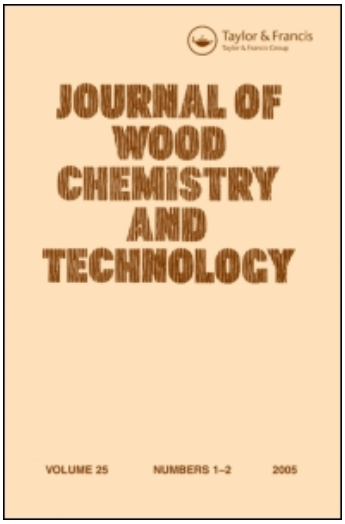

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The Role of Carbohydrates in Alkali Anthraqutnone Pulping

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THE ROLE OF CARBOHYDRATES IN ALKALI ANTHRAQUINONE PULPING

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Dedicated to the memory of Kyosti V. Sarkanen

ABSTRACT

The reactions of carbohydrates with anthraquinones in alkaline pulping processes are reviewed. AQ reacts mainly with the short-lived intermediates that are formed in the degradation reactions of wood polysaccharides. Oxidation of the reducing end groups of polysaccharides to stable aldonic acid end groups is marginal and corresponds to less than 1 % of all reactions of AQ. The stabilization of the polysaccharides may be enhanced by the use of salts of alkaline earth metals which increase the relative oxidation rate of sugar enediols and promote the hydride shift reaction of the intermediate aldos-2-ulose end groups to stable hexonic acid end groups. Analysis of the monomeric carbohydrate-derived oxidation products indicates that hardwood lignin probably contains more structures that react with anthrahydroquinone than does softwood lignin. This difference may partly explain the more facile delignification of hardwoods.

INTRODUCTION

A serious drawback of kraft pulping is the alkaline degradation of hemicelluloses starting from the reducing end groups and resulting in large material losses[1]. The mechanism of the degradation and particularly the possibilities of preventing it have been the objects of much research during several decades. Methods have been proposed to increase the carbohydrate yield

in kraft pulping but, among these, only polysulfide pulping has achieved some commercial importance[2].

In 1972, Bach and Fiehn[3] reported that cellulose was partly stabilized against alkaline degradation by a treatment with 2-anthraquinonesulfonic acid (AMS) or, alternatively, with certain other quinones. In the hope of a better carbohydrate yield, they made some alkali pulping experiments with wood chips, and found that AMS also accelerated the delignification of the chips. The results were encouraging, but the high cost of the relatively large amounts of AMS needed made it clear that its use was impractical for industrial production of wood pulp. The work of Bach and Fiehn, however, initiated vigorous research efforts to find practical applications for quinonoid additives as pulping catalysts.

In 1977, Holton[4] reported that unsubstituted anthraquinone (AQ) significantly accelerated the delignification of both hardwood and softwood in alkaline pulping even when using only very small charges of AQ. This finding initiated enormous interest in AQ among wood and pulping chemists throughout the world. In the beginning, there were great expectations for applying AQ commercially in alkaline pulping, but during recent years the initial enthusiasm has levelled off. Today, AQ is used as an additive in a number of kraft, soda, and sulfite pulp mills, but overall AQ has not broken through[2]. It may be noted, however, that among the sulfur-free pulping processes, soda-AQ pulping is the only one that could more widely challenge the kraft process.

In 1978 and 1979, Löwendahl and Samuelson[5], Fleming et al.[6], and Algar et al.[7] proposed that the effect of AQ in alkaline pulping is based on a reduction-oxidation cycle where AQ is reduced by carbohydrates and re-oxidized in the oxidative cleavage of lignin. Since then, many papers have been published on the degradation of lignin (model compounds) by the reduced forms of AQ. The reactions of AQ with carbohydrates have received less attention especially during the last ten years.

In this paper, the reactions of carbohydrates with AQ and related additives in alkaline pulping of wood are critically reviewed. The discussion of the reaction mechanisms and kinetics is largely based on the author's earlier studies with simple reducing sugars and their transient oxidation products. Some earlier unpublished results from studies with model compounds and pulping experiments are also presented.

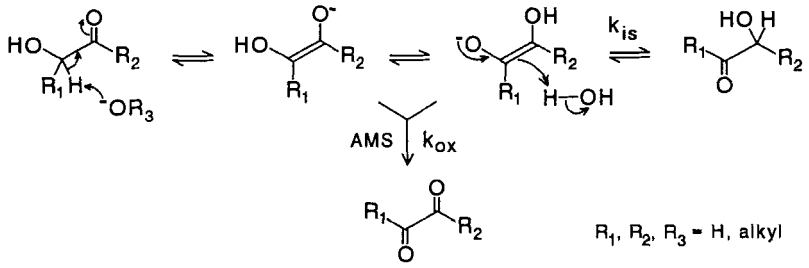
Although carbohydrates typically yield a great variety of degradation products, they are formed via a few general, consecutive reactions, such as enolization, ß-elimination, hydride and alkyl shifts, aldol cleavage, and oxidation. Many of the reaction intermediates can adopt several isomeric forms in equilibrium and their relative amounts finally determine the importance of the various competing reaction routes. To save space, only the general reaction mechanisms and the probable isomeric structures are shown in the text as schemes. However, by applying the general reaction mechanisms to individual isomers of of the intermediates, it is easy to understand how the specific reaction products are formed.

DISCUSSION

Oxidation of Sugar Enediols

Heikkilä and Sjöström[8] suggested in 1975 that, in alkaline solutions, the oxidation by quinones of reducing carbohydrates is preceded by enolization and yields an aldos-2-ulose intermediate as the primary product. The aldos-2-uloses are selectively cleaved by hydrogen peroxide to formic and the next lower aldonic acids. This specific reaction was applied to show kinetically that D-*arabino*-hexos-2-ulose is the only principal oxidation product from D-glucose[9]. Thus, in the presence of sufficient amounts of AMS and hydrogen peroxide, D-glucose gave almost exclusively formic and D-arabinonic acids. It may further be noted that Ciamician and Silber[10] were able to isolate D-*arabino*-hexos-2-ulose as its phenylosazone after a photochemical reaction of D-glucose with 1,4-benzoquinone.

By reacting D-glucose with AMS at several concentrations in aqueous sodium hydroxide, it was shown that the rate of formation of D-fructose was inversely proportional to the concentration of AMS[9]. On the other hand, the rate of oxidation of D-glucose at a high concentration of AMS was only slightly higher than the rate of formation of D-fructose in the absence of AMS. These two findings together proved that the oxidized intermediates were enediols, as the latter were known to be the major intermediates in the isomerization reaction



SCHEME 1

(Scheme 1). Later kinetic measurements of the rates of disappearance of reducing sugars and appearance of the reduced species of AMS were also applied in determinations of the relative oxidation rates (i.e., the ratio of oxidation and isomerization rates, designated as k_{ox}/k_{is})[11].

