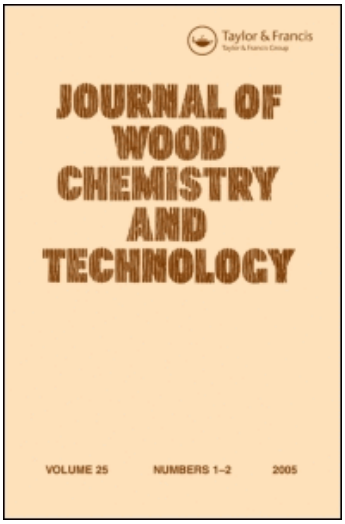

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Understanding Factors Contributing to Low Oxygen Delignification of Hardwood Kraft Pulps

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Abstract: We observed that the O_2 delignification pattern of aspen kraft pulps was distinctly different from that of pine pulps based on a reduction in the apparent pulp kappa number. Much of this phenomenon can be attributed to the variation of the residual extractives and hexeneuronic acid (HexA) unit content in the unbleached and O_2-delignified pulps, as they interfered with the conventional lignin determination methods. However, after a correction for contributions from these non-lignin components, the hardwood kraft pulps still displayed a lower response to O_2 delignification than the pine pulps. It appears that the relative reactivity of residual lignin in the hardwood and softwood pulps differs appreciably with the extent of kraft delignification, and is a significant factor affecting the overall O_2 delignification reaction.

Keywords: Residual extractives, hexeneuronic acid, kraft pulps, oxygen delignification, kappa number, lignin determination

INTRODUCTION

Oxygen delignification is a well-established process, and plays an important role in current production of bleached chemical pulps.[1] In a typical

This article is dedicated to the memory of Professor Josef S. Gratzl, a world-renowned scientist and a good friend.

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O_2 delignification of softwood kraft pulps, approximately 50% of the residual lignin can be removed without a serious effect on the pulp properties. Interestingly, it was generally reported[2–4] that hardwood kraft pulps are less responsive to the O_2 delignification process than softwood pulps. For example, in a survey of kraft mills,[2] the average O_2 delignification of softwood pulps (47.5%) was significantly higher than that of the hardwood pulps (40.2%). Also, for each unit of kappa number reduction, the softwood pulps required less alkali (0.13 *versus* 0.14%) and less O_2 (0.14 *versus*, 0.16%) than the hardwood pulps. In addition, a similar trend was observed[3] in an O_2–peroxide reinforced alkaline extraction stage (E_{op}), which resulted in a higher delignification (3.4%) for the softwood kraft pulps than for the hardwood pulps.

In view of the increasing significance of using hardwood in pulp production,[5] we have been interested in understanding the factors that contribute to a relatively poor performance of hardwood kraft pulps in the O_2 delignification process. Conceptually, structural variations of the residual lignin[6–15] in the softwood and hardwood pulps should play a role in the O_2 delignification reaction. It was reported[13] that the residual lignin in most hardwood kraft pulps has a lower phenolic hydroxyl group (PhOH) content than that of the softwood pulps. Because this functional unit represents one of the most reactive sites and has a significant impact[9] in the O_2 delignification of softwood pulps, it could be a contributing factor to the poorer performance of hardwood pulps. Although the hardwood lignin *in situ* is considerably less condensed than that of softwood, the condensed structures of residual pulp lignin in sweetgum kraft pulps was reported[14,15] being very comparable to that of the Douglas-fir pulps.

On the other hand, it is well known that the kappa number method of determining the residual lignin content of kraft pulps is affected by the presence of non-lignin components containing unsaturated groups, which consume permanganate during the kappa number determination.[17] Among these active non-lignin components, the influence of hexeneuronic acid (HexA) groups linked to xylan was well documented.[16–21] Because the content of these groups[20,21] is significantly higher in hardwood kraft pulps than in softwood pulps, and also is relatively resistant to O_2 delignification,[19] it could lead to an under-estimation of the O_2 delignification in hardwood pulps.

Our recent findings[22] further indicate that the residual extractives present in kraft pulps have a significant impact on the lignin content determination, notably by the Klason lignin method. In this study, the O_2 delignification efficiencies of pine, aspen, and birch kraft pulps were compared under similar conditions. The extent that the differences between the softwood and hardwood pulps in O_2 delignification may be attributed to the variation both in reactivity of the residual lignin, and in the content of residual extractives and the HexA units are discussed.

