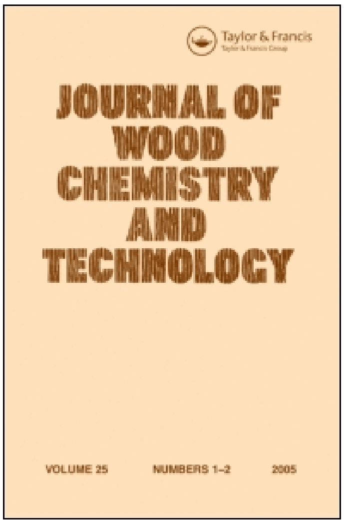


Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

IMPACTS OF ARYL-ETHER CLEAVAGES IN ALKALINE DELIGNIFICATION OF SOFTWOOD

Chun-Han Ko[a]; Yuan-Zong Lai[a]
[a] Empire State Paper Research Institute, Faculty of Paper Science and Engineering, State University of New York, College of Environmental Science and Forestry, Syracuse, New York, U.S.A.

To cite this Article Ko, Chun-Han and Lai, Yuan-Zong(2001) 'IMPACTS OF ARYL-ETHER CLEAVAGES IN ALKALINE DELIGNIFICATION OF SOFTWOOD', Journal of Wood Chemistry and Technology, 21: 1, 53 — 66
To link to this Article: DOI: 10.1081/WCT-100102654
URL: http://dx.doi.org/10.1081/WCT-100102654

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 21(1), 53–66 (2001)

IMPACTS OF ARYL-ETHER CLEAVAGES IN ALKALINE DELIGNIFICATION OF SOFTWOOD

Chun-Han Ko and Yuan-Zong Lai[1]

Empire State Paper Research Institute, Faculty of Paper
Science and Engineering, State University of New York,
College of Environmental Science and Forestry, Syracuse,
New York 13210

ABSTRACT

The cleavage of aryl ether linkages has been shown having a direct impact on the alkaline delignification of Norway Spruce up to approximately 90-95% level, and has little influence on further delignification reactions. Interestingly, such impacts were very comparable for both soda and kraft cooks, and were substantially reduced by lowering pulping temperatures. Thus, the lignin degradation and dissolution process were also affected by other chemical factors than aryl ether cleavages. The results also suggest that aryl ether units present in wood lignin vary significantly in reactivity.

INTRODUCTION

One of major drawbacks in the kraft process is its low selectivity, notably during the final phase in removing the last 5-10% of the lignin. The chemical aspect of the alkaline delignification process[2-6] has been generally thought to involve mainly the cleavages of aryl ether linkages, and this lignin degradation may be counteracted by condensation reactions. This contention, however, has been largely based on the studies of lignin model compounds.[2-6,9-14]

The overall kraft delignification is known to consist of three distinct phases.[4,7,8] An initial rapid removal of about 20-30% lignin is followed by a slower bulk delignification, which extends approximately to the 90% level. Further delignification proceeds very slowly and constitutes the so-called residual phase. Despite the cleavage of aryl ether structures is a key reaction in alkaline pulping, its impacts have not been quantified in details.

Lignins contain two major types of aryl ether structures: phenolic (I) and etherified (II) units (Fig. 1). Also, it is well known that soda cooks

