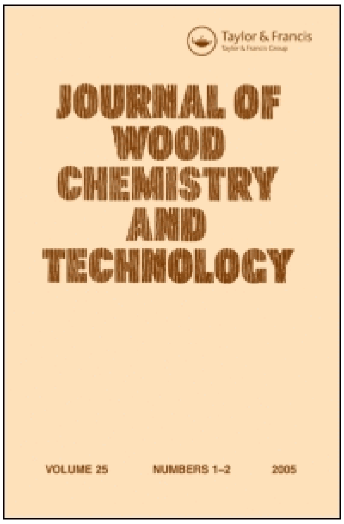

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Characterization of the Residual Kraft Pulp Lignin *In Situ* by Sulfite Treatments

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Abstract: The O_2 delignification of kraft pulps from Norway spruce was shown having a significant impact on the reactivity of the residual pulp lignin as revealed from their responses to sulfite treatments at pH 7.5. A substantial higher ratio of lignin sulfonation to the phenolic hydroxyl group content of residual pulp lignin was observed for the O_2-delignified kraft pulps ($\sim$0.8) as compared to a value of $\sim$0.3 for the unbleached samples and $\sim$1 for the spruce wood lignin. Under the prevailing sulfite treatment conditions, the sulfonation would be largely attributed to the phenolic lignin component and the etherified structures containing an α-carbonyl or -unsaturated group. The contribution from the latter units, evaluated by a borohydride pretreatment of pulps prior to the sulfite treatment, can only account for approximately 15% of the sulfonation observed for the O_2-delignified sample. Thus, the nature of phenolic structures in the O_2-delignified pulps was more similar to that of the wood lignin than that of the kraft pulps.

Keywords: Carbonyl groups, lignin analysis *in situ*, neutral sulfite treatment, O_2 delignification, residual kraft pulp lignin, wood lignin

INTRODUCTION

The kraft delignification process is known to consist of three district phases[1,2] (initial, bulk, and residual), which differ considerably in delignification selectivity. In order to minimize the fiber degradation, the commercial pulping is generally terminated near the interface because the bulk and the residual delignification. A complete removal of the residual pulp lignin (3–5%) requires a

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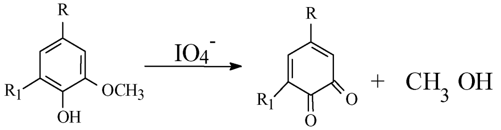
multiple bleaching sequence. Despite extensive studies,[3–8] the chemical nature causing the residual pulp lignin being so resistant to alkaline degradation still can not be fully quantified. Among possible causes, the association of residual pulp lignin with the lignin–carbohydrate complexes (LCC)[3,5,8–10] or with the condensed lignin structures[11,12] has received much attention. Recent reports showed[9,10] that the bulk of the residual kraft pulp lignin existed in the form of LCC and this appears to be a key factor affecting their reactivity. Although there is no general consensus on the formation of lignin diphenylmethane-type condensed structures in kraft pulping by an ionic mechanism,[13,14] the lignin condensation reaction was recently suggested to occur more likely by a radical pathway.[11,12]

Our current understanding on the delignification reaction has been derived largely from the characterization of the residual pulp lignin. Many prior studies were conducted on isolated lignin samples based on the hydrolysis of the carbohydrate matrix by a mild acid[15] or an enzymic treatment.[3,16,17] Significant improvements in the lignin isolation procedure were made in recent years,[18–22] and the lignin obtained can be analyzed by both chemical and spectroscopic methods, notably the powerful NMR (nuclear magnetic resonance) techniques.[14,23,24]

Our studies have emphasized the analysis of the wood or pulp lignin *in situ* to reveal its intrinsic characteristics. Among the available methods, the periodate oxidation technique based on the methanol formation (Eq. [1]) is a useful tool for a quantitative determination of the phenolic hydroxyl group (PhOH) in wood and pulp samples:[25–28]



(1)

We had quantified the impact of aryl ether cleavage reaction (as monitored by the PhOH formation) in kraft delignification of spruce wood ,[28] which also displayed three distinct phases (Figure 1). As indicated for the delignification at 170°C, the initial lignin removal up to about 20% level was accompanied by a very small increase in the PhOH content of residual wood lignin. The bulk phase extending to approximately 90% delignification was closely correlated with the aryl ether cleavages, whereas this cleavage reaction has only a slight effect on the residual delignification process.

