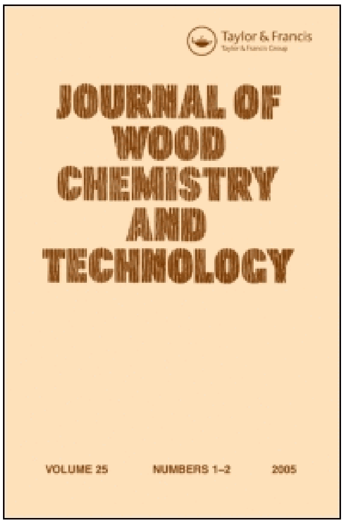

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THE INFLUENCE OF SULFIDITY IN KRAFT PULPING ON THE NATURE OF RESIDUAL LIGNIN

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ABSTRACT

The influence of sulfidity in kraft pulping of Norway spruce chips on the characteristics of residual lignin has been examined at two levels 25 and 40%. Comparing with the reference kraft cook at similar kappa number, the high sulfidity pulp lignin displayed a significantly lower phenolic hydroxyl group content, and a lower response to O_2 delignification, but it gave a slightly higher yield of nitrobenzene oxidation products, and was more responsive to a neutral sulfite treatment.

INTRODUCTION

One of the formidable challenges in kraft pulping is how to effectively remove the last 5-10% of lignin while maintaining the fiber quality. In the current trend of production of bleached chemical pulps, O_2 bleaching [1] has become a preferential process to follow kraft pulping. However, it can only readily delignify approximately 50% of the residual kraft lignin without causing an excessive fiber degradation. We have conducted studies aimed at understanding the nature of residual lignin [2,3] and how it may be affected by pulping conditions.

The nature of residual lignin, as revealed by the yield of nitrobenzene oxidation products, appears to be more condensed with increasing extent of kraft delignifications.[4] Recently, we have shown [2] that the content of phenolic hydroxyl groups in unbleached kraft pulp lignin increased steadily with the pulping reaction. The latter functional groups are one of the most reactive sites in lignin and are expected to facilitate the O_2-delignification process.

Sodium sulfide is well known for its enhancement of alkaline delignification.[5] However, its effects on the residual lignin have not been examined in detail. In this paper we report on an investigation of the characteristics of residual lignin from kraft pulping with a high sulfidity (40%) compared to that of a reference kraft cook at 25% sulfidity. The residual lignin was analyzed *in situ* for the phenolic hydroxyl group content, and for its response toward O_2 bleaching and neutral sulfite treatments.

EXPERIMENTAL

Kraft Pulping

The kraft pulping of Norway spruce chips (~400 g) was conducted in an M&K digester using a liquor-to-wood ratio of 4. A reference kraft cook employed a 18% active alkali charge and a 25% sulfidity, whereas a high-sulfidity cook used a 40% sulfidity with a similar active alkali charge (18%). The digester was heated from ambient temperature to 170°C in 90 min. and then kept isothermally for different durations to obtain pulps in the 15-80 kappa number range.

O_2 Bleaching

Oxygen bleaching was conducted in a Quantum reactor using 3% pulp consistency, a 5% alkali charge with $MgSO_4$ (0.5%), and an O_2 pressure of 90 psi at 100°C for 1 h.

Analytical Methods

Lignin (Klason plus acid-soluble) contents and kappa numbers were

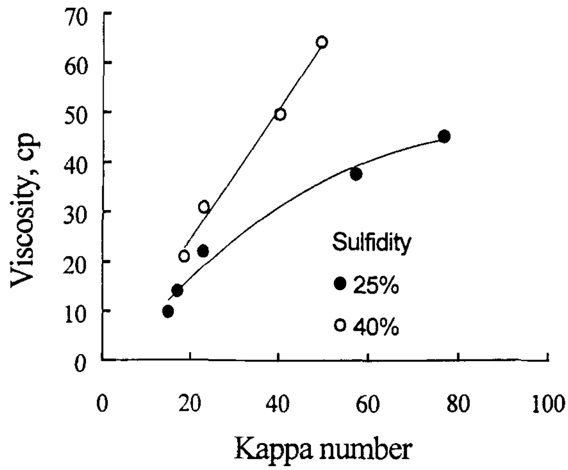

Figure 1. The influence of sulfidity on the alkaline delignification selectivity of Norway spruce at 170°C.

