Possible lignin reactions in the Organocell pulping process

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ABSTRACT *The interactions between organosolv cooking chemicals and lignins have not been studied in great detail. This report describes the reactions in the two-stage acid–alkali Organocell process. Lignin model studies show that α-aryl ether linkages are hydrolyzed by the alcohol–water mixture at high temperatures, forming phenolic groups and benzyl alcohol moieties during the first stage of the process. During the subsequent alkaline cooking stage, anthraquinone (AQ) is added. In the presence of AQ, the benzyl alcohols are preferentially oxidized to α-carbonyls, which are less susceptible to the secondary condensation reactions that occur in the presence of alkali. Similarly, the terminal methylol groups in the phenyl propane lignin structure are also oxidized, preventing further condensation reactions. The effective delignification obtained in this two-stage process is thus a function of (a) lignin fragmentation in the presence of water–alcohol during the first stage and (b) prevention of condensation reactions during the subsequent alkaline stage.*

KEYWORDS
Anthraquinone
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Nonsulfur pulping
Organosolv pulping
Phenol groups
Reaction kinetics

The kraft and the sulfite pulping processes have long been the dominant methods for producing pulp. During the past decade, however, several new pulping processes have gained acceptance. High-yield pulps such as thermomechanical and chemithermomechanical pulps, for example, are being used to manufacture utility-type paper grades. Nevertheless, the demand for high-purity chemical pulps remains strong, especially for such products as dissolving pulps and sanitary-grade fluff pulps.

Environmental issues have focused a great deal of attention on the conventional kraft and sulfite pulping processes. In the sulfite industry, the disposal of waste liquor is considered to be a problem because of sulfur dioxide emissions from chemical recovery plants. The kraft industry is bearing the brunt of public pressure to reduce or even eliminate emissions of mercaptans and other reduced-sulfur compounds.

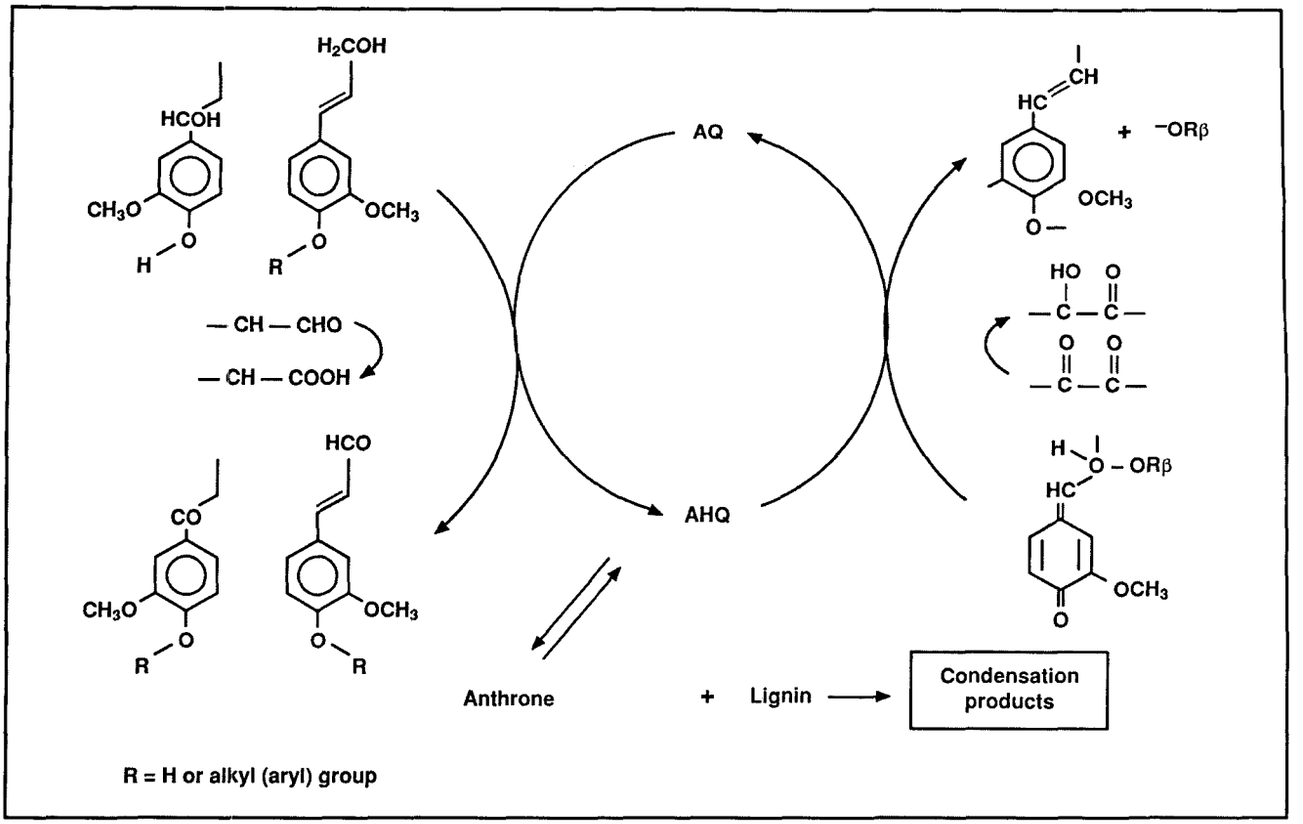
The rising cost of containing the sulfurous by-products generated by the conventional chemical pulping processes has focused renewed interest in alternative chemical pulping processes that do not use sulfur in their cooking-liquor formulations. Among these are the "organosolv" processes, which use methanol, ethanol, or butanol either exclusively or as one of the liquor components. Other organic solvents that can be used include acetic acid-ethyl acetate and aqueous phenol.