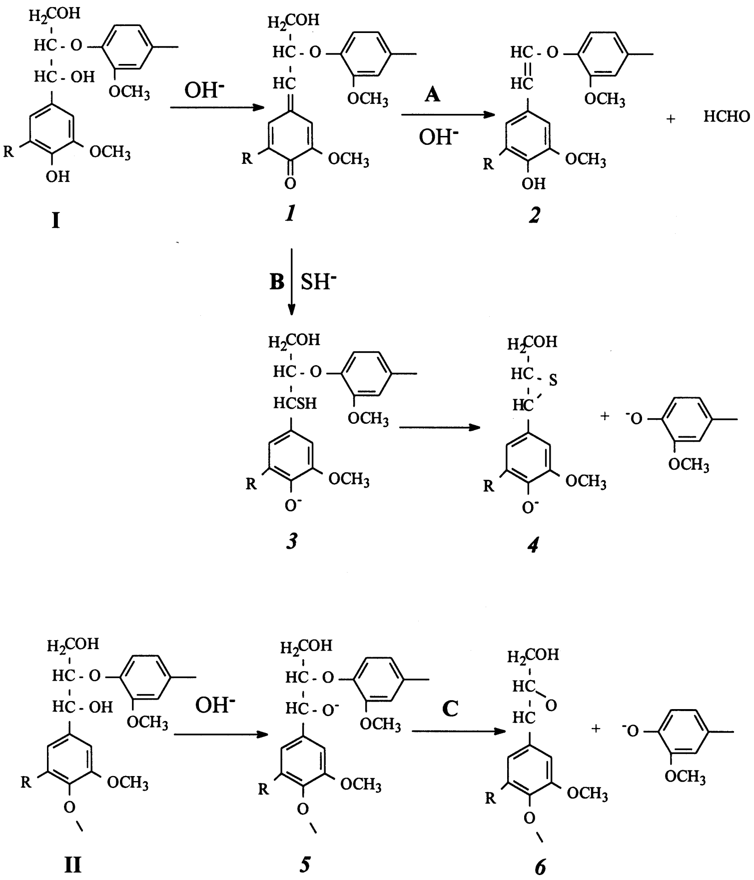


Figure 1. Alkaline degradation scheme of phenolic (I) and etherified (II) β-aryl ether units in soda and kraft cooks.

involve mainly the cleavage of phenolic aryl ether units, whereas the cleavages of both the phenolic and etherified types are important in kraft cooks. In this respect, it is of interest to examine the relative significance of different types of aryl ether cleavages in the delignification process.

The extent of aryl ether cleavages may be conveniently determined by the phenolic hydroxyl group (PHOH) formation. As anticipated, the reported content of this functional group in dissolved lignin is considerably higher than that of residual pulp lignin. Also, it has been suggested that a large number of PHOH groups must be formed prior to lignin dissolution.[15-18]

Previous reports[15-17] on the variation of PHOH in residual lignin during kraft cooking of pine seem to vary with the analytical method used. The content of this functional units in residual lignin, determined by permanganate oxidation methods,[16] was reported to increase with cooking up to the level of about 90% delignification, and then decreased sharply thereafter. However, the results based on aminolysis procedure displayed little variation within the 20-60 kappa number range.

We have conducted studies aimed at understanding controlling factors in the alkaline delignification process. In kraft pulping of softwood, we consistently observed[19,20] that the PHOH content of residual lignin, determined by a periodate method, increases steadily with decreasing kappa number of the unbleached pulp with a faster rate below the 30 kappa number range. A similar trend was also noted by others.[21,22]

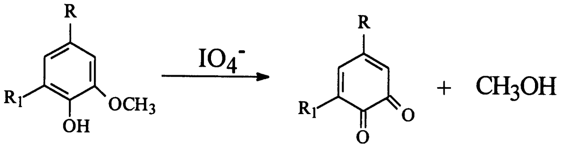
In this paper, the significance of aryl ether cleavages in the alkaline delignification of Norway spruce was further evaluated under typical soda and kraft cooking conditions. The influence of pulping temperature was also briefly examined.

RESULTS AND DISCUSSION

Methodology

In order to reflect the chemical role of aryl ether-cleavage reactions in the delignification process, and to alleviate possible interference of physical inaccessibility associated with chip substrates, all the experiments were conducted using wood-meal samples. Also, a high liquor-to-wood ratio of 20 was employed to minimize reduction in liquor concentrations during cooking. Alkaline cooks with soda (1 M NaOH) and kraft (0.8 M NaOH + 0.2 M Na_2S) liquors were carried out isothermally at several temperatures in the 100-180°C range.

The aryl ether-cleavage reactions were evaluated by the formation of phenolic hydroxyl groups (PHOH) in the residual lignin. This functional group was determined *in situ* by the periodate oxidation technique[23-25] based on the methanol formation as illustrated in Equation 1.



(1)

where R = Lignin side chain
R_1 = H, OCH_3 or lignin unit.

Although this procedure excludes detection of the methoxy-free phenolic units, the reported contents of catechol-type structures in typical residual kraft pulp lignins[26,27] were very small (< 1%). Thus, the periodate oxidation method should provide a fairly good estimate of the PHOH content in soda or kraft pulps.

Delignification

Figure 2A illustrates that cooking temperature has a significant influence in soda delignification of Norway spruce wood-meal samples. For the 180°C cook, a bulk delignification extending to approximately 10% lignin content followed by a slow phase was clearly indicated. As reported previously,[28] by lowering pulp temperature the bulk delignification was substantially retarded. Also, the transition between the bulk and residual phases occurred at a higher lignin content and became less pronounced. In the 100°C cook, there was a slight increase in the apparent lignin content likely resulting from a preferential dissoluton of the carbohydrate materials.

Also, the delignification patterns suggest that the amount of residual lignin resistant to soda cooks was substantially reduced by conducting pulping at high temperatures. Thus, pulping temperature affects not only the rate of soda delignification but also the characteristics of the residual pulp lignin. On the other hand, pulping temperature has little influence on delignification selectivity expressed by relative changes in pulp yield to lignin content (Fig. 2B). As indicated, the bulk and residual phases transition occurred at about 5% lignin content.

Similar temperature effects were observed in kraft cooking of Norway spruce in terms of delignification rate and selectively as shown in Figure 3. