lignin degradation requires more drastic conditions such as those prevailing during the bulk phase of

delignification. Cleavage of α− and β-aryl ether linkages in phenolic units, proceeding much faster, cannot be rate-determining during this phase. Instead, on account of similarities between the kinetic data, the cleavage of β-aryl ether bonds in non-phenolic units may be considered as the rate determining reaction in the overall bulk delignification. The cleavage of β-aryl ether linkages in non-phenolic structures is a relatively slow reaction that is dependent on the phenylpropane units having a hydroxyl group on the α− or γ-carbon. This group can dissociate under extreme alkaline conditions, forming an alkoxide anion. A nucleophilic attack on the β-carbon, through a neighboring group participation reaction, results in an oxirane intermediate with concomitant elimination of the β−aroxy substituent. Subsequent attack by the nucleophiles found in the cooking liquor (hydroxide and hydrosulfide ions) breaks the epoxide ring, producing diols or thioglycol-type structures as shown in Figure 9. Since hydrosulfide ions do not participate to an appreciable extent, the rate of cleavage of non-phenolic β-aryl ether linkages is independent of their concentration.
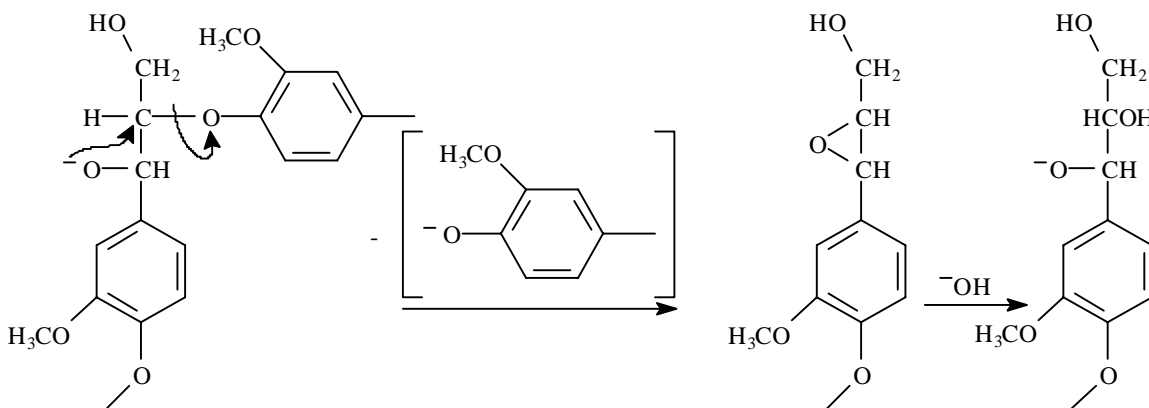

Figure 9.   Alkaline cleavage of β-aryl ether bonds in non-phenolic phenylpropane units.

Cleavage of β-aryl ether linkages in non-phenolic units also liberates new phenolic structures that may constitute the starting point for the two types of cleavage reactions operating during the initial phase, i.e., cleavage of α- and β-aryl ether bonds in phenolic

units. As a result of these reactions, lignin degradation during the bulk phase, initiated by the rate determining cleavage of β-aryl ether bonds in non-phenolic units, is extended to the point where dissolution takes place. Thus the subsequent fast reactions have no influence on the rate, but a great influence on the extent of lignin degradation. In this way, they contribute extensively to the rate of lignin dissolution during the bulk phase.

Unlike the fragmentation reactions of ether linkages, the cleavage of carbon-carbon bonds during kraft pulping accounts for only a small amount of the total lignin fragmentation. This cleavage occurs in side chains and between side chains and aromatic nuclei, often resulting in the formation of new carbonyl linkages. An example of the cleavage of carbon-carbon linkages is illustrated in Figure 10 with the retrograde aldol reactions.
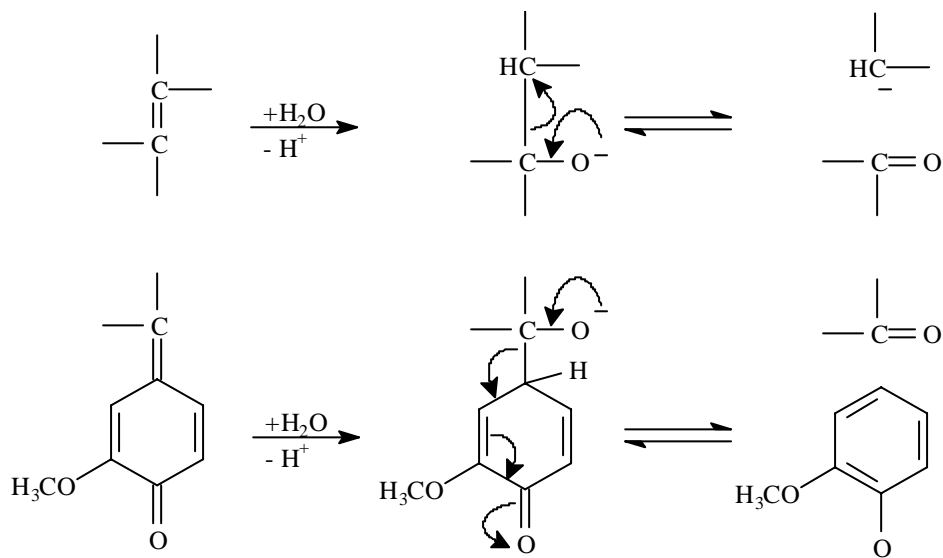

Figure 10. Alkaline cleavage of carbon-carbon linkages by retrograde aldol reactions.