EXPERIMENTAL

Preparation of Kraft Pulps

Kraft pulps were prepared from the loblolly pine (*Pinus taeda* L.), trembling aspen (*Poplus tremuloides* M.), and white birch (*Betula papyrifere* M.) wood chips in an M & K digester. The cooks used an effective alkali charge of 15 and 18% for the hardwood (aspen and birch) and pine chips, respectively, a 30% sulfidity, and a liquor-to-wood ratio of 4. The pulping temperature was maintained isothermally at170°C (T_{max}) and included a 1-h heating up period. A series of pulps with different kappa numbers was obtained by varying the H-factors: for the pine (1000, 1500, and 2200.), for aspen (650, 900, and 2300), and for birch (1000) cooks.

Oxygen Delignification

Oxygen delignification used a 2% NaOH charge, and 0.5% $MgSO_47H_2O$ based on an oven-dried pulp basis. It was conducted in a Quantum Mark IV reactor at 10% consistency, and 100°C under 90 psi of O_2 for one h.

Extraction of Pulps

Air-dried kraft or oxygen-delignified pulps (10 g, oven-dried basis) were extracted as described in TAPPI Test Method T204 cm-97. An ethanol-benzene mixture (1:2, v/v) was used as the extracting solvent.

Analytical Methods

Kappa numbers of the unbleached and O_2-delignified kraft pulps were determined according to TAPPI Test Method T236 om-99. The Klason lignin (acid insoluble lignin) content was determined following TAPPI Test Method T222-om-98, whereas the acid-soluble lignin was measured as described in TAPPI Useful Method UM 250.

The phenolic hydroxyl group (PhOH) content of the unbleached and O_2-delignified kraft pulps was determined *in situ* by a periodate oxidation methods.[23] The hexeneuronic acid (HexA) content of kraft pulps was determined by a selective hydrolysis of these units by mercuric chloride.[24]

RESULTS AND DISCUSSION

A series of kraft pulps with kappa number in the 10–26 range from the aspen, and in the 20–33 range from the loblolly pine chips were prepared by varying

the pulping H factors. Also, a single cook of white birch at 16 kappa number was included for comparison. All the cooking conditions were similar except using a lower effective alkali charge for the aspen and birch cooks (15%) than for the pine (18%). Table 1 summarizes the pulp yields and kappa numbers of the unbleached kraft pulps.

Delignification of Aspen, Birch, and Pine Kraft Pulps

Figure 1A compares the percent O_2 delignification of the aspen, birch, and pine kraft pulps based on a reduction in the apparent pulp kappa number. It is evident that for a given kappa number of the unbleached pulps, the delignification was significantly lower for the aspen pulp than the pine pulp. Also, the birch pulp had an even poorer performance than the aspen pulp. Unexpectedly, the delignification curve of the aspen kraft pulps displayed a clear maximum near the 15 kappa number region of unbleached pulps. This pattern differs distinctly from that of pine and spruce kraft pulps,[9] which show a steady increase in O_2 delignification with decreasing the unbleached pulp kappa number.

However, when the percent O_2 delignification was based on the reduction in the acid-lignin content (Klason lignin plus acid-soluble lignin), a nearly linear relationship with the acid-lignin content of unbleached pulps was observed for both the pine and aspen pulps (Figure 1B). Also, the difference between the pine and aspen pulps in O_2 delignification varied with the lignin content of unbleached pulps, and became apparent only in the region of lignin content above the 2.5% level. A nearly 20% lower delignification was shown for the aspen pulps compared at the 4.5% lignin level. These results support the general observation[2–4] that hardwood kraft pulp is less responsive to O_2 delignification. Figure 2 further illustrates that O_2 delignification of pine pulps resulted in larger reductions in kappa number and acid-lignin content than for hardwood pulps.

Table 1. Yields and kappa numbers of unbleached kraft pulps prepared from aspen, white birch, and pine

Species	H-factor	Pulp yield, %		Kappa number
		Screened pulp	Rejects	
Aspen	650	56.9	1.7	26.1
	950	56.2	0.5	16.0
	2300	54.9	0.2	9.5
Birch	1000	50.0	0.2	16.0
Pine	1000	46.6	1.4	33.6
	1500	45.3	1.3	24.0
	2200	43.7	1.1	20.3