Kinetic experiments in water and deuterium oxide indicated that AMS oxidizes both neutral enediols and their anions[11]. At high pH values, where the oxidation through the enediol anions was dominant, the relative oxidation rate depended on the ionic strength of the solution because AMS itself is an anion (Fig. 1). For the same reason, the relative oxidation rate decreased when the solvent polarity was decreased with an addition of organic solvents.

The salt and solvent effects on the oxidation are obviously very different when neutral AQ is used as the oxidant instead of ionic AMS. Because of the insolubility of AQ in cold aqueous solutions, it is practically impossible to determine its oxidation power under these conditions. However, in 40 % aqueous 1,4-dioxane the relative oxidation rate of D-glucose by AQ (25°C, 0.1 M NaOH; $k_{ox}/k_{is} = 1.7 \cdot 10^3$ M^{-1}) was only 5 % of the corresponding rate by AMS in water but under otherwise similar conditions.

The relative oxidation rates of different sugars were of the same order, although monosaccharides were generally oxidized a little easier than disaccharides (Fig. 1)[11,12]. The relative oxidation rates also depended on temperature. Thus, in 0.05 M sodium hydroxide, the relative oxidation rates (k_{ox}/k_{is}) of D-glucose were $2.0 \cdot 10^4$ and $0.23 \cdot 10^4$ M^{-1} at 25 and 52°C, respectively.

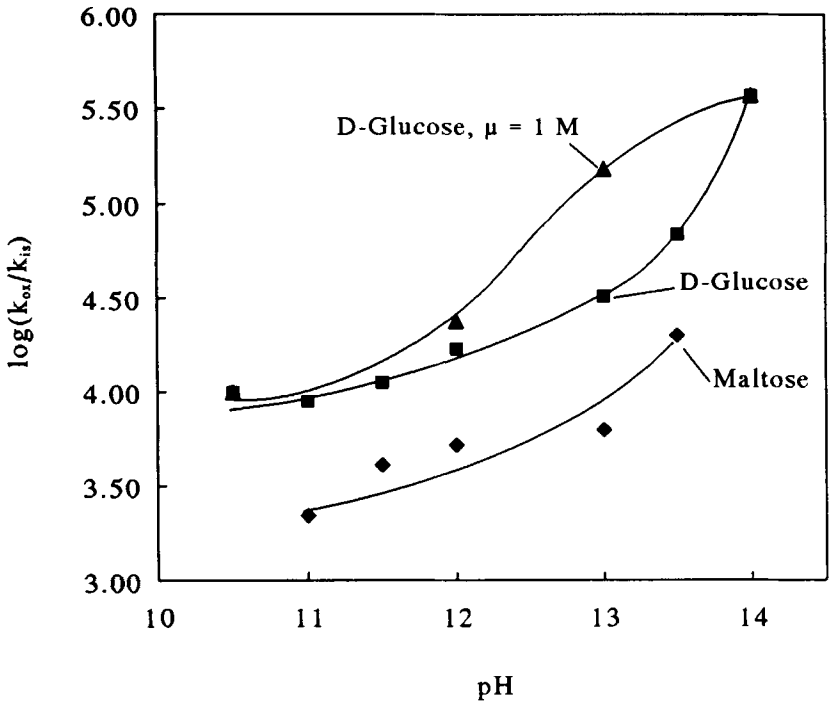
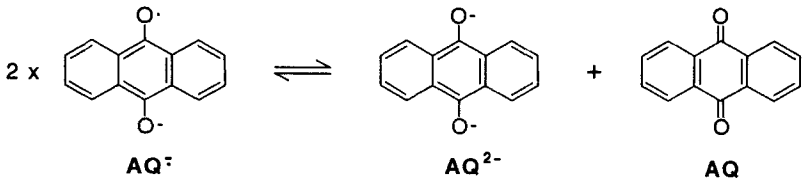


FIGURE 1. Effect of pH on the relative oxidation rates of D-glucose (▲,■) and maltose (♦) by AMS at 25°C. The ionic strength varied with the concentration of sodium hydroxide ($3 \cdot 10^{-4}$-1 M) used as the base (♦ ,■) or was kept constant (μ = 1 M) by adding sodium chloride (▲).

In conjunction with the partial reduction of a quinone, an equilibrium mixture of the quinone, the hydroquinone and its mono- and dianions, and the semiquinone radical and its anion is formed (Scheme 2)[13]. The pK_1 and pK_2 values of anthrahydroquinones are of the order of 8-9 and 11-12, respectively, whereas the pK values of the semiquinone radicals are 3-4[14-16]. Interestingly, aldoses were long ago applied as reductants in studies of these equilibrium mixtures of several quinones[65]. The oxidation of glycolaldehyde by AMS could quantitatively be described by the amount of AMS in equilibrium when the degree of reduction of the quinone was less than 0.5[11]. At higher degrees of



SCHEME 2

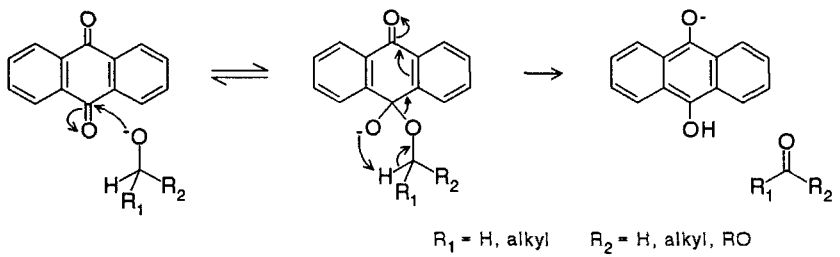
reduction the relative oxidation rate was higher than expected on the basis of the concentration of AMS. It was kinetically proved that glycolaldehyde was oxidized also by the semiquinone radical ion of AMS (9,10-anthradioxy-2-sulfonate radical anion, $AMS^{\cdot}$). Under the conditions applied (0.005 M NaOH, 13°C) the relative oxidation rates by AMS and $AMS^{\cdot}$ were $2.5 \cdot 10^4$ and $2.5 \cdot 10^3$ M^{-1}, respectively.

Oxidation of Non-Enolic Hydroxyl Groups

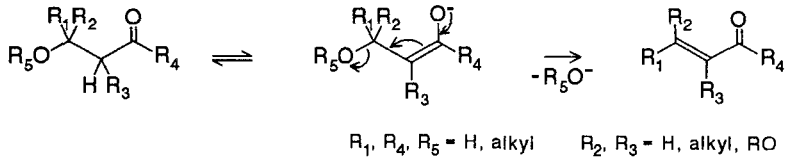
Free aldoses and ketoses are normally oxidized exclusively through the enediols derived from them by the action of alkali. When the formation of enediols is impossible, the oxidation may be extremely slow. Thus, 2-deoxy-D-*arabino*-hexose was oxidized by AMS at a rate that was only 0.1-1 % of the oxidation rate of D-glucose[9]. The oxidation products were not analyzed in this case, so it is not possible to say whether 2-deoxy-D-*arabino*-hexose was oxidized directly or through its degradation products.

Under the severe conditions of alkaline pulping, anthraquinones oxidized model compounds with primary and secondary hydroxyl groups to the corresponding ketones and aldehydes or acids[17]. Under milder conditions, AMS also oxidized alcoholic solvents such as ethanol and ethylene glycol[11]. A general mechanism of oxidation of alcohols by AQ is illustrated by Scheme 3.

Anthraquinones may generate carbonyl groups within cellulose chains according to Scheme 3. Irrespective of the site of oxidation (C-2, C-3, or C-6) the action of base on the resulting carbonyl structure will result in cleavage of the polymer chain via ß-elimination (Scheme 4). As a result of these consecutive



SCHEME 3

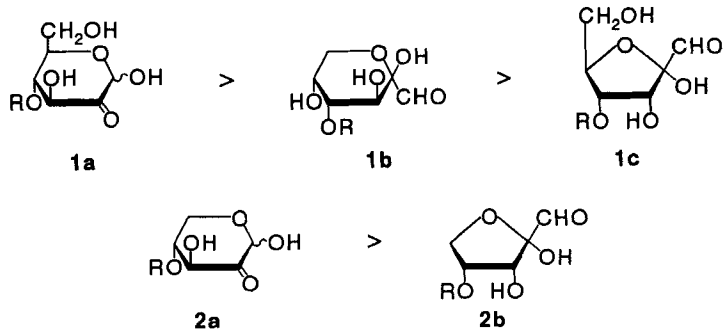


SCHEME 4

reactions, anthraquinones reduce the degree of polymerization of cellulose in alkali pulping[18].

Reactions of Aldos-2-ulose End Groups

The half-lives of aldos-2-uloses in strongly alkaline solutions (pH 12-14) are of the order of several minutes at room temperature[11,19,20]. Under these conditions, the degradation is much slower than the interconversion between isomeric ring forms[21,22]. The relative amounts of the isomeric forms, however, largely determine the importance of individual reaction pathways. The equilibrium compositions of pentos-2-uloses were recently determined by n.m.r[23]. The factors that determine the stabilities of the structures with free carbonyl groups were later discussed[24]. According to the relationships observed, the stabilities of the various forms of the D-*arabino*-hexos-2-ulose end groups of cellulose and glucomannan

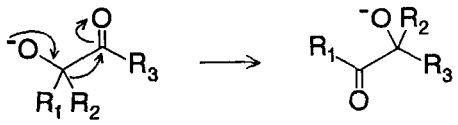


SCHEME 5

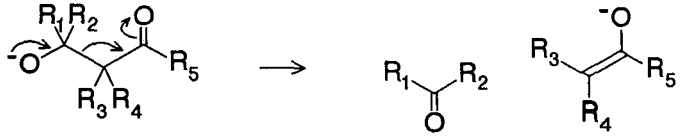
and the D-*threo*-pentos-2-ulose end groups of xylan decrease in the order shown in Scheme 5.

Even at fairly high temperatures structures **1a**, **1b**, **1c**, **2a**, and **2b** are less abundant than their hydrated analogues[23]. The unhydrated forms are, however, much more reactive, and they are responsible for practically all following reactions. Structures **1b**, **1c**, and **2b** are not especially reactive as there is no hydrogen atom at C-2 which is α to the free carbonyl group. In addition to a slow alkyl shift of C-3 to C-1 (Scheme 6), only an aldol cleavage between C-2 and C-3 may occur (Scheme 7). On the other hand, **1a** and **2a** can undergo several competing reactions. A hydride shift from C-1 to C-2 results in the formation of stable D-gluconic and D-mannonic (from **1a**) and D-xylonic and D-lyxonic acid end groups (from **2a**) (Scheme 6)[25-29]

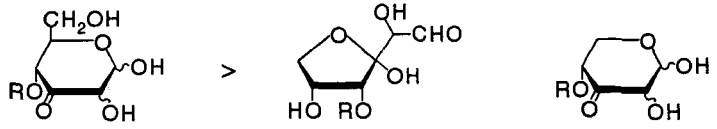
Another hydride shift from C-3 to C-2 (Scheme 6) generates C-2 epimeric aldos-3-ulose end groups which probably prefer the aldopyranoid structures **3a** and **4** in equilibrium in addition to their hydrated analogues (Scheme 8)[11]. The aldos-3-ulose end groups are obviously nearly exclusively degraded via elimination of formic acid from **3a** and **4** (Scheme 7)[30,31]. The products are the enediols of pentose and tetrose end groups which very easily undergo ß-elimination of the polysaccharide chain. The liberated 3-deoxy-D-*glycero*-pentos- and 3-deoxytetros-2-uloses undergo almost quantitatively a hydride shift reaction to 3-deoxypentonic and 3-deoxytetronic acids (Scheme 6)[20,32]. It may be noted that



SCHEME 6



SCHEME 7



SCHEME 8

the enediolic pentose and tetrose end groups are not very easily converted to the corresponding tetros- and pentos-2-ulose end groups because the oxidation must compete with the rapid ß-elimination.

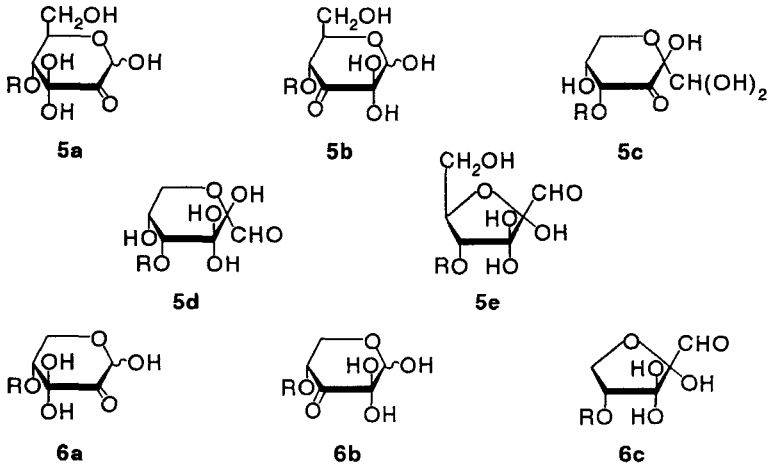
A third important reaction of **1a** and **2a** is the formation of the 2,3-enediols[11]. In principle, the (cyclic) enediols could directly undergo ß-elimination of the rest of the polysaccharide chain (Scheme 4). However, experiments with cellobiose and maltose indicated that the elimination did not compete with the oxidation of the 2,3-enediols over a wide concentration range of AMS (0.4-20