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1.1.3.2 Condensation reactions

The degradation and fragmentation reactions are believed to be counter-balanced by condensation reactions during kraft pulping. Primary condensation reactions occur when quinone methide intermediates are formed by the elimination of an α-substituent while secondary condensation reactions occur with quinone methide structures formed after an initial ether cleavage. Condensation reactions may be viewed as conjugate additions (Michael reactions) in which quinone methides, extended quinone methides or side chain enone structures function as acceptors, and carbanions from phenolic or enolic units serve as adding nucleophiles.

Figure 11 illustrates the alkali-promoted condensation of phenolic units.   In these reactions, formaldehyde, liberated from quinone methide intermediates, constitutes another important acceptor for carbanions from phenolic structures. A hydroxybenzyl alcohol is generated from the addition of a carbanion to a quinone methide intermediate. This primary addition product is converted to the corresponding *o*-quinone methide. Another carbanion reacts with the *o*-quinone methide, affording the corresponding diarylmethane structure. The role of formaldehyde in cross-linking lignin units has been recently question in several publications.

The external nucleophiles (hydroxide and hydrosulfide ions) present in the cooking liquor have to compete with internal nucleophiles, in particular carbanions from phenolic and enolic structures, for quinone methide structures. The addition step of the nucleophile to the quinone methide is reversible and is therefore dependent on not only the nucleophilicity of the species, but also the ability of the addition product to undergo a fast irreversible reaction. Thus, in structures containing a good leaving group (e.g. the aroxy substituent or R=OAr) at the β−carbon, fragmentation by neighboring group participation reactions will outweigh condensation reactions by virtue of the greater nucleophilicity of the external nucleophile (hydroxide and hydrosulfide ions) compared to the internal competitors or carbanions. However, if the quinone methide structure has a β-substituent

that cannot be readily eliminated (e.g. alkyl or aryl groups), the addition of an internal nucleophile, like cyclohexadienone, is followed by a fast, irreversible proton abstraction and subsequent rearomatization reaction step. This competitive addition between external and internal nucleophiles is outlined in Figure 12. Thus, the external nucleophiles, although stronger in some cases than their internal counterparts, do not prevent, but possibly retard condensation reactions.
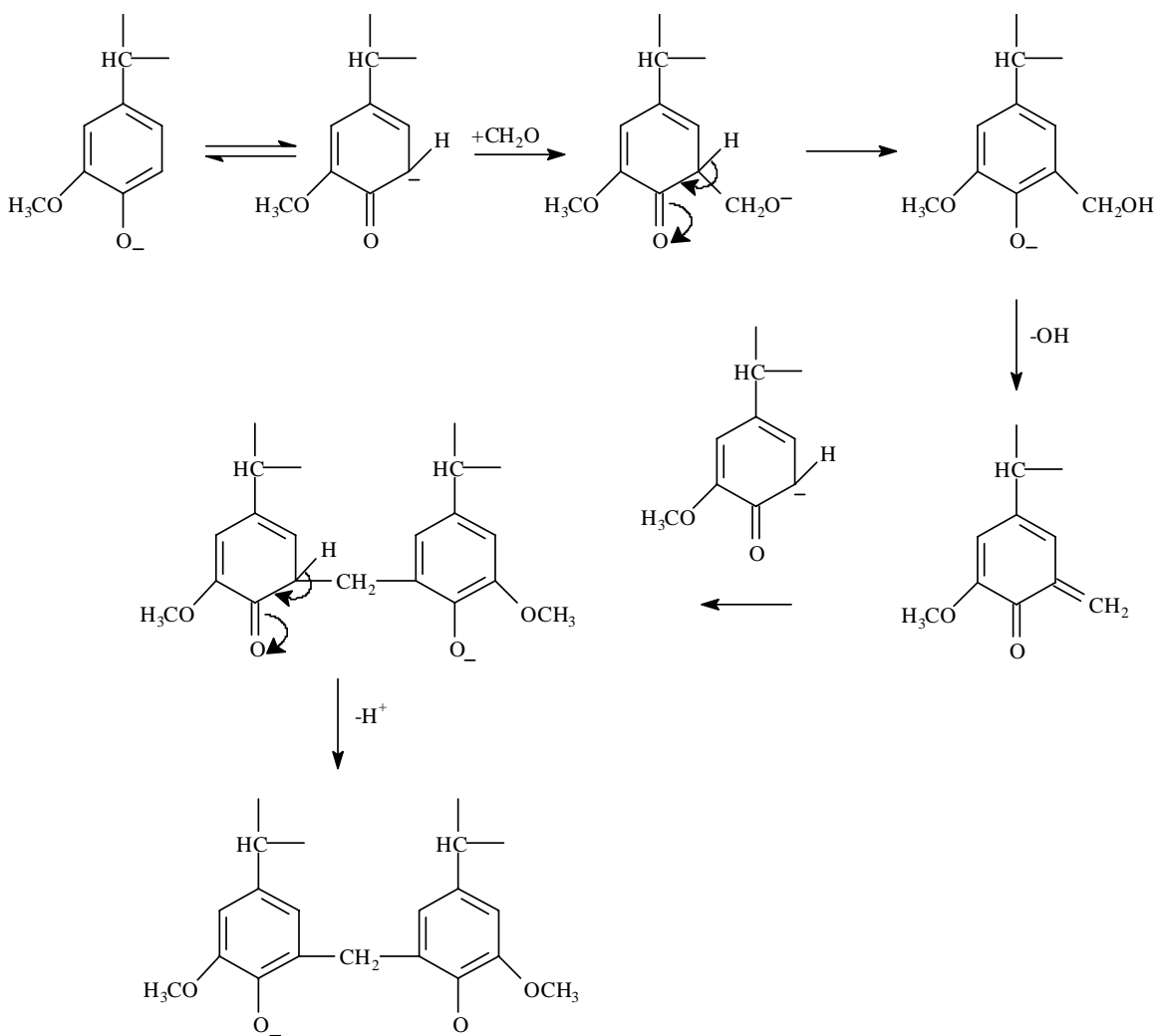
Figure 11.   Alkali-promoted condensation reaction of phenolic units.
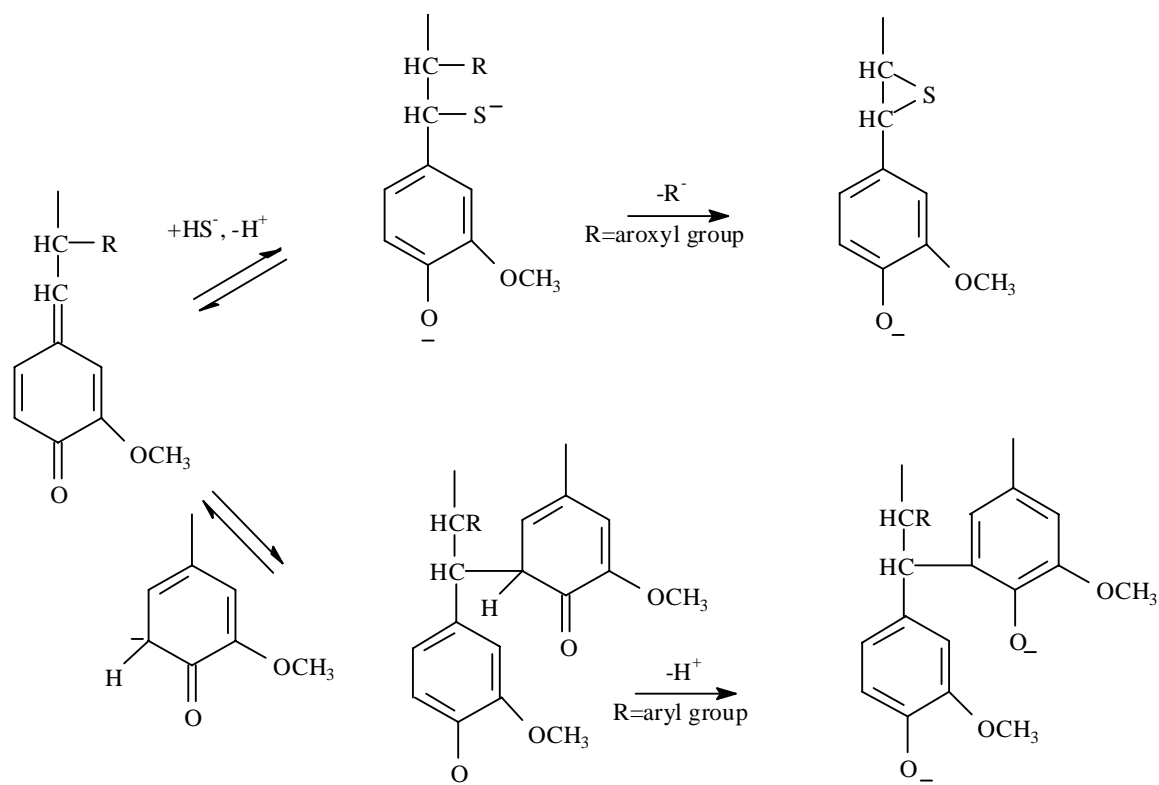
Figure 12.   Competitive addition of external and internal nucleophiles to quinone methide intermediates. OAr=aroxy group; Ar=aryl group.