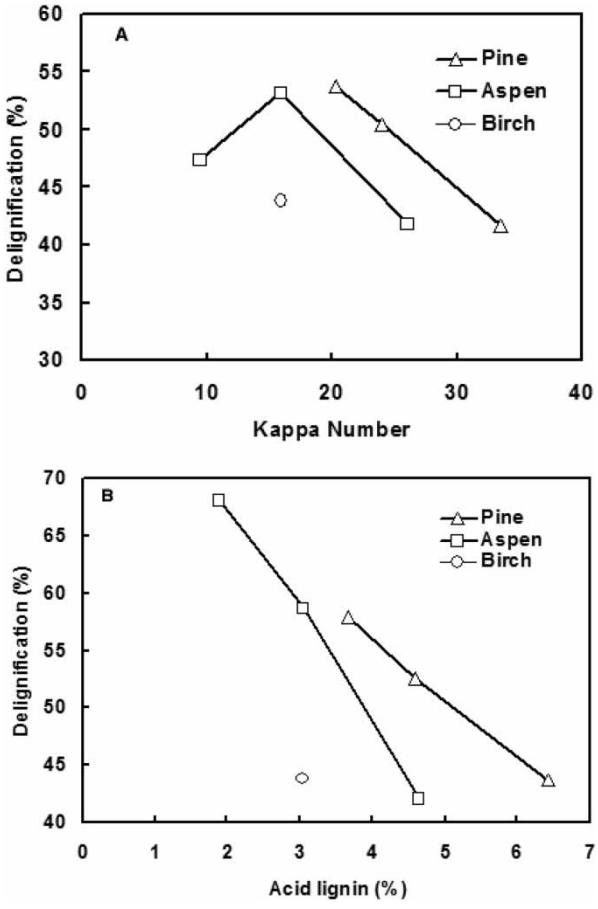

Figure 1. A comparison of the oxygen delignification of pine, aspen, and birch kraft pulps in relation to the lignin content of the unbleached pulps as determined by the kappa number (A) and acid-lignin content (B) methods.

It is evident that the delignification pattern of the aspen pulps differed distinctly between the two methods of lignin determination, the kappa number (Figure1A) and acid-lignin procedure (Figure 1B) method. This phenomenon most likely results from interference of the non-lignin components in the lignin analyses, which is discussed further with regard to the impact of residual extractives and the HexA units.

Impact of Residual Extractives

We have observed recently[22] that a significant amount of extractives remains after kraft pulping, even after O_2 delignification in the case of hardwood pulps.

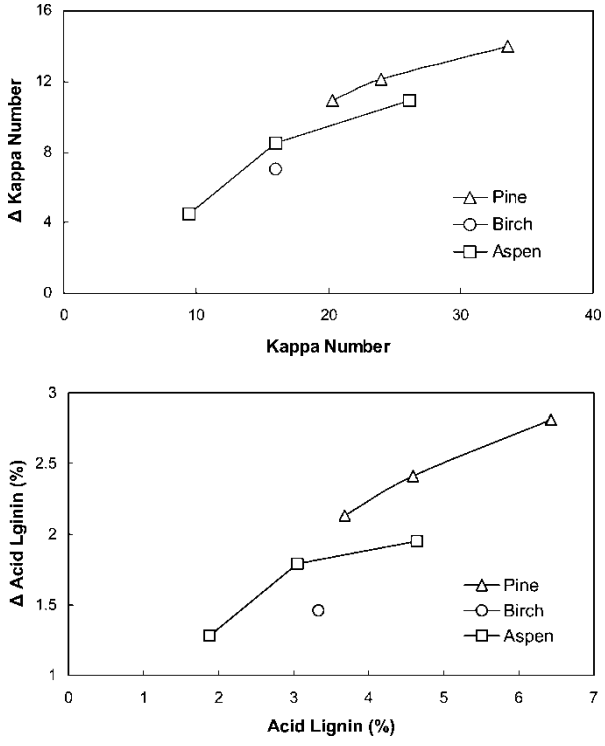

Figure 2. A comparison of the changes in kappa number (A) and acid-lignin content (B) on oxygen delignification of pine, aspen, and birch kraft pulps in relation to the lignin content of the unbleached pulps.

Tables 2 and 3 summarize the residual extractives contents of the unbleached and oxygen-delignified kraft pulps from aspen, birch, and loblolly pine, as well as their impact on the lignin content analysis. It is evident that the residual extractives had more of an impact on the acid-lignin determination than the kappa number procedure. The impact of residual extractives on the kappa number decreased from 11.3–13.8% in the aspen and birch unbleached pulps to 5.3–12.0% in the oxygen-delignified pulps. However, the relative impact of extractives on the acid-lignin analysis increased from 15.5–23.4% in the aspen and birch unbleached pulps to 21.9–41.7% in the oxygen-delignified pulps. On the other hand, the contributions of extractives in the pine pulps to the kappa number or acid-lignin analysis were minimal.