mM)[12]. A probable explanation is that the cyclic enediols are at least partly converted to acyclic reductone-type enediols which are then easily oxidized to the corresponding aldos-2,3-diulose end groups[33]. It may be noted that a strong u.v. absorption at 310 nm indicated the presence of significant proportions of the conjugated enediols in solutions of unsubstituted aldos-2-uloses[34]. The latter can adopt a number of isomeric forms and undergo several reactions (Scheme 9). Among these, an alkyl shift of C-1 to C-3 (**5b**, **5c**, and **6b**) or C-4 to C-2 (**5a** and **6a**) generates 2-C-carboxy-D-pentose (from **5a**, **5b**, and **5c**) and 2-C-carboxy-D-tetrose end groups (from **6a** and **6b**) (Scheme 6). The other major reaction is an aldol cleavage between C-2 and C-4, which results in the formation of D-erythronic (from **5d** and **5e**) and D-glyceric acid end groups (from **6c**) (Scheme 7).

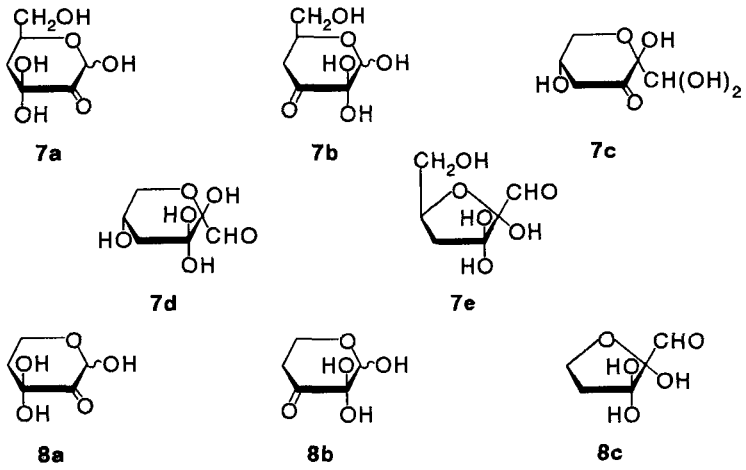
The ß-elimination products of **1a** and **2a** are 4-deoxy-D-*glycero*-hexos- and 4-deoxytetros-2,3-diuloses, respectively. They are mainly degraded via an aldol cleavage between C-2 and C-4 (**7d**, **7e**, and **8c**) (Schemes 7 and 10) or via an alkyl shift of C-1 to C-3 (**7b**, **7c**, and **8b**) or C-4 to C-2 (**7a** and **8a**) (Scheme 6). The products from these reactions consist of 2-deoxy-D-*glycero*-tetronic acid (from **7d** and **7e**), 3-hydroxypropanoic acid (from **8c**), 2-C-carboxy-3-deoxypentoses (from **7a**, **7b**, and **7c**), and 2-C-carboxy-3-deoxytetroses (from **8a** and **8b**)[12,29]. Formation of large amounts of these products in the oxidation of cellobiose and maltose by AMS showed that the aldos-2-ulose end groups can undergo ß-elimination even under strongly oxidizing conditions. An explanation may be that the ß-elimination is not necessarily preceded by enolization.

The 2-C-carboxy-3-deoxyaldoses were degraded during a prolonged treatment, probably to carbon dioxide and the enediols of 3-deoxyaldoses (Scheme 7)[12]. The latter are easily oxidized to the 3-deoxyaldos-2-uloses and converted further to the 3-deoxyaldonic acids.

The significance of each of the competing reaction routes is largely determined by the reaction conditions. For example, the formation of hexonic acid end groups in cellobiose and maltose was promoted by high hydroxyl ion concentrations (Fig. 2) and the presence of small amounts of alkaline earth metal ions[11,25,35].



SCHEME 9



SCHEME 10

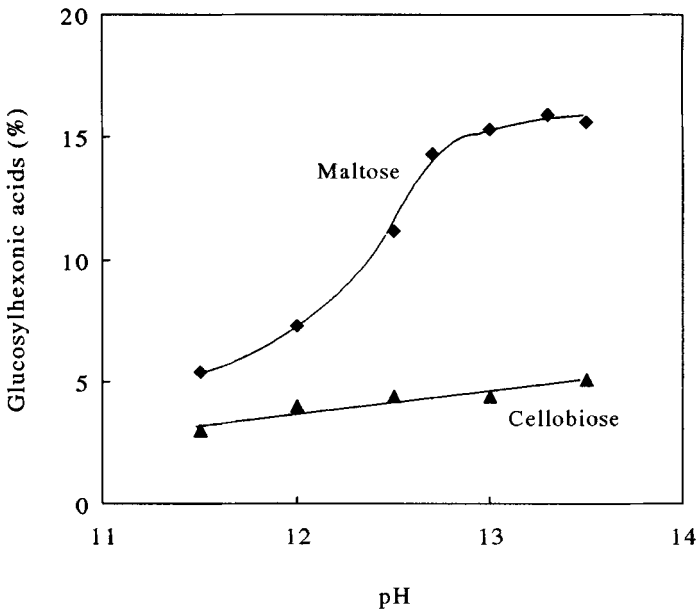
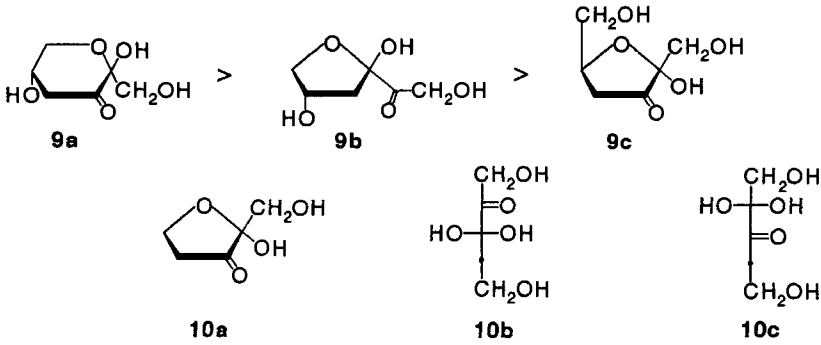


FIGURE 2. Effect of pH on the formation of glucosylhexonic acids from cellobiose (▲) and maltose (♦) by 4 mM AMS in aqueous sodium hydroxide (0.003-0.3 M) at 50°C.