It is evident that the residual phase delignification was accompanied by a significant increase in PhOH units of the residual wood lignin. Because a high content of this functional group would facilitate the residual lignin removal in alkalis, its resistance to dissolution must be caused by some chemical factors. Thus, the results support the contention that the presence of LCC or the formation of lignin-condensed structures is an important factor affecting the reactivity of residual pulp lignin.

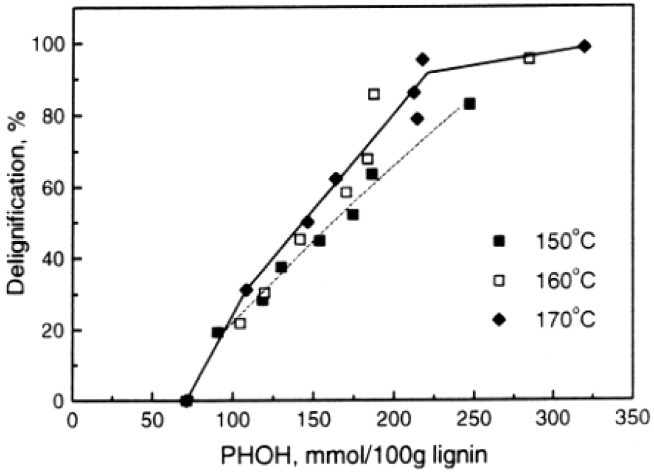


Figure 1. The impact of aryl ether cleavages (as indicated by the PhOH content in residual pulp lignin) in kraft delignification of Norway spruce wood.[28]

Now, the O_2 delignification[29] is nearly a standard process to follow kraft pulping in the current production of bleached pulps and is generally attributed to the degradation of the phenolic structure. However, approximately 50% of the phenolic structures in kraft pulps were resistant to a typical O_2 delignification process.[30] Available data[6,7,31,32] indicate that phenolic structures of the 5,5-biphenyl, p-hydroxylpropyl, or C-5 condensed type were less reactive to the O_2 delignification. On the other hand, there were indications, from the lignin model dimer reactions[33,34] and from the analysis of residual kraft pulp lignin,[31] that the oxidation of etherified structures is also involved under the O_2 delignification conditions.

We have been interested in further understanding the nature of phenolic structures present in the residual kraft pulp lignin, especially those resistant to the O_2 delignification and also on the oxidative degradation of the etherified structures, as this information would help to plan a strategy for a facile removal of the residual pulp lignin. In this study, the sulfite treatments at pH 7.5 were used as a tool to evaluate the nature of phenolic units in kraft pulps with respect to their modification at the benzylic position and also to detect the presence of oxidized etherified lignin structures in kraft pulps.

LIGNIN REACTIONS IN NEUTRAL SULFITE TREATMENTS

As summarized by Gellerstedt[35] on the reactions of the lignin model compounds (Figure 2) under neutral sulfite pulping conditions at 180°C, a key