Origins of organosolv pulping

The use of alcohol in solvent pulping dates back to 1931 and was extensively investigated by Kleinert and Tayenthal (*1*). Numerous pulping studies with alcohol as one of the main pulping liquor components showed that aspen could be delignified extensively to around kappa no. 10 with good viscosity. However, red oak and eucalyptus could only be pulped to around kappa no. 30, and these pulps suffered a loss in viscosity (*2*).

Based on these findings, Repap Inc. started up a commercial-scale demonstration plant that produces approximately 30 tons/day of aspen pulp using an ethanol extraction procedure known as the Alcell® process (*3*). Typically, the wood chips are extracted in several stages with aqueous ethanol at temperatures up to 200°C. Under these conditions, the lignin is partially hydrolyzed, and the degradation products from the wood components are dissolved by the organic solvent. The Alcell® process, however, appears to be suitable only for the pulping of hardwoods and not softwoods. For example, spruce wood chips did not respond to the solvent treatment at all. It was found that

1. Proposed redox mechanisms (6)



softwood chips present in the aspen furnish were insufficiently pulped and contributed substantially to the rejects in the knotter screens.

It was not until the early 1980s that it became possible to produce acceptable organosolv pulps from spruce and pine. Baumeister and Edel (4) showed that an initial extraction of softwood chips with methanol or ethanol in water at an elevated temperature—followed by a subsequent cook with aqueous alkali in the presence of residual alcohol from the first stage—yielded pulps with kappa nos. 20-30. Furthermore, they found that addition of a small amount of anthraquinone (AQ) to the cooking liquor in the second stage helped delignify spruce and pine wood chips.

In the absence of detailed mechanistic studies, it was originally assumed that organosolv pulping processes were governed by hydrolytic reactions. It is well known that the pH of the cooking liquor in alcohol-water pulping is in the acidic range because of the acids (e.g., acetic acid, etc.) generated by hydrolysis of polysaccharides (hemicelluloses). Thus, alcohol-water pulping constitutes a mild hydrolysis of wood components.

In a recent series of lignin model compound studies, Meshgini and Sarkanen (5) showed that, in mildly acidic ethanol-water mixtures, an α-aryl ether linkage in a nonphenolic α-β diaryl ether structure is cleaved to form a benzylic alcohol moiety and a free phenolic group. Only upon heating to higher temperatures could β-aryl ether linkages be hydrolytically cleaved to corresponding alcoholic and phenolic hydrolysis products. This seems to explain the high temperatures required in the Alcell® process, whereby degradation of the abundant lignin β-aryl ether side units results in the observed extensive delignification of aspen wood chips.

A two-stage organosolv process

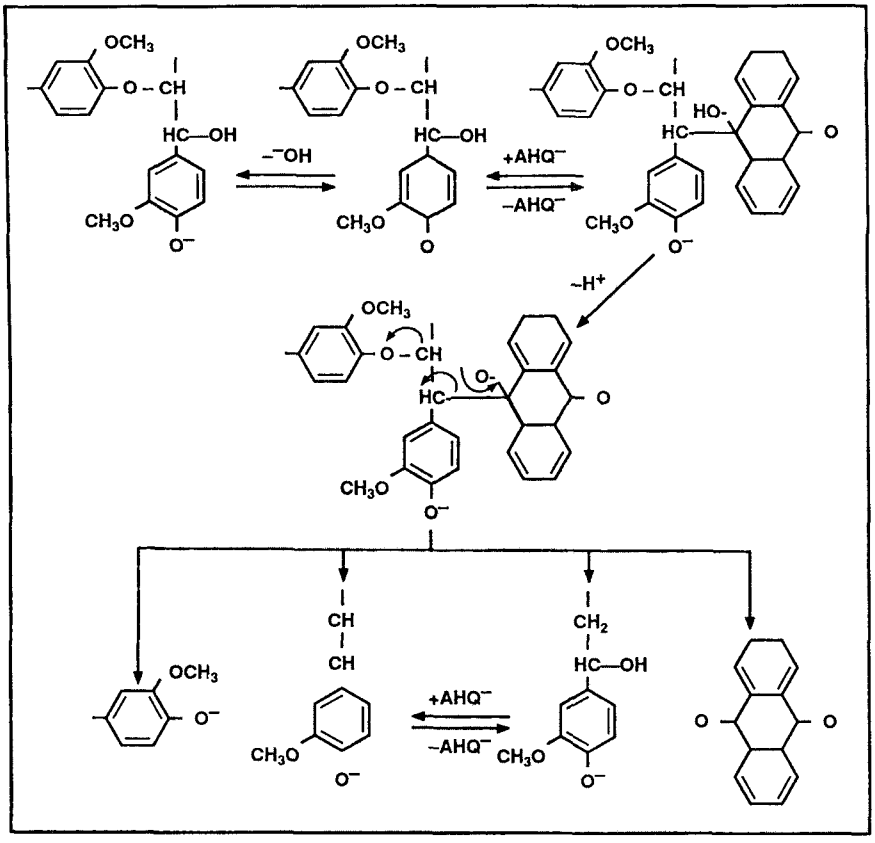
Acid stage

During development of the original acid-alkaline Organocell process, it was found that pH control in the first stage is important for overall delignification. If the pH is allowed to remain too high, i.e., if cooking temperature is not high enough to deacetylate the wood components, then delignification in the second stage will be unsatisfactory, and the resulting pulp will invariably have a high kappa number. On the other hand, if the temperature in the first stage is too high, the formation of acids during the initial phase of the cook may become too great. This can lead to lignin condensation, requiring excessive amounts of alkali in the second stage to degrade and remove lignin and to neutralize the acids. Therefore, in the first stage of the Organocell process, cooking temperature is maintained such that lignin α-aryl ether linkages are cleaved by mild acid hydrolysis without undergoing secondary condensation reactions.