Figure 3 illustrates the impact of a correction for the residual extractive contribution to the lignin analysis on the O_2 delignification of aspen, birch, and pine pulps. As indicated, the impact was more for the aspen pulp than for the pine pulp, and also was more in the kappa number method than in the acid-lignin procedure. For the two high kappa number aspen pulps, the

Table 2. Impact of residual extractives[a] on the lignin content of unbleached pulps

Pulp[b]	Pulp extractives, %	Extractives contribution to kappa number, %	Extractives contribution to acid lignin, %
AK 650	1.0	13.8	15.5
AK 950	1.0	11.3	16.4
AK 2300	0.5	11.6	23.4
BK 1000	0.6	11.3	18.3
PK 1000	0.2	2.4	3.0
PK 1500	0.2	0.8	2.8
PK 2200	0.2	3.0	2.7

[a]Extraction with ethanol-benzene (1:2, vol).
[b]AK: trembling aspen, BK: white birch, and PK: loblolly pine kraft pulps. The number is the H-factor for the kraft pulping.

extractives correction resulted in a lower O_2 delignification (2–6%) determined by the kappa number method, whereas the impact on the pine pulp was minimal.

Impact of Hexeneuronic Acid Groups (HexA)

The HexA content of the unbleached and O_2-delignified kraft pulps was determined by a selective hydrolysis of these units with mercuric chloride.[24] Tables 4 and 5 summarize the HexA contents and their contributions to the

Table 3. Impact of residual extractives[a] on the lignin content of O_2-delignified kraft pulps

Pulp[b]	Pulp extractives, %	Extractives contribution to kappa number, %	Extractives contribution to acid lignin, %
AO 650	0.52	5.3	21.9
AO 950	0.50	6.7	33.3
AO 2300	0.43	12.0	41.7
BO 1000	0.32	7.8	24.1
PO 1000	0.11	0.5	1.7
PO 1500	0.05	2.5	3.7
PO 2200	0.05	0.0	5.2

[a]Extraction with ethanol-benzene (1:2, vol).
[b]AO: trembling aspen, BO: white birch, and PO: loblolly pine O_2-delignified kraft pulps. The number is the H-factor for the kraft pulping.

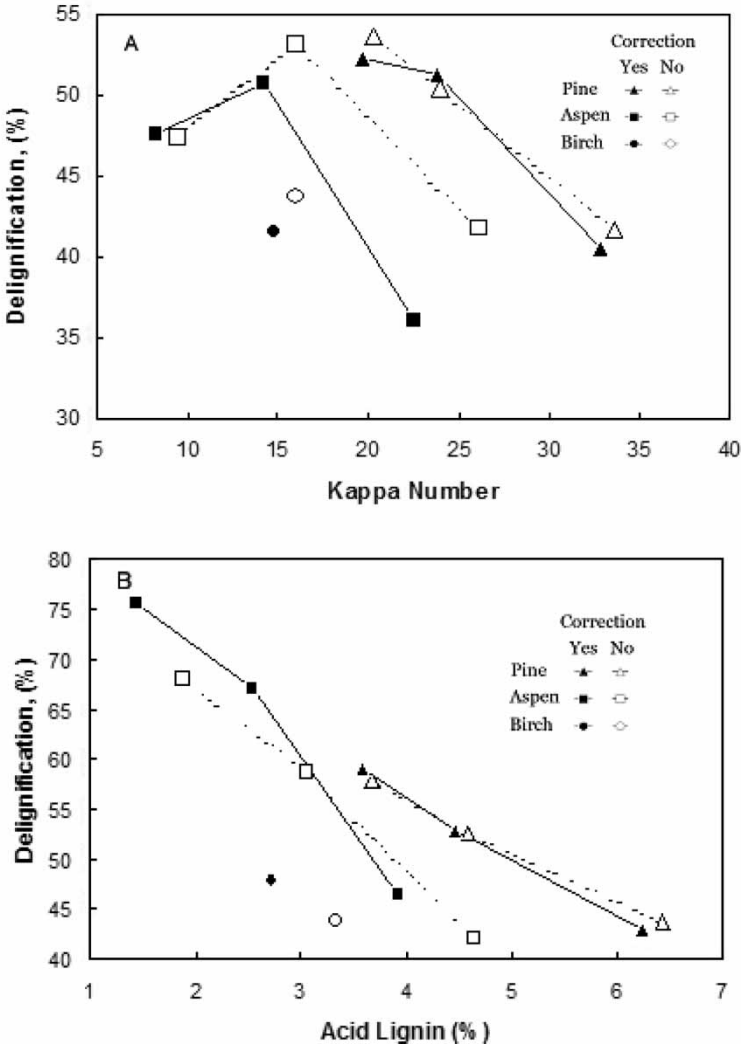

Figure 3. Impact of residual extractives on the O_2 delignification determined by the kappa number (A) and acid-lignin (B) methods. (The dotted lines are for the original data, whereas the solid lines are the data after correction for the residual extractives contribution).