In general, condensation reactions counteract lignin degradation and fragmentation reactions. However, in certain instances, the initial condensation may be followed by a fragmentation step. Figure 13 depicts possible fragmentation reactions that occur after condensation reactions. Gierer *et al*. found that primary condensation products may subsequently undergo neighboring group participation reactions, resulting in cleavage of the β-aryl ether linkage.[13] There are several types of fragmentation reactions that have been observed with condensation products from β-aryl ether structures.   In these products, the original condensed phenolic structure, in its ionized form, attacks the β-carbon atom and eliminates the β-aroxy substituent. As a result these aryl (upper reaction in Figure 13) and phenolate ion (lower reaction in Figure 13) participation reactions give rise to stilbene and phenylcoumaran, respectively.
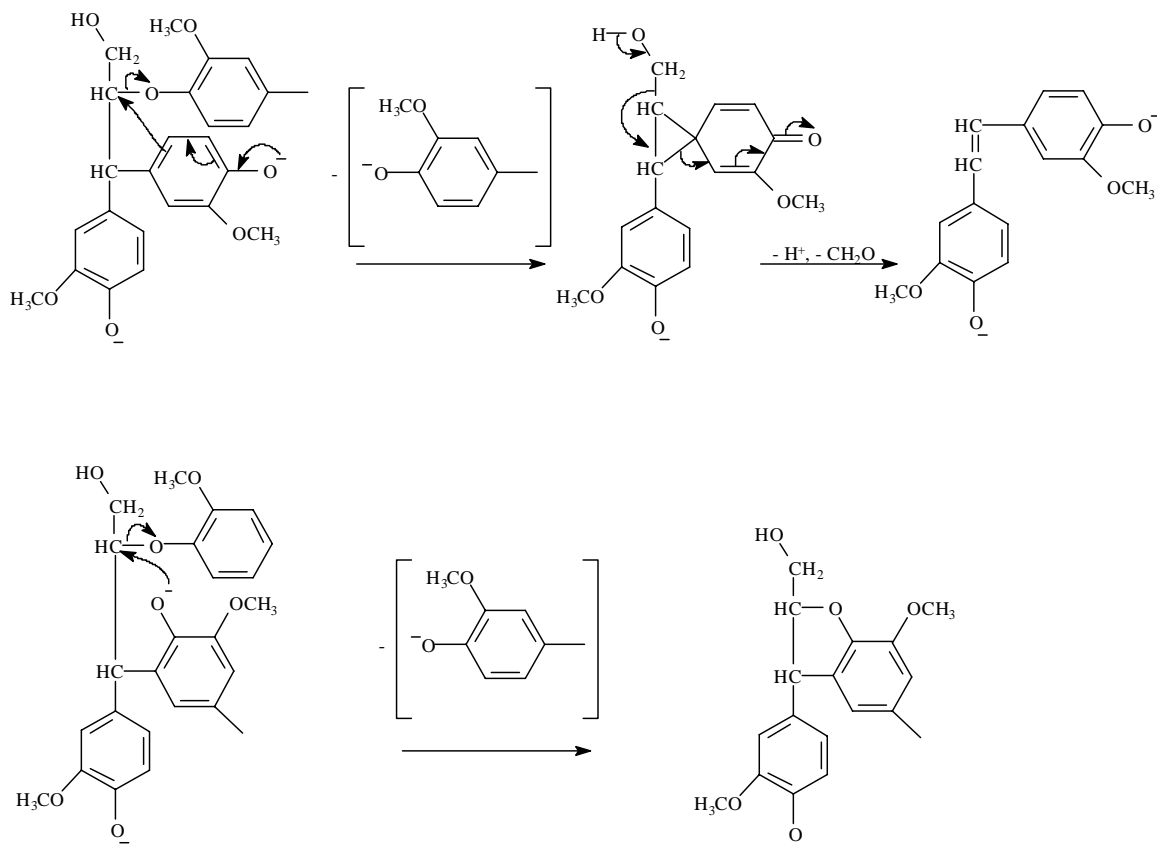
Figure 13. β-Aryl cleavage with participation of condensed phenolic structures.