Alkaline stage

The second stage of the acid-alkaline organosolv process can be looked upon as a soda-AQ cook in the presence of methanol. After extensive modeling studies, the reactions of the major wood components (polysaccharides and lignin) are well understood. With

2. Adduct formation and subsequent Grob fragmentation of phenolic β-aryl ether structures with AHQ (*9*)



the addition of AQ, both quinone and anthrahydroquinone (AHQ, the reduced form of AQ) participate in a very complex system of redox reactions and hydrolytic processes (*6*). The high efficiency of AQ (0.1-0.2% on o.d. wood) is due to the cyclic nature of the reductive and oxidative processes, as illustrated in **Fig. 1.**

Polysaccharide reactions. The reactions between the carbohydrates and the AQ-AHQ redox system are predominantly oxidative. The reducing end groups are easily oxidized by AQ to the corresponding aldonic acid structures, thus stabilizing the polysaccharides against base-induced stepwise depolymerization or "peeling" reactions. Studies by Wallis *et al.* (*7*) demonstrated that some oxidation of carbinol to carbonyl groups along the polysaccharide chains may occur, leading to a base-induced cleavage of the glycosidic bond of the subsequently formed ketol structures. Splitting the glycosidic bonds along the polysaccharide chains weakens the fiber and reduces sheet strength properties.

Lignin reactions. In contrast to the polysaccharides, lignin is subject to reductive as well as oxidative reactions involving both AQ and its reduced form, AHQ. It is well documented that the interaction between the reductant in the system, AHQ, and the quinone methide of phenolic β-aryl ether structures leads to the formation of an adduct that is subject to the Grob fragmentation cleavage of the β-aryl ether bond and formation of the vinyl-type structure and the quinone, AQ (*8, 9*). This is illustrated in **Fig. 2.**

Oxidation of lignin structures by AQ (including sodium anthraquinone monosulfonate) has been studied extensively by Schroeter (*10*), Hawes *et al.* (*11*), and Hise *et al.* (*8*). These studies have provided valuable information about the lignin reactions induced by the conversion of alcohol groups in lignin side chains to corresponding carbonyls. Schroeter demonstrated that alcohol groups in the α position in both phenolic and nonphenolic structures can be oxidized, thus reducing condensation while enhancing the splitting of the β-aryl ether linkages by base. Hawes *et al.* showed that α-keto β-aryl ether structures are subject to reductive splitting by reacting with AHQ.

Model studies by Hise *et al.* (*8*) clearly showed that cinnamyl alcohol structures as well as the terminal methylol groups in lignin side chains can be oxidized to carbonyls. The conversion of the terminal methylol group to an aldehyde group gives rise to extensive fragmentation, regardless of whether the moiety is phenolic or nonphenolic. If there is an α-position hydroxyl group on the side chain, then the structure is subject to a reverse aldol reaction, leading to cleavage of the side chain between the α and β carbon atoms. If there is an ether linkage in the α position of the side chain, then this linkage will be cleaved by a β-elimination reaction, leading to structures prone to reversed aldol reactions (*12*). This reaction pattern is shown in **Fig. 3.**

In summary, both reductive and oxidative reactions between lignin structures and the components of the AQ-AHQ redox system result in extensive fragmentation. Adduct formation between AHQ and quinone methides, which are very prone to condensation, helps prevent lignin condensation. It is the combination of enhanced fragmentation and diminished condensation that contributes greatly to the removal of lignin in this stage of the process.

Conclusion

Based on extensive lignin model studies, the principal reactions of lignin in both stages of the Organocell process are reasonably well understood. The presence of methanol in both stages of the process helps increase lignin removal because lignin fragments are soluble in this organic solvent. It appears that the lignin condensation reactions are suppressed in the first stage, where the alcohol concentration is high. In the second stage, where the alcohol concentration is low, the added anthraquinone assumes a major role in suppressing condensation reactions in the mildly acid-hydrolyzed lignin structure.□

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3. Postulated mechanism for the reaction of nonphenolic α-ether lignin structures with AQ (*8*)