kappa number determination for the unbleached and O_2-delignified kraft pulps, respectively. The equivalent kappa number contribution was calculated on the basis of work by Li and Gellerstedt.[16] As anticipated, the aspen kraft pulp had a considerably higher HexA content than the pine pulps. Also, the bulk of these groups were retained after O_2-delignification. Thus, the HexA units had an enormous impact on the kappa number determination of aspen

Table 4. Impact of hexeneuronic acid on the kappa number of unbleached kraft pulps

Pulp[a]	Kappa number[b]	Hexeneuronic acid (μmol/g pulp)	Kappa equivalent	% Contribution to kappa number
AK 650	22.5	50.09	4.1	18.2
AK 950	14.2	53.12	4.3	30.3
AK 2300	8.4	36.65	3.0	35.7
PK 1000	32.8	34.77	2.8	8.5
PK 1500	23.8	21.33	1.7	7.1
PK 2200	19.7	20.96	1.7	8.6

[a]AK: trembling aspen, BK: white birch, and PK: loblolly pine kraft pulps. The number is the H-factor for the kraft pulping.

[b]Based on extractives-free pulp.

pulps, especially for the O_2–delignified pulp. For example, the HexA groups contributed to more than 50% of the pulp kappa number for the two most delignified aspen samples (AO 950 and AO 2300).

Figure 4 illustrates that HexA groups had a considerable impact on the determination of O_2 delignification by the kappa number method, especially for the hardwood pulps. After correction for the HexA content, the delignification of both the pine and aspen pulps was nearly a linear relationship with respect to the kappa number of the unbleached pulps. This trend is consistent with an earlier observation.[9] Interestingly, an extrapolation of the curve for the pine pulp would intersect with the aspen line near the 10 kappa number region. It follows that the relative response of the pine and aspen pulps to O_2 delignification would vary significantly with the extent of kraft delignification. Comparing pulps near the 20 kappa number region, the aspen pulp showed a 30% lower delignification than the pine pulp. An opposite trend, however, would be anticipated for pulps below the 10 kappa number region.

Table 5. Impact of hexeneuronic acid on the kappa number of O_2-delignified kraft pulps

Pulp[a]	Kappa number[b]	Hexenuronic acid (μmol/g pulp)	Kappa equivalent	% Contribution to kappa number
AO 650	14.4	47.17	3.8	26.4
AO 950	7.0	44.16	3.5	50.0
AO 2300	4.4	35.85	3.2	72.7
PO 1000	19.5	32.99	2.6	13.3
PO 1500	11.6	22.21	1.8	15.5
PO 2200	9.4	19.94	1.6	17.0

[a]AO: trembling aspen, BO: white birch, and PO: loblolly pine O_2-delignified kraft pulps. The number is the H-factor for the kraft pulping.

[b]Based on extractives-free pulp.

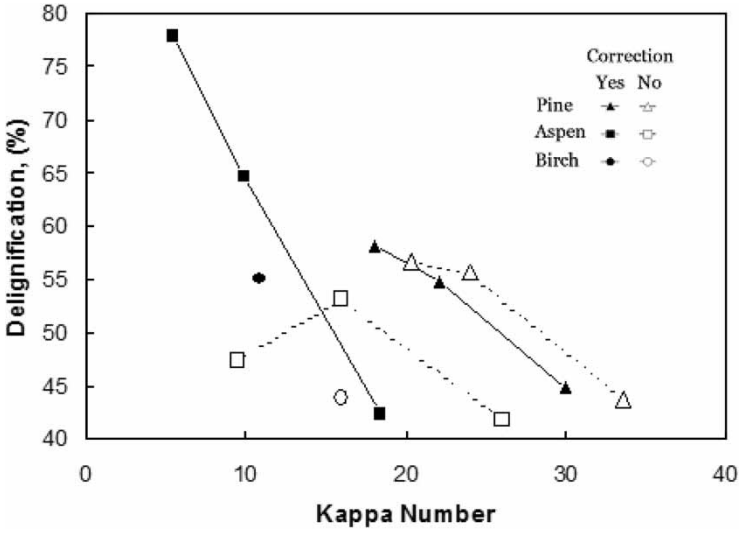

Figure 4. Impact of HexA units on the O_2 delignification of kraft pulps determined by the kappa number method. (The dotted lines are for the original data, whereas the solid lines are for data corrected for the HexA contribution).