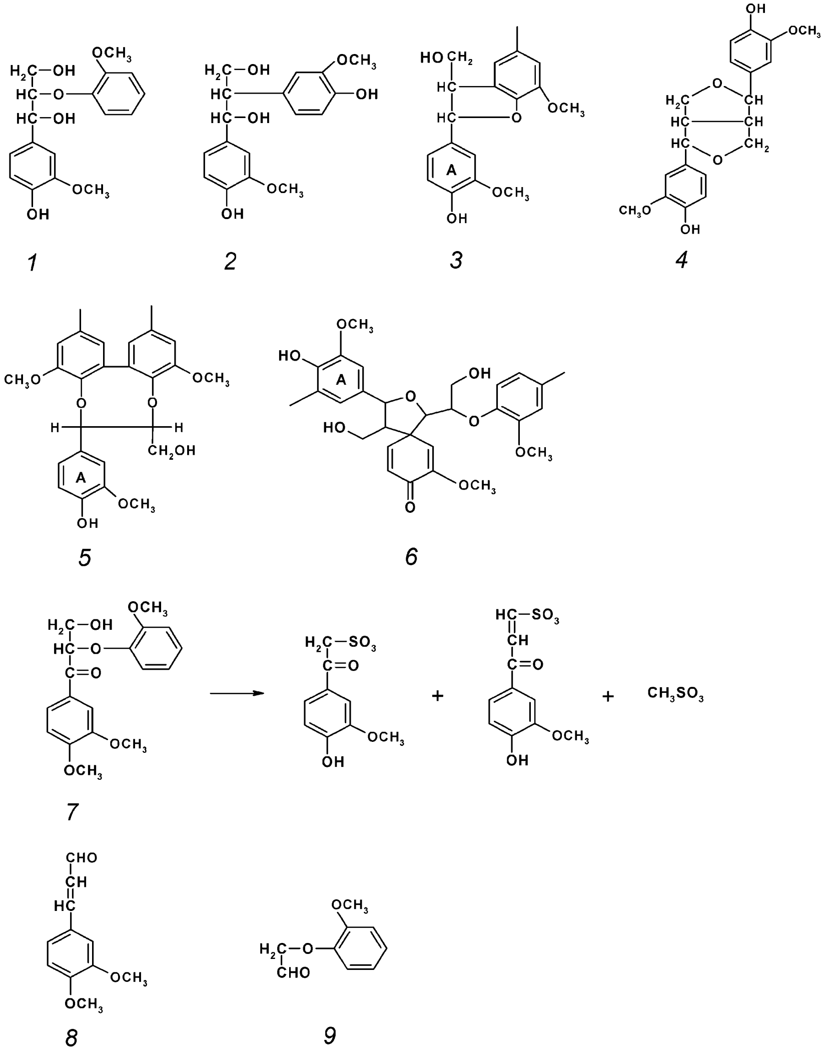


Figure 2. Active lignin model compounds under neutral sulfite pulping conditions[35] (with exception of compounds 5 and 6 that have not been examined).

reaction is the sulfonation at the benzylic position. This α-sulfonation was observed for all phenolic structures associated with the β-O-4 **1**, β-1, **2**, β-5 **3**, and β-β **4**. Also, the sulfonation occurred for the etherified units containing an α-carbonyl group **7** or an unsaturated unit **8** and **9**. The reaction of the oxidized etherified unit is of special interest, as the α-carbonyl group **7** would induce the sulfitolytic β-aryl ether cleavages, β-elimination, or demethylation reactions (Figure 2).

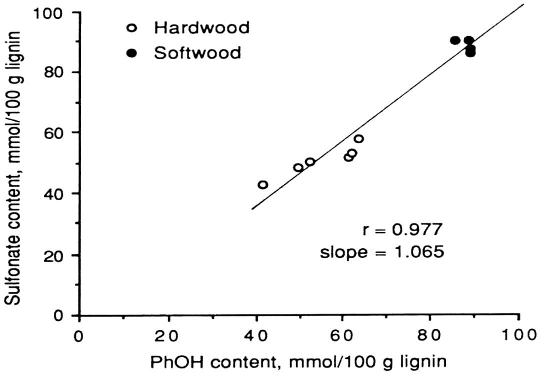


Figure 3. The extent of lignin sulfonation as related to the PhOH group content of wood lignin for the sulfite-treated wood samples at pH 7.5.[41]

Although the reactivity of dibenzodioxocin **5**,[36] spirodienone **6**,[37] enol ether,[38] and stilbene[39] type units has not been examined in detail, they are expected to be reactive under neutral sulfite cooking conditions. On the other hand, the phenolic units containing a α-reduced unit such as CH_2 would be un-reactive in neutral sulfite treatments.

Heitner et al.[40] reported that the maximum sulfonation of black spruce wood chip on neutral sulfite treatment (6% SO_2 solution) at 140°C required about 1 h. We adopted this condition except for using a slightly higher pH (7.5 vs. 7) to examine the sulfonation for a series of wood samples. Figure 3 illustrates an excellent correlation between lignin sulfonation and the PhOH group content of the sulfite-treated samples for both softwood and hardwood species.[41] The average ratio of lignin sulfonate group to PhOH units was 1.03 for the softwood and 0.92 for the hardwood species. The small difference may be attributed partly to the variation of wood lignin in the carbonyl or unsaturated group content.