determined by the Tappi Standard Methods. The lignin contents of O_2-bleached samples, because of their low values, were generally estimated from the kappa number by a multiplication factor of 0.15. Phenolic hydroxyl groups were determined by the periodate oxidation procedure.[6] Nitrobenzene oxidation was carried out as described earlier.[3] Sulfite treatments of pulps were performed at pH 7.5 and 140°C for 1 h as previously outlined.[7] The sulfonate group content was measured by a conductometric method.[8]

RESULTS AND DISCUSSION

Characteristics of Unbleached Pulps

Two series of kraft pulps in the 15-80 kappa number range were prepared from Norway spruce chips at two levels of sulfidity (25 and 40%) under otherwise similar cooking conditions. As anticipated, the high-sulfidity cook resulted in a considerably higher delignification selectivity (Fig. 1), and its beneficial effects on pulp viscosity was especially pronounced above the 30 kappa number level.

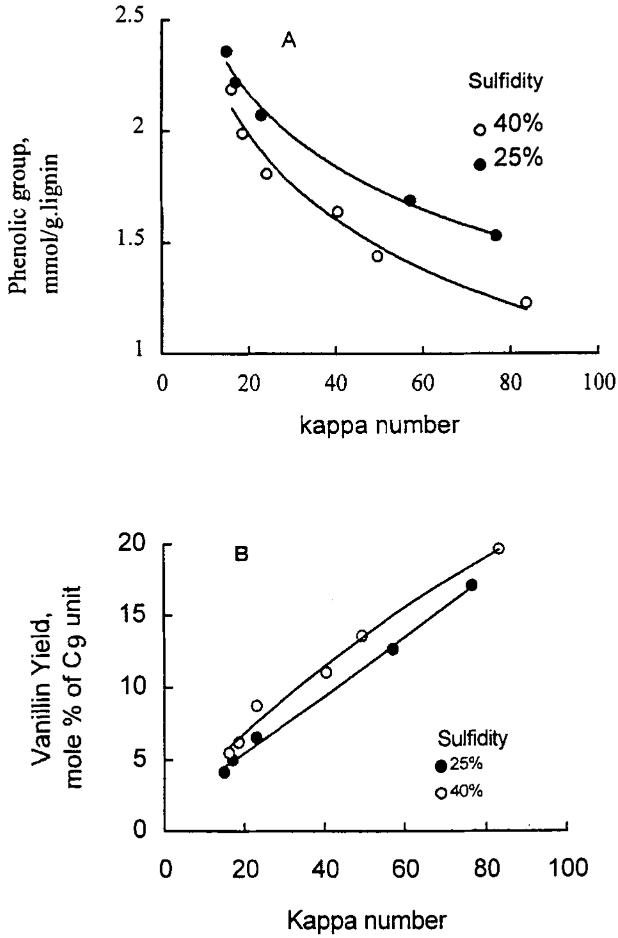

Figure 2. The influence of sulfidity on phenolic hydroxyl group content (A) and nitrobenzene oxidation products (B) of kraft pulp residual lignin.

Figure 2A illustrates the phenolic hydroxyl group content of the residual pulp lignin as related to the pulp kappa number. Consistent with our earlier findings,[2] the phenolic hydroxyl group content increased steadily with a decrease of the pulp kappa number. It is clearly shown that the two series of kraft cooks displayed distinctly different curves. Compared at similar kappa number, the high sulfidity pulp had a lower phenolic hydroxyl group content than the reference kraft pulps.