Reactions of 4-Deoxyhexo- and 4-Deoxypento-2,3-diuloses

4-Deoxy-D-*glycero*-hexo- and 4-deoxypento-2,3-diuloses are the major primary products from the alkaline degradation of cellulose and glucomannan and xylan, respectively[1,60]. The equilibrium compositions of these intermediates have not been determined. However, on the basis of data from related structures, the stabilities of the cyclic unhydrated forms of 4-deoxy-D-*glycero*-hexo-2,3-diulose are expected to decrease in the order **9a** > **9b** > **9c** (Scheme 11)[23,24]. 4-Deoxypento-2,3-diulose can adopt only one unhydrated cyclic structure (**10a**, two enantiomers), and obviously the acyclic structures **10b** and **10c** are involved in most reactions.

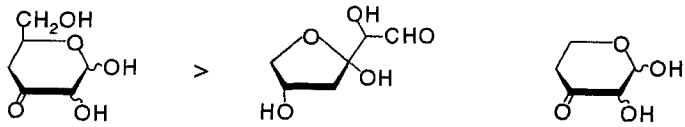
Each of the cyclic and acyclic structures can undergo an alkyl shift reaction of either C-1 to C-3 or C-4 to C-2 (Scheme 6)[36]. In every case, the products



SCHEME 11

are epimeric 2-deoxy-2-C-hydroxymethylpentonic (from **9a**, **9b**, and **9c**) and enantiomeric 2-deoxy-2-C-hydroxymethyltetronic acids (from **10a**, **10b**, and **10c**). Another major reaction of **9b** and **10b** is a hydride shift from C-1 to C-2 (Scheme 6). Among the reactive carbonyl structures of the products, epimeric 4-deoxy-hexos-3-uloses and enantiomeric 4-deoxytetros-3-uloses (**11a** and **12**) dominate (Scheme 12). These are obviously almost exclusively degraded via an aldol cleavage between C-1 and C-2 to formic acid and the enediols of a 3-deoxy-pentose (from **11a**) and a 3-deoxytetrose (from **12**) (Scheme 7). Under oxidative conditions, the latter may yield epimeric 3-deoxypentonic and enantiomeric 3-deoxytetronic acids as was discussed above. In the absence of oxidants, the 3-deoxypentose and 3-deoxytetrose enediols are partly isomerized to 3-deoxy-D-*glycero*-2-pentulose and 3-deoxy-2-tetrulose, respectively, which may be degraded via an aldol cleavage between C-3 and C-4 or ß-hydroxy elimination (Schemes 1, 4, and 7). The latter reaction finally results in the formation of enantiomeric 3,4-dideoxypentonic and 2-hydroxybutanoic acids.

Another reaction of **9b** and **10b** is the formation of the corresponding 1,2-enediols which may further be isomerized to the epimeric 4-deoxyhexos-3-uloses and enantiomeric 4-deoxypentos-3-uloses or form the corresponding acyclic reductone-type enediols (Scheme 1). The latter are sensitive to oxidation, and are therefore a potential source of 4-deoxy-D-*glycero*-hexos- and 4-deoxypentos-2,3-diuloses and their degradation products[33].



11a **11b** **12**

SCHEME 12

An aldol cleavage between C-1 and C-2 may generate 3-deoxy-D-*glycero*-pentos-2-ulose (from **9a** and **9c**) and 3-deoxy-tetros-2-ulose (from **10a** and **10c**) which are then converted to 3-deoxypentonic and -tetronic acids via a hydride shift from C-1 to C-2 (Scheme 6).

Finally, **9a** and **10c** may yield 1-hydroxybutadione through an aldol cleavage between C-4 and C-5 (Scheme 7). This intermediate yields enantiomeric 2-C-methylglyceric acids via alkyl shift reactions (Scheme 6).

Aldonic Acid End Groups in Wood Polysaccharides

When hydrocellulose was treated with an excess of AMS (0.06 M AMS, > 10 eq. AMS per reducing end group) in 0.25 M sodium hydroxide at 90°C, 70 % of the reducing groups were oxidized[8]. The relative composition of the aldonic acid end groups was: 60 % D-erythronic acid, 12 % D-arabinonic acid, 7 % D-gluconic acid, and 21 % D-mannonic acid. The large proportion of D-erythronic acid indicates that the oxidation of the D-*arabino*-hexos-2-ulose end groups was a significant reaction under these conditions. The applied analytical procedure did not allow the detection of the 2-C-carboxypentose end groups (the other major products of the D-*erythro*-hexos-2,3-diulose end groups) because these are unstable during hydrolysis with acids[12].

A relatively mild treatment (1 M sodium hydroxide, 80°C, 2 h) of wood meal from Scots pine with 1 % AQ generated 1.9 mmol of aldonic acid end groups per kg wood[37]. This amounted to ~40 % of all the analyzed reducing and acidic end groups. More than half of these aldonic acid end groups (0.9-1.3 mmol per kg wood) were still present after normal soda or kraft cooking of Scots pine

or Norway spruce with an addition of 1 % of AQ[5,38]. Small amounts of aldonic acid end groups (0.3-0.4 mmol per kg wood) were generated during both soda and kraft pulping even when AQ was not used. An addition of 0.1 % of AQ only slightly increased (by 0.3 mmol per kg wood) the amount of aldonic acid end groups from this blank value. The use of AQ never increased the amount of D-erythronic acid end groups from the blank value, which indicates that in AQ pulping, oxidation of the aldos-2-ulose end groups did not occur. On the contrary, the majority of the aldonic acid end groups consisted of D-gluconic, D-mannonic, D-lyxonic, and D-xylonic acids and were formed via direct hydride shift reactions of the aldos-2-ulose intermediates.

The polysaccharide content of a soda-AQ pulping liquor (0.1 % AQ on wood) from Scots pine was 1.86 % of wood[39]. A corresponding kraft cooking liquor contained only 0.58 % of dissolved polysaccharides of wood. In both cases, the major monosaccharide components of the dissolved polysaccharides were arabinose, galactose, and mannose. Apparently, the water-soluble arabinogalactans and other partially soluble hemicelluloses were stabilized more efficiently than the insoluble polysaccharides against the alkaline degradation by generation of aldonic acid end groups by AQ. The end groups of the dissolved wood polysaccharides have not been determined.

It may be noted that the 4-O-linked aldonic acid end groups (D-gluconic and D-mannonic acid end groups of cellulose and glucomannan and D-lyxonic and D-xylonic acid end groups of xylan) mostly survive the conditions of soda and kraft pulping, whereas the other aldonic acid end groups are less stable and, if formed, can bring about only a partial stabilization of the polysaccharide chains[40].