Thus, the aforementioned observations suggest that the bulk of phenolic structures in wood lignin were able to undergo neutral sulfonation and contained very little of the α-condensed units. In this study, the similar sulfite treatment was used to evaluate the differences between the unbleached and the O_2-delignified spruce kraft pulps in the reactivity of phenolic structures. Also, the presence of oxidized etherified structures in the kraft pulps was examined by a borohydride pre-treatment of pulps prior to the sulfite treatment.

EXPERIMENTAL

Kraft Pulp Preparation

Kraft pulps prepared from Norway spruce chips were conducted using an 18% active alkali charge (as Na_2O) and a 25% sulfidity at a liquor-to-wood ratio of

4 in an M&K digester. The digester was heated from ambient temperature to 170°C in 60 min. and then kept isothermally for different duration to obtain a series of samples with kappa number in the 15–80 range.

Oxygen Delignification

The oxygen delignification was conducted in a Quantum reactor using a 5% alkali charge (as NaOH) at 10% consistency and 100°C for 1 h under an O_2 pressure of 90 p.s.i.

Sulfite Treatment

Samples of kraft pulps placed in small autoclaves were mixed with a sulfite solution (6% SO_2) at a liquor-to-wood ratio of 10. The sulfite solution was prepared by adjusting the sodium bisulfite solution to pH 7.5 with alkalis. The autoclave was then heated in an oil bath at 140°C for 1 h. The treated samples after thorough washing with distilled water were air-dried and analyzed for the content of residual lignin, PhOH, and sulfonate groups.

Borohydride Reduction

The borohydride reduction of kraft pulps was carried out in an Erlenmeyer flask using a 5% charge of sodium borohydride at 3% consistency with an initial pH of 10.5 at ambient temperatures for 12 h. The pulp mixture after acidification with a dilute HCl solution was filtered, washed thoroughly with distilled water, and then air-dried.

Analytical Methods

The kappa number of pulps was determined by the TAPPI test method T236 om-99. Klason lignin (acid-insoluble lignin) was measured following the procedure of TAPPI test method T222 om-98, whereas the acid-soluble lignin was determined according to TAPPI useful method UM 250. A good correlation between lignin content and kappa number was observed for all the unbleached samples. The lignin content of the O_2-bleached samples, because of their low values, was estimated from the kappa number by multiplying a factor of 0.15. The PhOH units were determined by a periodate oxidation procedure,[25] whereas the sulfonate group was measured by a conductometric titration.[42]

RESULTS AND DISCUSSION

Influence of Kraft and O_2-Delignification on the Phenolic Units

Figure 4 illustrates that the PhOH content of residual pulp lignin increased steadily with decreasing the pulp kappa number for a series of kraft pulps from Norway spruce in the 15–80 range. This trend is consistent with earlier observations.[27,28,30,43] A similar pattern is also shown for the O_2-delignified samples, which were prepared from the series of kraft pulps shown in Figure 4 using a 5% alkali charge at 100°C for 1 h. A comparison from the two curves indicated that approximately 50% of the phenolic units in unbleached kraft pulps were removed during the O_2-delignification process.

In kraft cooks, the PhOH units are generated from the β-aryl ether cleavages reactions. The existing phenolic unit along with those generated *in situ* would be modified to some extent either on the aromatic ring or the side-chain unit. The analyses of residual pulp lignin from the unbleached softwood kraft by permanganate oxidation[44] or the ^{31}P NMR methods[13,31] generally revealed a gradual decrease in the uncondensed guaiacyl units with increasing the delignification while the content of C_5-condensed and 5,5′-biphenyl structures was increased. Although the identification of diphenylmethane-type structures in the isolated lignin samples was reported by a ^{31}P NMR method,[14] this may require further confirmation.[6] The modified side-chain units identified in kraft