Since the periodate oxidation method used to determine the phenolic hydroxyl groups was based on the methanol formation, it excludes the detection of methoxy-free phenolic units. The content of catechol-type units had been reported to be small (<1%) in conventional kraft or O_2-bleached pulps.[3,9] Thus, it appears that a lower phenolic hydroxyl group content of the high-sulfidity pulp may be partly related to its lignin being less condensed.

The contention that a high-sulfidity cook reduces the extent of condensed units in the residual lignin is also consistent with the results of nitrobenzene oxidation analysis. As indicated in Figure 2B, the vanillin yield of high-sulfidity pulps was slightly higher than that of the conventional kraft pulps.

Sulfonation

Since fiber sulfonation under neutral or slightly alkaline conditions is generally limited to the phenolic units of lignin,[10] it may be used to reveal the extent of substitution at the α position. As shown in Figure 3, the high-sulfidity pulps, compared to the reference cooks, were slightly more responsive to sulfite treatments, and contained more reactive sites capable of undergoing sulfonation under slightly alkaline conditions despite their lower phenolic units. Thus, the phenolic component of the high-sulfidity pulp lignin appears to be less condensed or substituted at the benzylic positions.

O_2-Delignification

Figure 4 illustrates the influence of the unbleached pulp kappa number on the percent kappa number reduction in O_2 bleaching at 100°C for 1 h. The bleaching conditions used would have completed the rapid delignification phase. It is evident

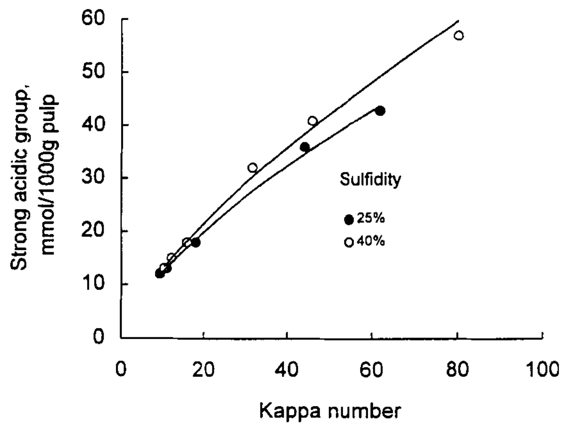

Figure 3. The influence of sulfidity on the response of kraft pulps to neutral sulfite treatments as indicated by the formation of strong acidic groups.

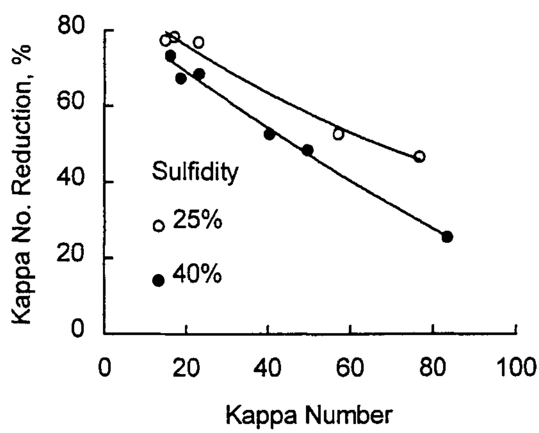

Figure 4. The influence of sulfidity on O_2 delignification of kraft pulps.

that the O_2 delignification increased significantly with decreasing kappa number of the unbleached pulps. Also, compared at similar kappa number, the high-sulfidity pulp was less reactive toward O_2 bleaching than the reference kraft pulp. This apparent difference in reactivity, however, is closely related to the variation in their phenolic hydroxyl group content (Fig. 2A).

CONCLUSIONS

Sulfidity has been shown to have a significant influence on the nature of the residual pulp lignin, and its response toward neutral sulfonation and O_2 bleaching. A high sulfidity cook significantly reduced the phenolic hydroxyl group content of the residual lignin, and this may be largely responsible for a reduced O_2 delignification of the high-sulfidity pulp.

ACKNOWLEDGMENTS

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