Gierer *et al*. have shown that fragmentation reactions may follow the initial condensation reactions through model compound studies and by cooking extracted spruce wood meal in the presence of xylenol under conditions similar to a kraft cook (white liquor, heated to 170°C). They found that there are several requirements to be met if the neighboring group participation reactions after condensation are to occur. First, the structure must contain a free phenolic hydroxyl group and an α-substituent that can be eliminated to give a quinone methide intermediate. Second, the added phenol has to compete successfully with external nucleophiles present in the cooking liquor for the quinone methide intermediate. Finally, the phenolic β-aryl ether structure must not be condensed to an adjacent phenyl propane unit at the C5 position.

Condensation reactions in kraft pulping have been the subject of much debate. Axegard and Wiken knew of the possibility that formaldehyde, which is formed during a kraft cook, might cause lignin condensation, as depicted in Figure 11.[14] These researchers tested this hypothesis by soaking wood chips in formaldehyde. Their results indicated that residual lignin is not caused by formaldehyde condensation. Meanwhile, Robert *et al*. [58] investigated structural changes in dissolved kraft lignins to further elucidate the chemistry of the kraft cooking process. In this research, it was not possible to find any clear indication of condensation reactions assumed to contribute to the slow rate of delignification in the residual phase of the kraft cook. Studies by Gellerstedt and Lindfors on the structural changes of lignin during kraft pulping showed that no comprehensive condensation involving the aromatic rings of the residual lignin had taken place during the cook.[15] The same conclusion seemed also valid for a soda pulp that gave analytical data very similar to those for the kraft pulps. Gellerstedt suggests that electron transfer reactions are taking place between the residual fiber lignin and dissolved phenols present in the pulping liquor during the residual phase of the kraft cook. These reactions could increase cause an increase in molecular weight of the residual lignin, as observed during the residual phase of kraft pulping.

1.1.3.3 *Other lignin reactions*

Besides degradation and condensation reactions, there are a variety of other reactions that occur in kraft pulping that are believed to contribute to the low reactivity of residual lignin. These reactions do not assist in the fragmentation and dissolution of lignin. Enol ethers and stilbenes can also be formed during pulping, as shown in Figure 14. These structures are, to a large extent, alkali-stable and are not desirable in kraft pulping. The formation of these structures involves the elimination of the terminal hydroxymethyl group as formaldehyde.[16] Stilbenes may be formed from phenolic phenylcoumaran structures by alkali-promoted opening of the five-membered coumaran ring, followed by formaldehyde elimination from the resulting quinone methide as shown in Figure 15. Stilbene structures should constitute important structural elements in dissolved as well as

residual lignins. These ring-conjugated structures are important to consider when studying the structure of residual and dissolved lignins because their presence, although in small quantities, may contribute to the dark color of kraft pulp. A variety of reduced structures have been suggested to be present in the residual and dissolved lignins, as evidenced by the increase in the number of methylene and methine groups in the residual and kraft lignins. However, the formation of these structures is not well understood.
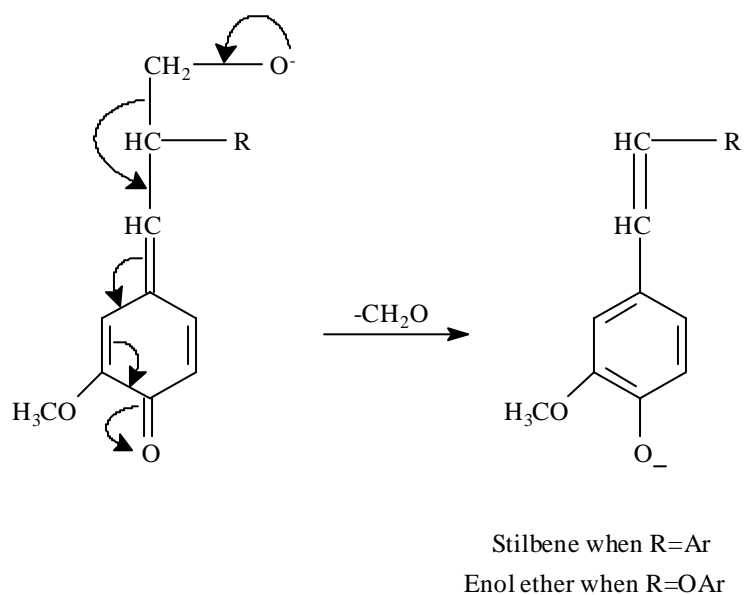