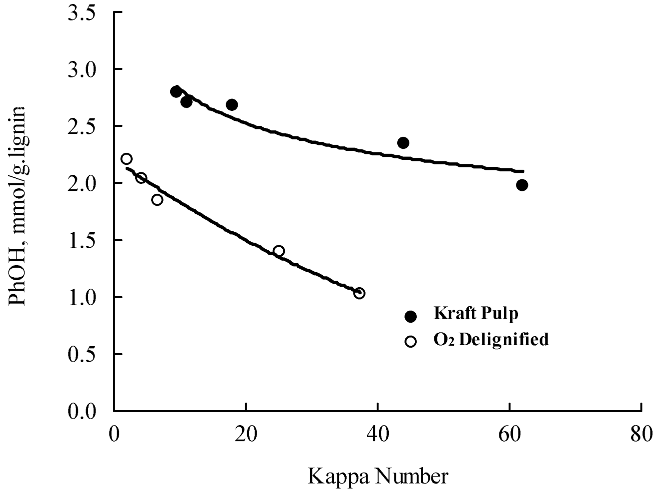


Figure 4. Variation of the PhOH content in residual pulp lignin with the kappa number of the unbleached and O_2-delignified kraft pulps from Norway spruce.

pulps included the formation of enol ether,[38] stilbene,[39] reduced,[6,13] and coniferyl alcohol[45,46] structures.

In O_2 delignification of kraft pulps, about 50% of the PhOH units (~50%) were removed as noted earlier and the resistant phenolic structures remained were shown to contain a higher content[13,31,44,47] of the C_5-condensed, 5,5′-biphenyl, and p-hydroxyphenyl units as well as a higher content of reduced side-chain units (-CH_2-).[13] It is anticipated that the structures of the enol ether,[38] stilbene,[39] and coniferyl alcohol[45,46] types generated in kraft cooks would be largely degraded in O_2 delignification based on their high reactivity observed in model compound reactions.[48]

Response of Unbleached Kraft pulps to Sulfite Treatments

The aforementioned series of the unbleached kraft pulps was then treated with a sulfite solution at pH 7.5 (at 140°C for 1 h). Figure 5 illustrates the extent of lignin sulfonation as related to the PhOH content of the residual kraft pulp lignin. The curve displayed a distinctly different pattern from that of the wood lignin *in situ* under similar sulfite treatment conditions (Figure 3). For the sulfite-treated kraft pulps, the apparent ratios of lignin sulfonation

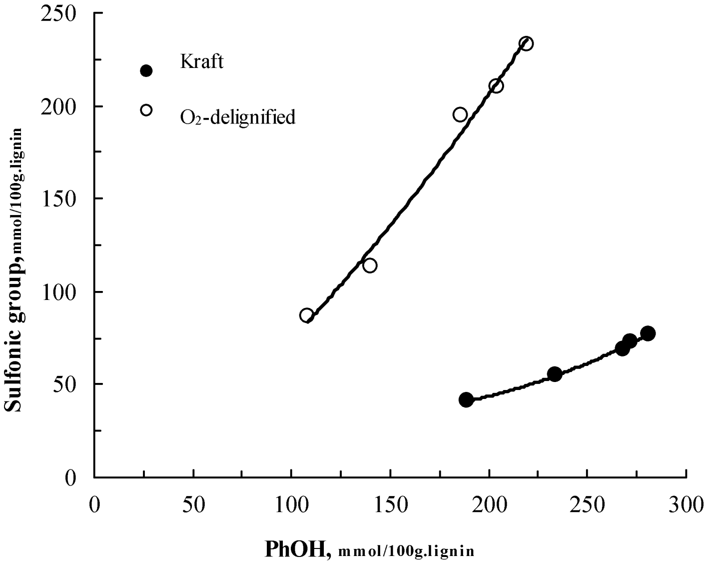


Figure 5. The extent of lignin sulfonation as related to the phenolic hydroxyl group (PhOH) content of residual pulp lignin for sulfite-treated unbleached and O_2-delignified kraft pulps from Norway spruce.