Fate of Phenolic Units

As noted earlier, the phenolic hydroxyl units (PhOH) are the most reactive sites of residual lignin under O_2 delignification conditions, and thus should be a factor affecting the relative reactivity of the hardwood and softwood pulps. This functional group was determined *in situ* by a periodate oxidation procedure.[23] Figure 5 illustrates the PhOH content of the unbleached and O_2-delignified pulps in relation to their lignin contents. It should be noted that all the kappa number and acid lignin data have not been corrected for contributions from the non-lignin components. In the kappa number method, the residual lignin content was estimated by multiplication of a factor of 1.8. With the exception of the O_2-delignified pulps determined by the kappa number method (Figure 5A), all other curves displayed a similar pattern showing a steady increase of the PHOH units with decreasing lignin content of the pulps. A different trend, however, was shown for the O_2-delignified pulps determined by the kappa number method. This unusual pattern, as will be discussed later, can be attributed to the interference by the HexA units in the kappa number determination.

Figure 6 illustrates the adjusted PhOH content of the unbleached and O_2-delignified pulps after correction for contributions by the non-lignin components. The correction included the residual extractives and HexA units in the kappa number method, whereas only the residual extractive was corrected for in the acid-lignin determination method. Several interesting

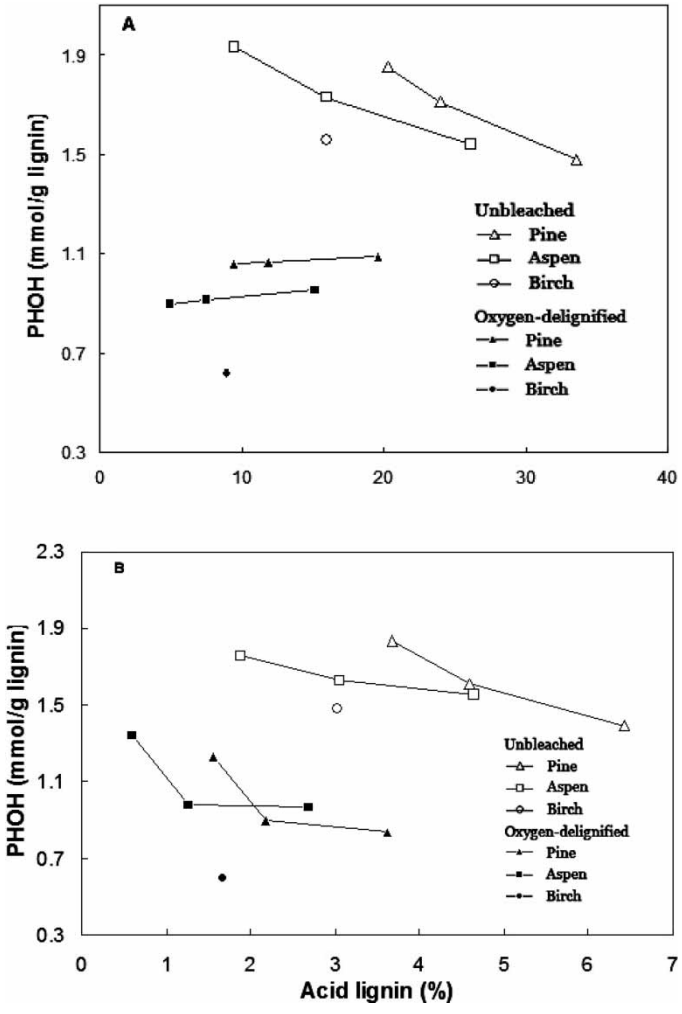

Figure 5. The PhOH content of unbleached and O_2-delignified kraft pulps relative to their residual lignin content determined by the kappa number (A) and acid lignin (B) methods without correction for contributions from the non-lignin components.

features are evident. Both the kappa number and acid-lignin methods gave a very similar pattern for both the pine and aspen pulps showing a steady increase of the PHOH content with decreasing the lignin content of pulps. For the unbleached pulps, all the data points of the pine, aspen, and birch pulps fit well into a single line. This is consistent with the contention that the basic mechanism of kraft delignification is essentially the same for both softwood and hardwood involving the cleavage of aryl ether linkages.