Stilbene when R=Ar
Enol ether when R=OAr

Figure 14. Formation of enol ethers/stilbene by the elimination of formaldehyde from a quinone methide intermediate structure.

Another reaction that occurs in kraft pulping involves the cleavage of methyl aryl ether bonds. Hydrosulfide ions, possessing a strong nucleophilic character, bring about this type of cleavage. The products of this reaction, generated after demethylation, are methyl mercaptan and a catechol. The methyl mercaptide ion may cleave another methyl aryl ether bond (methoxy group) to generate dimethyl sulfide, or it may get oxidized to yield dimethyl disulfide. An example of these demethylation reactions by hydrosulfide and methyl mercaptide ions is illustrated in Figure 16.
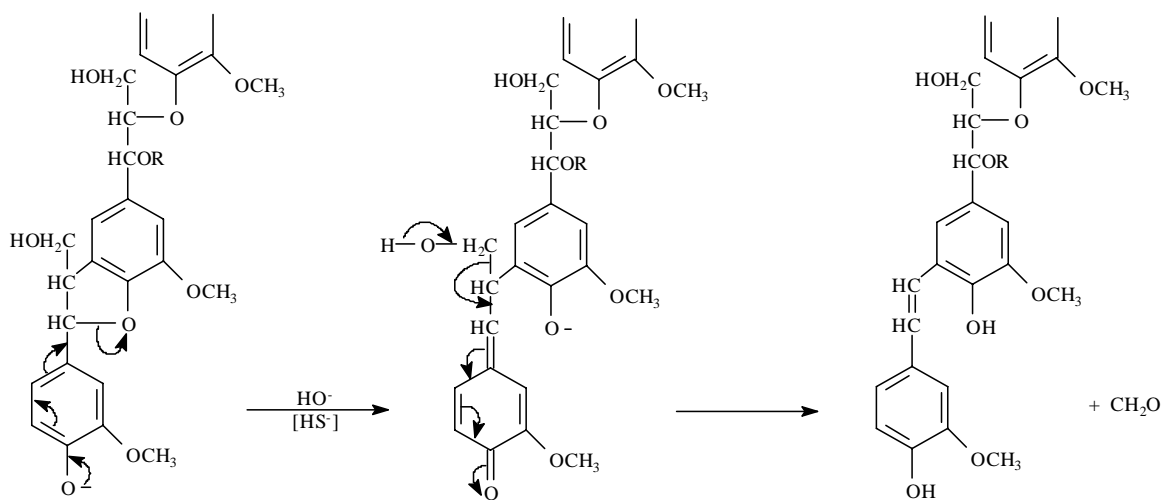
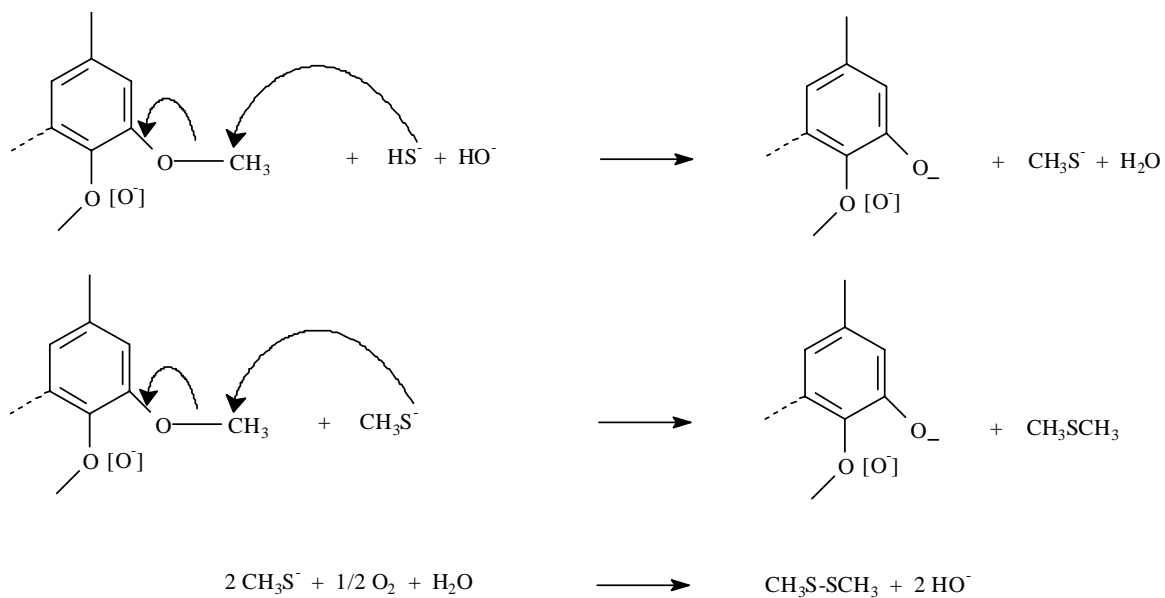**Figure 15.   Formation of stilbenes from phenolic phenylcoumaran moieties.**

$$2\ CH_3S^- + 1/2\ O_2 + H_2O \longrightarrow CH_3S\text{-}SCH_3 + 2\ HO^-$$

Figure 16.   Demethylation by hydrosulfide and methyl mercaptide ions.