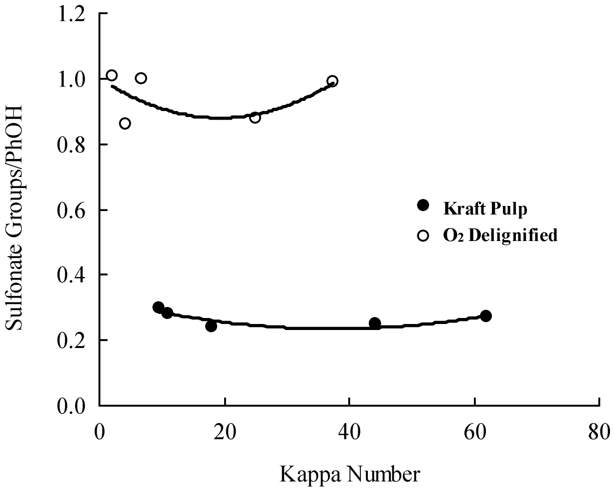


Figure 6. The apparent ratio of lignin sulfonation to the PhOH group content of residual pulp lignin for the sulfite-treated unbleached and O_2-delignified kraft pulps from Norway spruce.

to the PhOH groups were fairly low, being in the 0.25–0.3 range (Figure 6), as compared to that of the wood lignin (0.9–1) (Figure 3). Thus, the bulk of phenolic units in the residual kraft pulp lignin were unable to achieve the α-sulfonation and this may be attributable to the alkali-induced modification of the side-chain units encountered in kraft cooks. The modified side-chain units, as noted earlier, include the α- reduced units,[13] which would be stable under neutral sulfite treatment conditions. Also, the α-condensed or -linked to a carbohydrate moiety, if present, would be un-reactive in sulfite treatments. Because the enol ether or the stilbene types would be reactive in neutral sulfite treatments, it would appear that the presence of reduced side-chain unit, α-condensed or α-substituted with a carbohydrate moiety, would be an important factor contributing to the low reactivity of the residual kraft pulp lignin. Also, it is unclear on the extent that the phenolic units might contain an α-thio group and how they would respond to the sulfite treatment.

Response of O_2-Delignified Kraft Pulps to Sulfite Treatment

Similarly, the series of the O_2-delignified pulps was submitted to the same sulfite solution (at pH 7.5 and 140°C for 1 h). As indicated in Figure 5, the lignin sulfonation was closely related to the PhOH content of the residual pulp lignin and was substantially higher than that of the unbleached kraft pulp when comparing at a given PhOH content. In contrast to a low sulfonation/PhOH ratio (0.25–0.3) for the unbleached sample, a considerably high ratio (0.8–1.0) was found for the O_2-delignified samples (Figure 6). Because the O_2-delignification is known to increase the reduced side-chain units in the residual pulp lignin,[13] which is un-reactive toward sulfite treatments, the high lignin sulfonation /PhOH ratio for the O_2-delignified pulp would suggest two possibilities: the O_2-delignification has removed those extensively modified units or the observed sulfonation was also contributed from the oxidized etherified unitcontaining an α-carbonyl group.[31,34] The latter oxidized etherified structure such as **7** of Figure 2 was known to be quite reactive in neutral sulfite treatments.[35] This contention is examined and discussed in the following.

Influence of a Borohydride Pre-treatment in Sulfite Treatment

To evaluate the possible contribution of oxidized etherified structures to the neutral sulfonation, an unbleached spruce kraft at 66 kappa and an O_2-delignified spruce kraft sample at 22 kappa were reduced with sodium borohydride prior to the sulfite treatments. Table 1 illustrates the influence of borohydride reduction on the lignin sulfonation and the PhOH content of sulfite-treated samples.

As indicated, the borohydride pre-treatment reduced the lignin sulfonation of the unbleached kraft by about 40% (Samples KS vs. KBS), whereas a lower percent reduction (15%) was observed for a borohydride pre-treatment of the O_2-delignified sample (Samples KOS vs. KOBS). The observed reduction in sulfonation was likely resulted from elimination of the oxidized etherified units containing α-carbonyl group. It should be noted that the actual reduction in sulfonation (16–17 mmol/100 g lignin) was essentially identical for both unbleached and the O_2-delignified samples, and this would translate into an aryl α-carbonyl group content of 0.03 per phenylpropane (C_9) unit. Because

Table 1. The influence of sodium borohydride pre-treatment on the sulfite treatment of spruce kraft pulps at pH 7.5 and 140°C for 1 h