Degradation Products of Polysaccharides in Pulping Liquors

The published data on the degradation products of wood polysaccharides in soda-AQ and kraft-AQ pulping liquors are very limited. Samuelson and Sjöberg[39] analyzed the aliphatic hydroxy carboxylic and dicarboxylic acids in a soda-AQ pulping liquor from Scots pine, but unfortunately they did not include a blank experiment without AQ. Thus, the only valid conclusion from this

analysis was that the major components of soda-AQ and kraft pulping liquors were the same. More recently, Alén et al.[41] performed a similar analysis of the aliphatic carboxylic acids in soda-AQ and kraft pulping liquors from Scots pine and Norway spruce. Once again, an analysis of the effect of AQ on the product composition is difficult because data from a soda pulping liquor were not given.

The influence of AQ on the generation of aliphatic carboxylic acids became more apparent in recent work of Niemelä et al.[42], who used kraft as a reference for kraft-AQ. In this study, birch wood was pulped with and without an addition of 0.15 % of AQ. At a constant cooking time, the use of AQ decreased the amount of hydroxy acids by 3.5 % of wood at maximum. By the end of the cook, this difference decreased to 1.6 % of wood. Under similar conditions, AQ increased the carbohydrate yield by ~1.0 % of wood at a constant cooking time[43]. Thus, at least at the end of the cook, the increase in the carbohydrate yield roughly corresponded to the decrease in the amount of the carbohydrate-derived hydroxy carboxylic acids.

The amount of 2-deoxytetronic acid was very low (3 mmol per kg wood) both in kraft and kraft-AQ pulping liquors, which reveals that 4-deoxy-D-*glycero*-hexos-2,3-diulose was not generated from cellulose and glucomannan in significant amounts[42]. In other words, oxidation of 4-deoxy-D-*glycero*-hexo-2,3-diulose through its enediols was negligible and only trace amounts of D-*arabino*-hexos-2-ulose end groups underwent ß-elimination. Because ß-elimination is the main reaction of the D-*arabino*-hexos-2-ulose end groups, the oxidation of the reducing end groups of cellulose and glucomannan by AQ was unimportant[12]. Analogously, little 3-hydroxypropanoic acid (~10 mmol per kg wood) was formed and its generation was little enhanced when AQ was applied. Thus, oxidation by AQ of both 4-deoxypento-2,3-diulose and the reducing end groups of xylan was very limited. In agreement with this, the formation of 3,6-dideoxyhexonic acids from the L-rhamnose unit second to the original D-xylose end group of xylan was not retarded by AQ[44].

In kraft pulping of birch wood, the major product from xylan or 4-deoxy-pento-2,3-diulose was 2-hydroxybutanoic acid[42]. When the kraft pulping was carried out with an addition of 0.15 % of AQ, the yield of 2-hydroxybutanoic acid was halfed. Simultaneously the yield of 3-deoxy-2-C-hydroxymethyltetronic acids

was lowered only by ~20 % or by the same amount as the total amount of the hydroxy carboxylic acids, whereas the yield of 3-deoxytetronic acid was markedly increased. Clearly, AQ oxidized the 3-deoxytetrose enediols, in part, and thus retarded the competing ß-hydroxy elimination reaction of these enediols.

AQ had an analogous effect on the reactions of 4-deoxy-D-*glycero*-hexo-2,3-diulose derived from cellulose and glucomannan in kraft pulping of birch wood[42]. AQ increased the yield of 3-deoxypentonic acids and decreased the yield of 3,4-dideoxypentonic acids more than the yield of 3-deoxy-2-C-hydroxymethylpentonic acids. Thus, AQ partially oxidized the 3-deoxysugar enediols in this case too.

The influence of AQ on the formation of 2-hydroxybutanoic, 3-deoxytetronic, 3,4-dideoxypentonic, and 3-deoxypentonic acids is illustrated by Figs. 3 and 4. The 3-deoxyaldonic acids were generated in relatively large amounts even when AQ was not used. Although 3-deoxypentonic acids are formed to some extent from pure 1,4-linked hexosans such as cellulose and amylose, it is likely that the 3-deoxyaldonic acids in soda and kraft pulping are generated mostly in different types of oxidation reactions. Recently, Janson and Fullerton[45,46] showed that compounds that are able to form enediols promote the cleavage of ß-aryl ether bonds in phenolic lignin structures in a way similar to anthrahydroquinone with a simultaneous oxidation of the enediols. The wood itself may contain compounds that are able to act as reduction-oxidation catalysts (e.g., quinones and catechols) or these may be formed during pulping (e.g., quinones and polysulfide)[61,62].

The use of 0.15 % of AQ in kraft pulping of birch wood increased the total yield of 3-deoxytetronic and -pentonic acids by ~60 mmol per kg wood (Figs. 3 and 4). On the other hand, the yield of 2-hydroxybutanoic acid alone was decreased by >100 mmol per kg wood. AQ also enhanced the formation of glycolic (+50 mmol/kg at a constant degree of degradation) and oxalic acids (+35 mmol/kg), whereas the formation of lactic acid was retarded[42]. Changes were also observed in the amounts of several minor products. Although the routes of formation of glycolic, oxalic, and lactic acids remain uncertain, it seems probable that 100-200 mmol of AQ was involved in all oxidation reactions of carbohydrates. A similar analysis of soda-AQ pulping of pine wood (0.2 % AQ)

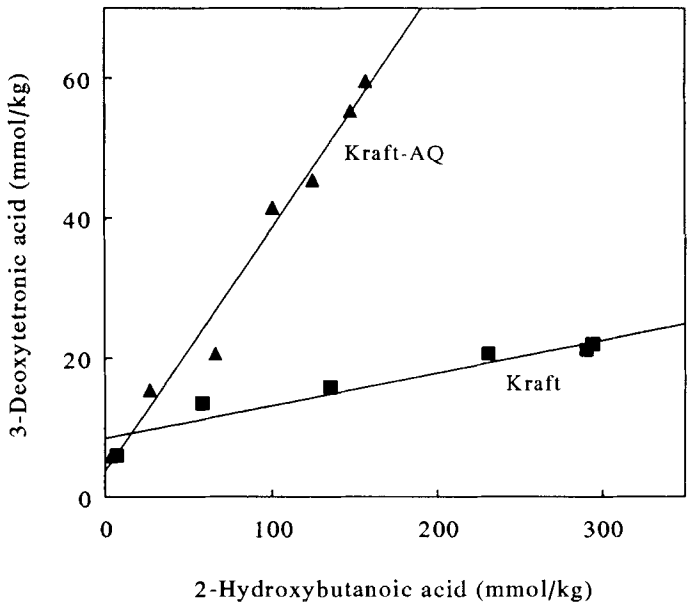


FIGURE 3. Formation of 2-hydroxybutanoic and 3-deoxytetronic acids in kraft (■) and kraft-AQ pulping (▲; 0.15 % AQ) of birch wood. The yields (mmol/kg wood) increase with increasing cooking time. The data were taken from ref. 42.

reveals that possibly 50-100 mmol of AQ were consumed in oxidation of products derived from carbohydrates[41]. This value is, however, less certain because the reference data were taken from kraft pulping.