1.1.3.4 Carbohydrate reactions

The process of delignification during kraft pulping is accompanied to varying extents by degradation of the carbohydrate constituents, i.e., cellulose and hemicelluloses. One type of reaction that is responsible for this degradation, namely the peeling reaction, starts at temperatures of about 100°C and may lead to considerable losses in pulp yield. The peeling reaction, like the cleavage of α-aryl ether linkages in phenolic units, commences under the relatively mild conditions of the initial phase. In the peeling reaction, a stepwise depolymerization of the carbohydrate occurs at the reducing end sites of the polymer chain, as shown in Figure 17. The reaction generates a monosaccharide that undergoes a benzilic acid rearrangement (BAR) to form an isosaccharinic acid. The reaction also forms a new reducing end on the remainder of the polymer, which can undergo further peeling reactions. The carbohydrate material lost in the peeling reaction is converted to various hydroxy acids that consume alkali and reduce the effective concentration of the pulping liquor.

The peeling reaction continues in carbohydrates until the introduction of a carboxyl group at the reducing end. This stopping reaction stabilizes the carbohydrate against further peeling. During the stopping reaction, the diketone intermediate rearranges via a BAR scheme to create a carboxylic acid group on the terminal end of the polymer chain. The carbohydrate chain no longer has a terminal carbonyl group, and the peeling reaction cannot proceed, as outlined in Figure 18.
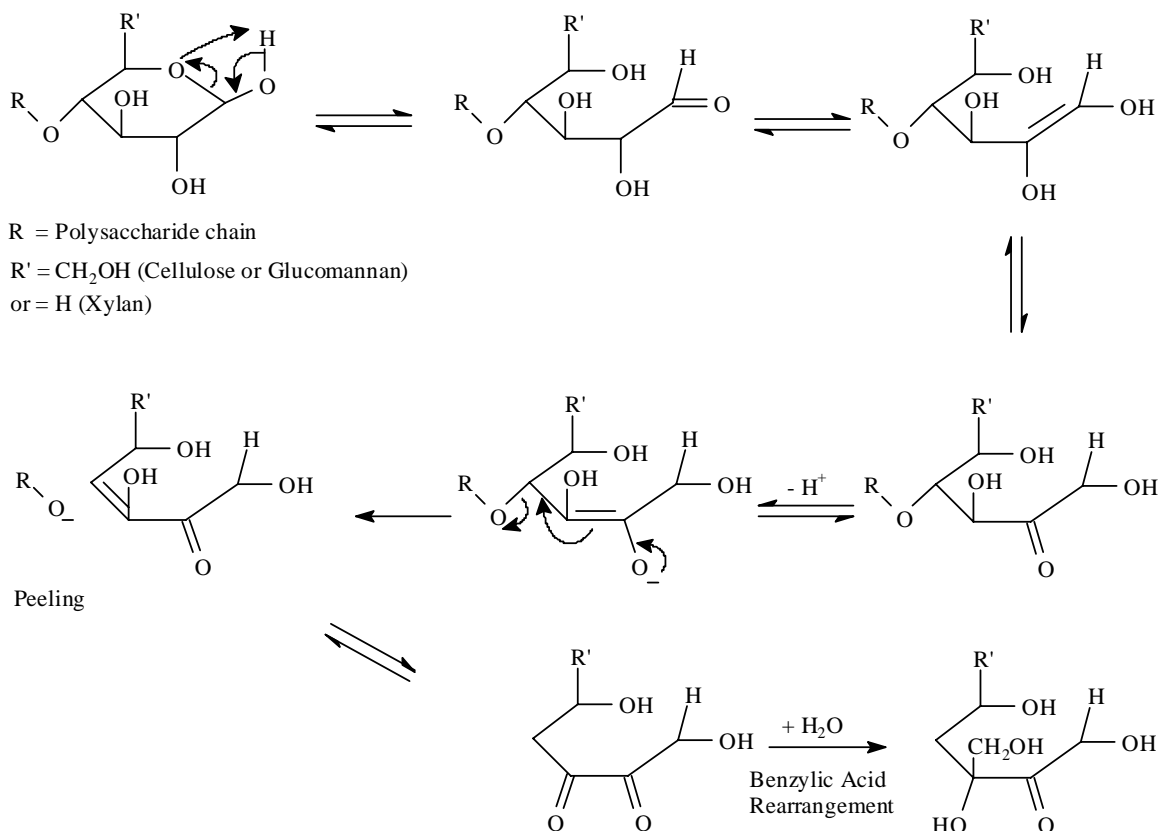
Figure 17. Peeling of 1,4-linked polysaccharides such as cellulose, xylans, or glucomannan.

Considering all these analogies between the alkaline degradation reactions of both lignin and carbohydrate polymers, the selectivity of alkaline delignification could be interpreted in terms of differences in the state of order or crystallinity of these substrates. However, there are purely chemical reasons for this selectivity. Namely, aroxy anions, due to their polarizability and weaker basicity, constitute more efficient leaving groups in the cleavage via oxiranes than do alkoxide anions. In addition, lignin degradation during both the initial and bulk phase is partly due to the sulfidolytic cleavage of β-aryl ether linkages, a reaction that has no parallel in carbohydrate degradation reactions. Finally, the alkaline cleavage of a-aryl ether bonds does not have to compete with a stabilizing reaction, as the peeling reaction competes with the stopping reaction for carbohydrates.[17]
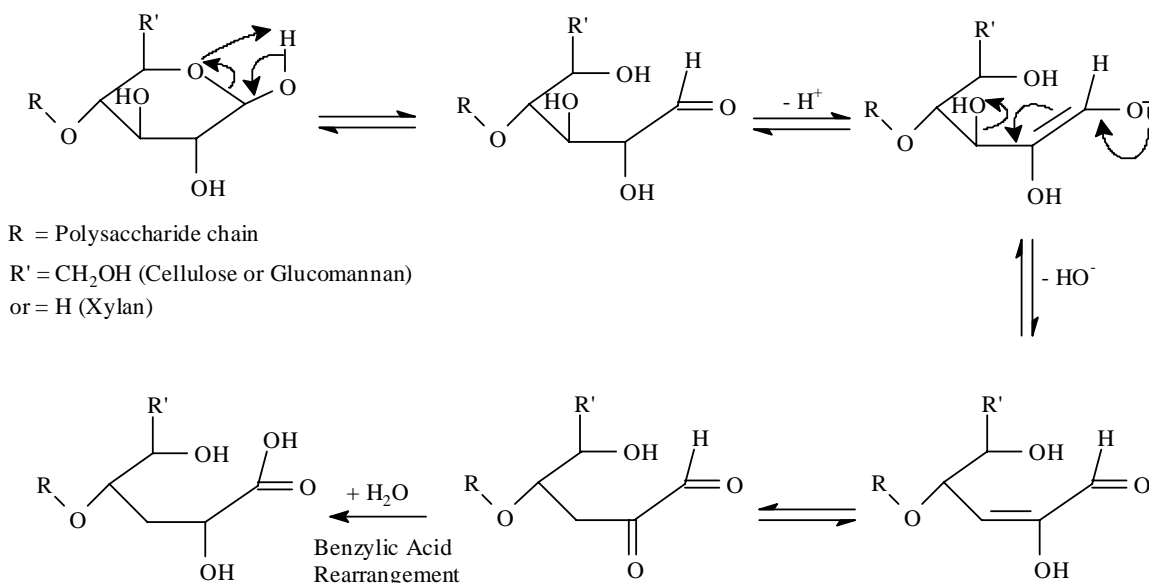
Figure 18. The formation of metasaccharinic acid during the stopping reaction involving carbohydrates.

Another important reaction involving carbohydrates is the formation of hexenuronic acids during kraft pulping. Clayton initially postulated the formation of hexenuronic acids during kraft pulping.[18] He proposed that the removal of the 4-O-methyl-α-D-glucuronic acid groups could be initiated by β-elimination of methanol during the alkaline pulping of wood. Later, Johansson and Samuelson employed 2-*O*-(4-*O*-methyl-α-D-gluco-pyranosyluronic acid)-D-xylitol as a model compound to provide evidence for the formation of hexenuronic acids upon treatment with alkali at elevated temperatures, as well as its slow degradation with time.[19]

Although it has been clear from the literature that 4-O-methyl-D-glucuronic acid must undergo β-elimination during kraft pulping, the occurrence of hexenuronic acid in kraft pulps or in the dissolved xylans was not verified until 1995.[20] After these investigations, it became readily apparent that hexenuronic acids contributed to pulp bleachability, influenced the retention of non-process elements in kraft pulps, and impacted pulp brightness values.[21] In addition, the amount of hexenuronic acids in kraft pulp is strongly affected by the pulping conditions and attention has therefore been given to

monitoring the existence and changes of hexenuronic acid during kraft pulping.[22] The formation of hexenuronic acids during kraft pulping is illustrated in Figure 19. During this reaction, β-elimination of methanol results in the formation of hexenuronic acid.
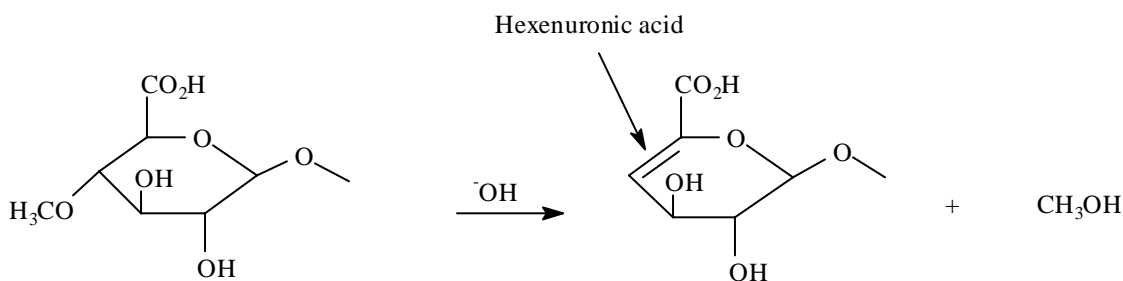

Figure 19.   Formation of hexenuronic acids during kraft pulping.

1.1.3.5 _Lignin-Carbohydrate Complexes_

Lignin-carbohydrate complexes (LCCs) are believed to be present in the native wood lignin.   There are possibly several different linkage types between lignin and carbohydrates. These linkage types can be generalized as either alkali-stable or alkali-sensitive.   The alkali-sensitive linkages are readily cleaved under the harsh alkaline conditions of the kraft cook while the alkali-stable linkages survive the kraft cook and have been suggested to be present in kraft pulps.[23] By surviving the kraft cook, these alkali-stable linkages may be enriched and contribute to the difficulty in removing lignin at the end of the cook. In addition to the native alkali-stable LCCs surviving the cook, alkali-stable LCCs may be formed during the cook.[24] This has been demonstrated in model compound studies of both phenolic and non-phenolic model compounds and by analysis of the lignin-carbohydrate bonds present in dissolved kraft lignins. Iversen _et al_. performed a methylation analysis of a material enriched in residual lignin and isolated by enzyme-catalyzed hydrolysis of the polysaccharides.[25]   The results of these studies indicated the presence of alkali-stable lignin bonds, mainly to cellulose, but also to other polysaccharides.