Samples	Borohydride pre-treatment	Kappa no.	Functional groups, mmol/100 g lignin	
			$-SO_3H$	PhOH
K	—	65.8	—	165
KS	—	60.1	50	188
KBS	Yes	59.3	32	179
KO	—	22.4	—	101
KOS	—	21.1	110	134
KOBS	Yes	19.6	93	115

K, krat pulps; S, sulfite treatment; B, borohydride treatment; O, O_2 delignification; SO_3H, sulfonate groups; PhOH, phenolic hydroxyl group.

these oxidized etherified structures are reactive and degraded[49] under the O_2-delignification conditions, a similar content for both unbleached and the O_2-delignified samples would suggest that they are also generated during the O_2-delignification as reported by others.[31]

For a reference, the above-estimated aryl α-carbonyl group of 0.03 per $C_9$for the residual kraft pulps lignin compares well to a reported value of 0.06 for the spruce milled wood lignin,[50] especially in view of the distinctly different methods and pulp samples used.

Also indicated in Table 1, the sulfite treatment of the unbleached kraft resulted in a 10% increase in the PhOH content of residual lignin (K vs. KS) and an even higher increase of this functional group (30%) was observed for a similar sulfite treatment of the O_2-delignified sample (KO vs. KOS). These would be equivalent to an increase in PhOH of 0.04 and 0.06 per C_9 unit for the unbleached and O_2-delignified samples, respectively. This PhOH generation may be attributed to the sulfitolytic cleavages of β-aryl ether linkages[35] of the phenolic type**1** or the oxidized etherified units **7** (Figure 2). Interestingly, the borohydride pretreatment reduced the PhOH formation by about 50%, and this further supports the presence of oxidized etherified units in both the unbleached kraft and the O_2-delignified samples.

The aforementioned results indicate that only a small portion of the enhanced sulfonation in the O_2-delignified kraft pulps could be attributed to the presence of the oxidized etherified structures. Thus, the phenolic structures presented in the O_2-delignified sample were clearly more responsive to the sulfite treatments than those that existed in the unbleached kraft pulps. Because O_2 delignification reduced the PhOH content of unbleached kraft by approximately 50%, it is unclear on the extent that the phenolic structures present in the O_2-delignified samples were originated from the unbleached kraft or modified or generated during the O_2 delignification.

IMPLICATIONS

The response of kraft pulps to sulfite treatments at pH 7.5 provides further insight into the nature of the phenolic lignin structures. In kraft delignification, the phenolic unit content is continued to increase in the residual pulp lignin. Interestingly, less than 30% of these structures were able to achieve the neutral sulfonation (Figure 6) as compared to nearly 100% for the wood lignin *in situ* (Figure 3). Thus, extensive modifications must have occurred at the benzylic position during the kraft cooks, and the reactions may include the formation of reduced units[13] or condensed structures, which were resistant to neutral sulfite treatments. Also, there is a possibility that the reduced sulfonation may be partly attributed to the presence of α-thio group or its condensed products,[51] which are resistant to neutral sulfonation, and this hypothesis merits a further clarification.

In contrast, the phenolic units of O_2-delignified pulps were very responsive to the neutral sulfite displaying a high ratio ($\sim$0.85) of lignin sulfonation to the PhOH groups. Because this ratio was only slightly affected by elimination of the oxidized etherified structures units with a borohydride reduction, the phenolic structures of the O_2-delignified sample appear to differ distinctly from that of the unbleached kraft in lignin reactivity. Conceptually, the enhanced sulfonation of O_2-delignified pulps would suggest that O_2-delignification preferentially removed those phenolic units resistant to sulfonation or generated additional reactive sites. This subject will be examined further.

CONCLUSIONS

The response of kraft pulps to sulfite treatments provides further insight into the chemical nature and reactivity of the residual lignin as reflected in the extent of sulfonation and aryl ether cleavages reactions. The present data suggest that O_2 delignification resulted in a significant modification and degradation of the existing phenolic structures in kraft pulps as well as in the formation of new types of phenolic units. The nature of phenolic structures in the O_2-delignified kraft appears to be more similar to that of the lignin in wood than that of the unbleached kraft. This study shows that the sulfite treatment at pH 7.5 would be a useful tool to determine the nature of phenolic structures at the benzylic position and the content of the oxidized etherified structures in lignin-containing materials.

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