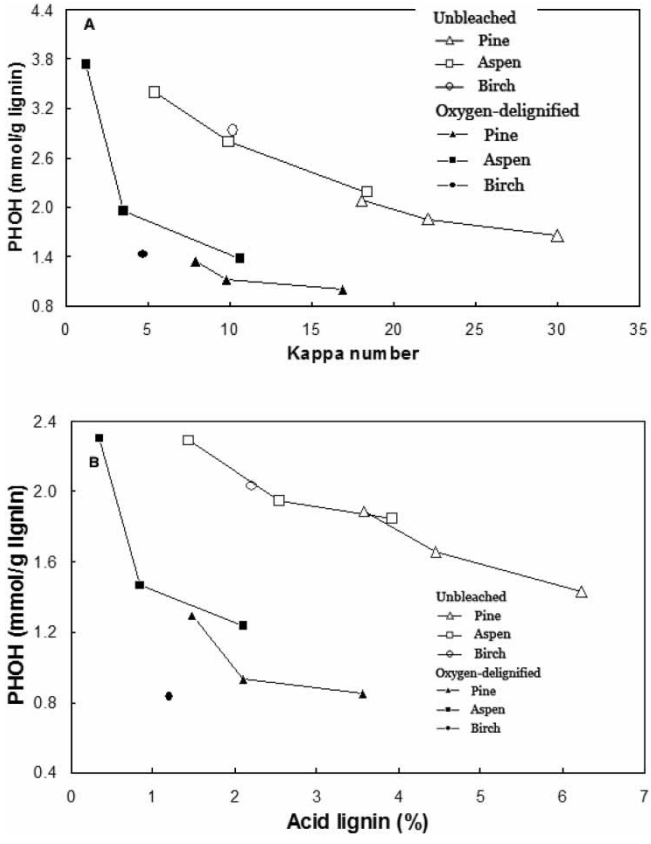

Figure 6. The adjusted PhOH content of unbleached and O_2-delignified kraft pulps in relation to their residual lignin content determined by the kappa number (A) and acid lignin method (B) after correction for contributions by the residual extractives plus HexA units in A and for the extractives contribution in B.

When comparing the O_2-delignified pulps at a given lignin content, the aspen pulps had a slightly higher PhOH content than the pine pulps. This may suggest that the reactivity of this functional unit in the aspen residual lignin was slightly lower than that of the pine lignin. This contention is consistent with the finding that a lesser amount of PhOH units was removed in O_2 delignification from the aspen residual lignin than from the pine residual lignin for pulps with lignin contents above 15 kappa number or 3.5% acid lignin level (Figure 7). However, in the lower lignin content region, the reactivity of PhOH units in the aspen pulps would be comparable to or higher than that of the pine pulps. Thus, it appears that kraft delignification has a significant impact on the relative reactivity of softwood and hardwood residual lignin. The extent to which this contention may be

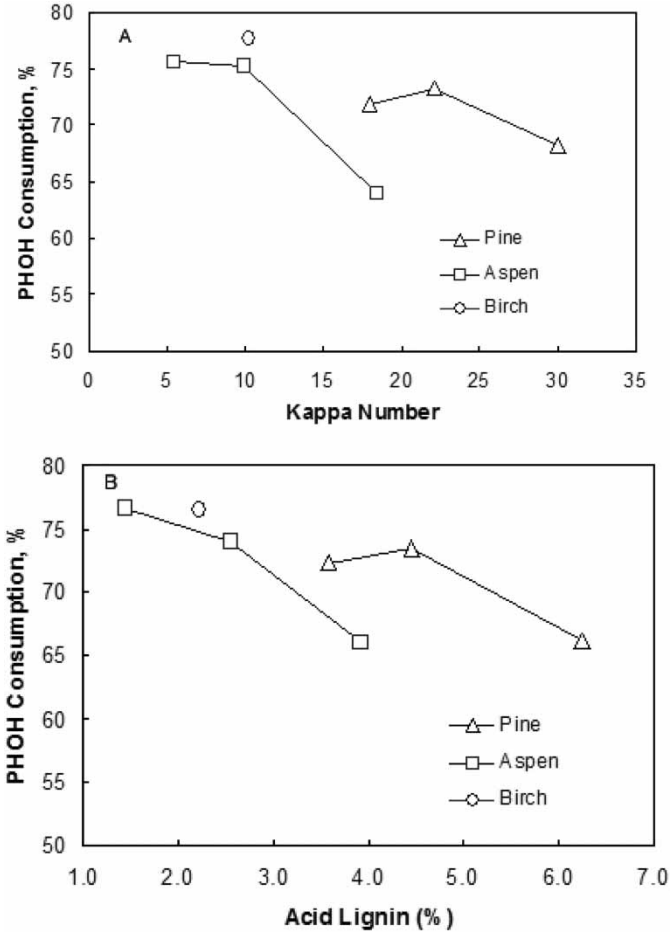

Figure 7. The percent consumption of PhOH units in O_2 delignification in relation to the kappa number (A) and acid lignin (B) of the unbleached kraft pulps.

related to the nature of lignin-carbohydrate complexes and lignin condensation reactions merits a further study.

Implication in O_2 Delignification

The results of this study clearly indicate that the relative O_2 delignification of softwood and hardwood pulps can vary considerably with how the residual lignin is determined (Figure 1). This can be attributed mainly to the interference of residual extractives and HexA units in the lignin analysis.