Carbohydrate Yield in AQ Pulping

AQ increases the yield of soda and kraft pulps from both hardwoods and softwoods[43,47]. Mostly, this yield increase results from a faster delignification (shorter cooking time) and less from the stabilization of the polysaccharides through oxidation of the reducing end groups. At the end of an soda-AQ or kraft-AQ cook, the increase in the carbohydrate yield is typically 1 % of wood or less (0.1-0.2 % AQ on wood). There is, however, strong evidence that the AQ-induced

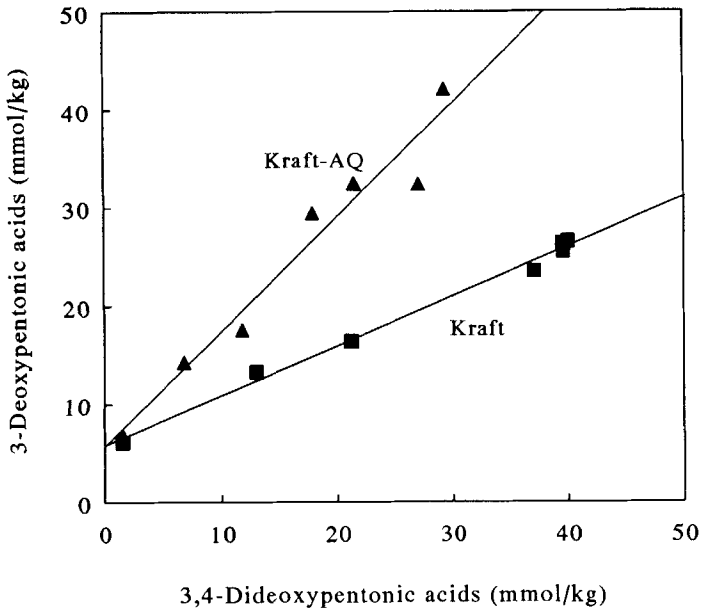


FIGURE 4. Formation of 3,4-dideoxypentonic and 3-deoxypentonic acids in kraft (■) and kraft-AQ pulping (▲; 0.15 % AQ) of birch wood. The yields (mmol/kg wood) increase with increasing cooking time. The data were taken from ref. 42.

change in the carbohydrate yield is larger during intermediate stages of the cook[63]. Thus, AQ smoothly decreased the generation of aliphatic hydroxy carboxylic acids during the heating-up period of kraft pulping of birch wood, but by the end of the cook the difference between the yields of these degradation products of carbohydrates was markedly decreased[42].

When wood meal from Norway spruce was cooked in an excess of 0.1 M sodium hydroxide, an addition of 1 % AQ decreased the losses of carbohydrates by 2 % of wood by the end of the heating-up period (Fig. 5). At the maximum temperature, AQ enhanced the degradation of the residual polysaccharides, and at the end of the treatment the carbohydrate yield in the presence of AQ was similar, if not lower than, in the absence of AQ. Similar results were obtained when the cooking liquor contained sodium hydroxide, sodium carbonate, and sodium

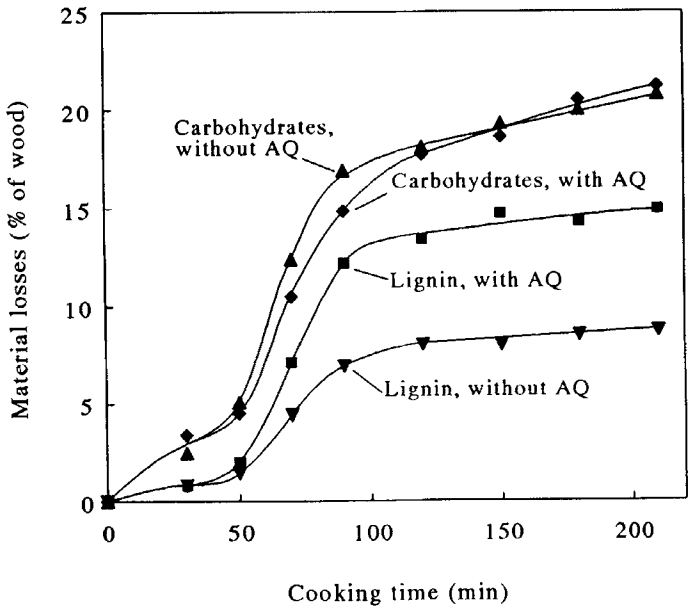


FIGURE 5. Dissolution of carbohydrates (▲,◆) and lignin (▼,■) during pulping of spruce meal in 0.1 M sodium hydroxide in the absence (▲,▼) and presence of AQ (◆,■; 1 % on wood). The liquor-to-wood ratio was 75:1.

bicarbonate at various concentrations, although the influence of AQ was less marked at lower alkalinities.

The enhanced degradation of carbohydrates at the maximum cooking temperature is probably caused by the oxidation of the non-enolic hydroxyl groups in the polysaccharides by AQ, which is followed by chain cleavage via ß-elimination and degradation starting from the newly formed reducing end groups[18]. Another possibility would be degradation starting from polysaccharide chains with 2-O- or 3-O-linked aldonic acid end groups. Such groups are, however, not generated by AQ in significant amounts[37].

Small additions of barium salts had a profound effect on the dissolution of carbohydrates in AQ-soda pulping of spruce wood meal (Fig. 6)[64]. Even though the barium salts also increased the carbohydrate yield when AQ was not used, it

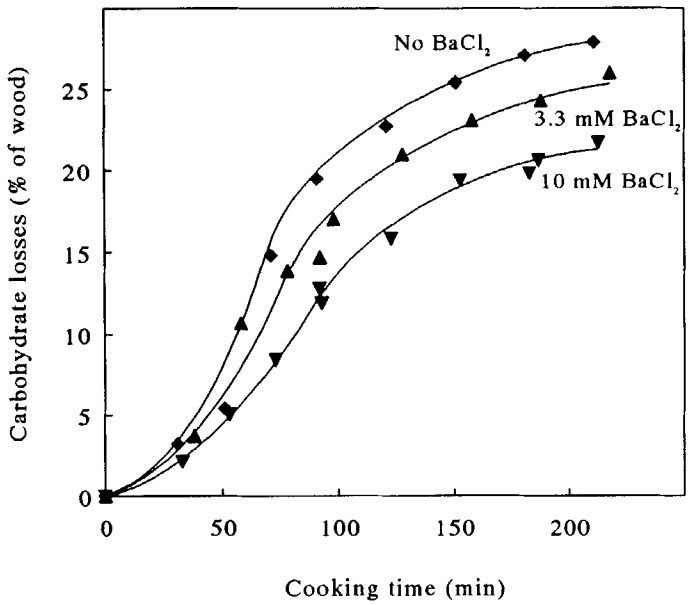


FIGURE 6. Effect of barium ion (♦, 0 mM; ▲, 3.3 mM; ▼, 10 mM) on dissolution of carbohydrates during pulping of spruce meal with AQ (1 % on wood) in 0.5 M sodium hydroxide. The liquor-to-wood ratio was 75:1.

is probable that the higher relative oxidation rate of the enediols and especially the more selective hydride shift reaction of the aldos-2-ulose intermediates resulted in a more extensive formation of the stable 4-O-linked aldonic acid end groups. The influence of calcium salts was similar but less efficient, possibly because of the lower solubility of calcium ions in the basic solutions. In the presence of both barium and calcium ions, the delignification of the wood meal was retarded. It may be noted that calcium ions have a stabilizing effect on the wood polysaccharides also in polysulfide pulping, probably because of enhanced formation of stable aldonic acid end groups[48,49].