Alkaline cleavage of β-aryl ether bonds in non-phenolic units, the dominant reaction during kraft pulping, may also result in the formation of covalent ether bonds between lignin and carbohydrate constituents of wood. Such bonds may prevent lignin fractions from being dissolved in the final or residual phase of the kraft cook. The formation of an LCC with a non-phenolic β-aryl ether-type structure is believed to occur by a carbohydrate hydroxyl group, acting as a nucleophile, reacting with an epoxide that is formed during the elimination of the β-aroxy substituent, as shown in. Thus, the reaction has to compete with the alkaline-mediated opening of oxirane intermediates in lignin. The lignin fragment of the native LCCs is believed to be linked exclusively with hemicelluloses, while the lignin fragment of the LCCs that are formed during pulping may be more frequently linked to cellulose.

The formation of lignin-carbohydrate complexes requires predissociation of alcoholic hydroxyl groups followed by nucleophilic attack to form the oxirane intermediate. The presence of a nucleophilic species stronger than alkoxide ions, such as the hydrosulfide ion, will inhibit or reduce the formation of LCC linkages. Thus, the hydrosulfide ions not only facilitate lignin fragmentation via sulfidolytic cleavage of the β-aryl ether units, but also scavenge reactive intermediates of the oxirane type and prevent these from undergoing coupling reactions with carbohydrates. Thus, a high sulfidity during the transition stage from the initial to the bulk phase is desired. The reason for this is because at this stage of the kraft cook, extensive lignin fragmentation takes place through cleavage of β-aryl ether linkages in non-phenolic units. Thus, the conditions for the formation of lignin-carbohydrate complexes involving the reaction between oxirane intermediates and ionized hydroxyl groups in carbohydrates are favorable at this stage of the kraft cook.
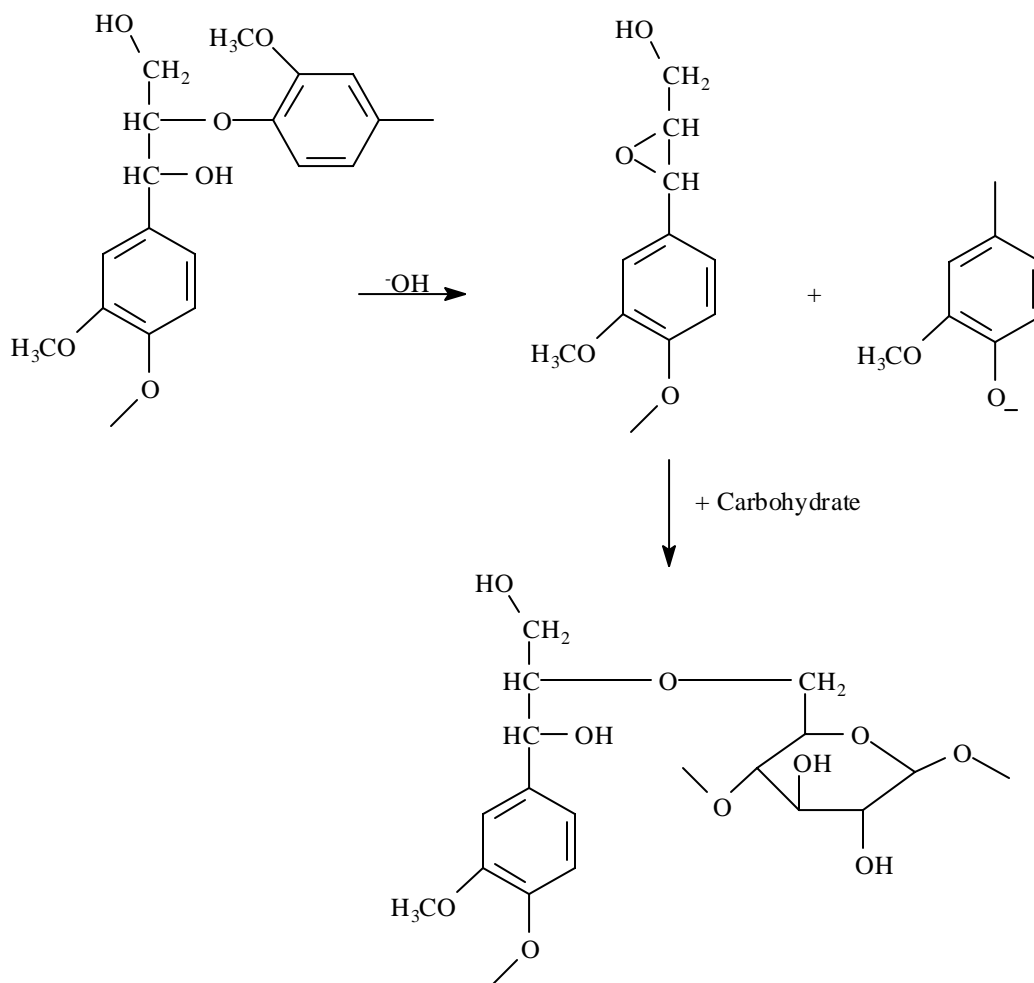
Figure 20. Formation of an LCC under kraft pulping conditions by the reaction between a carbohydrate and a non-phenolic β-aryl ether lignin model.

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