The impact of these non-lignin components in lignin determination was more for hardwood pulps than for softwood pulps. Because the content of these non-lignin components varies considerably with the wood species and pulping conditions, their contribution to the lignin analysis should be corrected for to obtain a proper evaluation of the O_2 delignification efficiency.

Figure 8 illustrates a comparison of the O_2 delignification among the aspen, birch, and pine pulps after correction for the impact from the residual extractives and HexA units in the kappa number analysis, and for

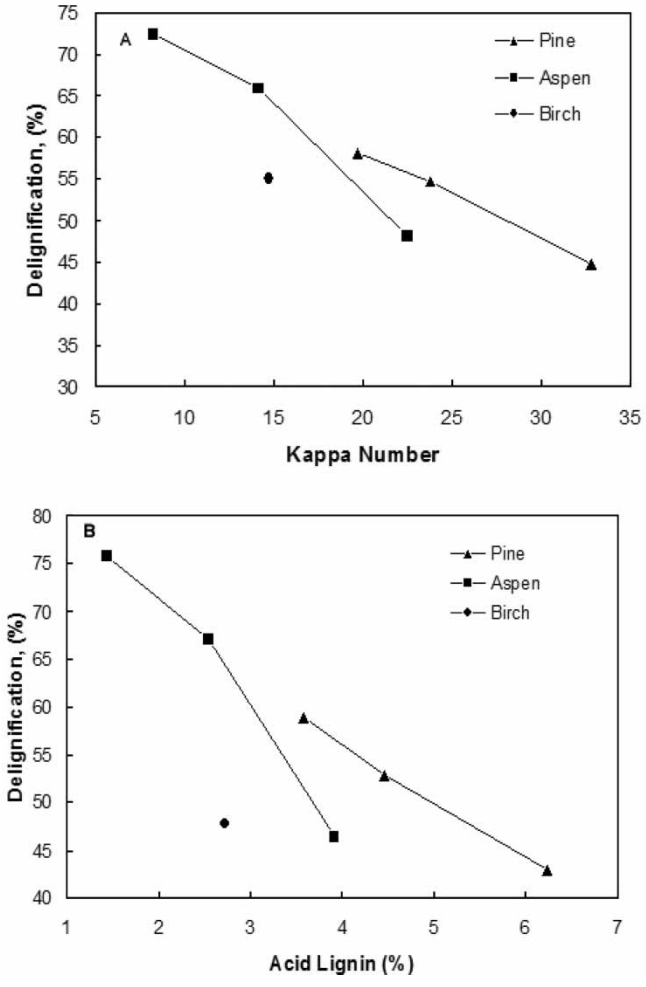

Figure 8. Comparison of the adjusted O_2 delignification of kraft pulps in relation to their residual lignin content determined by the kappa number (A: Corrected for the effects of residual extractives plus HexA units) and acid-lignin (B: Corrected only for the effect of residual extractives) methods.

impact from the residual extractives in the acid-lignin determination. It is evident that both lignin determination methods gave very comparable results. Interestingly, the difference between the pine and aspen pulps in O_2 delignification varied considerably with the lignin content of the unbleached pulps, and was more pronounced in the high-lignin content region. An extrapolation of the pine curve would intercept the aspen line near the 15 kappa number region or 2.5% lignin content. Below this region, the aspen pulp would be very comparable to or even more reactive than the pine pulp. This contention suggests that extended kraft cooking has a different impact on the softwood and hardwood pulps with respect to the nature and reactivity of the residual lignin. This contention is being investigated further.

CONCLUSIONS

The O_2 delignification of the hardwood kraft pulps was less extensive than that of softwood pulps, and displayed a distinctly different pattern based on an apparent reduction in the pulp kappa number. The residual extractives in kraft pulps, like HexA units, interfered with the residual lignin content determination, and the impact was greater for hardwood pulps than for softwood pulps.

After correction for contributions from the residual extractives and HexA units, the O_2 delignification of both pine and aspen kraft displayed similar patterns showing a steady increase in delignification with decreasing lignin content of the unbleached pulps. The difference between the pine and aspen pulps in O_2 delignification increased with increasing the lignin content of unbleached pulps, and was 10–15% lower for the aspen pulp at about 22 kappa number or 4% acid-lignin content. However, there are indications that for extensively delignified kraft pulps ($<$15 kappa number), the aspen pulps would be comparable to or more reactive than the pine pulps. The overall performance of hardwood and softwood kraft pulps in O_2 delignification is closely related to the content and condensed structures of the phenolic units in the residual pulp lignin.

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