The Reduction-Oxidation Cycle in AQ Pulping

Visual examination and polarographic studies indicated that AQ is reduced in the very beginning of soda or kraft pulping[6,50,51]. In a soda-AQ cook of black

spruce, the degree of reduction of AQ reached a maximum value of 0.8 at 120°C, which implies that below this temperature, the reduction of AQ by carbohydrates was faster than its regeneration in reactions with lignin. The degree of reduction of AQ decreased to a minimum value of 0.3 when the temperature was raised from 120 to 170°C. In this range, both delignification and degradation of carbohydrates were fast (cf. Fig. 5), and the change in the ratio of the reductive and oxidative reactions possibly resulted from dissimilar activation energies. By the end of the cook, the degree of reduction of AQ increased again to 0.4 as a result of decreased selectivity of delignification.

Mortimer[52] found that relatively large amounts of coniferyl alcohol were formed during the initial delignification phase of soda-AQ and kraft-AQ pulping. This observation was very important, because for the first time it proved that anthrahydroquinone cleaved ß-aryl ether bonds in lignin in a way that was earlier predicted by several authors[53-55]. The maximum yield of coniferyl alcohol was ~25 mmol per kg wood. Later, Kondo and Sarkanen[56a] reported that up to ~45 mmol of coniferyl alcohol per kg wood were analyzed in soda-AQ pulping (0.2 % AQ) liquors from western hemlock. Because coniferyl alcohol reacted further under prolonged pulping, the analyzed values were lower than the amounts actually generated.

It is interesting to note that both coniferyl alcohol and the oxidation products of carbohydrates were formed mostly during the initial phase of AQ-soda pulping of softwood and, moreover, in roughly equal amounts (50-100 mmol/kg wood). It may be concluded from this that AQ (0.2 % = 10 mmol/kg wood) underwent the reduction-oxidation cycle at least 5-10 times during the pulping. Although a major portion of the anthrahydroquinone was consumed in generation of coniferyl alcohol, it represented only a minor part of the dissolved lignin during the initial stage (an addition of 0.2 % AQ increased the amount of dissolved lignin by 6 % of wood, whereas the yield of coniferyl alcohol was 0.8 % of wood)[56].

Hardwoods yielded both coniferyl and sinapyl alcohols in soda-AQ pulping[52,57]. Their generation continued at the maximum temperature, as did the formation of the oxidation products of carbohydrates. The amount of the oxidation products of carbohydrates (100-200 mmol/kg wood) indicates that in a soda-AQ

cook, AQ (0.15 % = 7 mmol/kg wood) underwent the reduction-oxidation cycle 15-30 times.

Because little oxidation products of carbohydrates were formed during the bulk and residual delignification of softwood, in particular, it is uncertain how important the reduction-oxidation cycle really is for a successful delignification.

An addition of 0.1 % of AQ in soda pulping of spruce wood increased the amount of aldonic acid end groups in the pulp by an amount that corresponded to 0.3 mmol/kg wood or 2-5 % of the original amount of reducing end groups in wood. This also implies that less than 1 % of the reactions of AQ with carbohydrates resulted in the formation of aldonic acid end groups in the pulp.

EXPERIMENTAL

The relative oxidation rates of the reducing sugars were determined as described earlier[9,11]. The oxidation products of disaccharides were analyzed by gas-liquid chromatography as their trimethylsilyl derivatives[12].

The wood material consisted of acetone-extracted (20 h) spruce (*Picea abies*) meal (0.2-0.4 mm). Its lignin content was 28.5 % (by the acetyl bromide method)[58,59].

The wood meal (2.0 g) was cooked under a nitrogen atmosphere in rotating stainless steel autoclaves (200 ml) in an oil bath. The charge of the cooking liquor was 150 ml. The oil bath was heated linearly from 30 to 170°C in 85 min and maintained at 170°C for up to 135 min. After the chosen cooking times, the autoclaves were cooled in cold water.

The washing procedure was varied with the cooking base. When barium or calcium ions were present in the cooking liquor, the treated material was washed successively with hot water, 0.02 M hydrochloric acid, and hot water. After pulping in sodium bicarbonate, the material was extracted with 0.1 M sodium hydroxide before washing with hot water. In other cases, only hot water was applied.

The amount of dissolved lignin in the spent liquor (or alkaline extract) was determined by UV-spectroscopy at 282 nm. The absorptivity value (28.6 $lcm^{-1}g^{-1}$) was obtained by means of parallel determinations of the residual lignin content of

the wood meal by the acetyl bromide method[58,59]. The amount of dissolved carbohydrates was calculated as the difference of the decrease in total yield and the amount of dissolved lignin.

CONCLUSIONS

As proved by others, a reduction-oxidation cycle, where AQ oxidizes mostly carbohydrates and the resulting anthrahydroquinone cleaves ß-aryl ether bonds in lignin with concurrent regeneration of AQ, is operating in soda-AQ and kraft-AQ pulping. The number of the reduction-oxidation cycles can be evaluated from specific oxidation products of carbohydrates. The larger amounts of the oxidation products in pulping liquors from hardwoods indicate that hardwood lignin probably contains more structures that react with anthrahydroquinone than does softwood lignin.

AQ reacts mainly with the monomeric intermediates that are formed in conjunction with degradation of wood polysaccharides. The introduction of stable aldonic acid end groups to the polysaccharides is marginal, and corresponds to less than 1 % of all reactions of AQ. Thus, oxidation by AQ causes no or little increase in the carbohydrate yield in alkaline pulping processes.

Any attempts to increase the stabilizing effect of AQ towards the wood polysaccharides should be directed at increasing the relative oxidation rate of sugar enediols by the quinone, or at enhancing the hydride shift reaction of the intermediate aldos-2-ulose end groups to hexonic acid end groups. These effects may be brought about by an addition of alkaline earth metal salts to the cooking liquor. A disadvantage is that the delignification is simultaneously retarded.

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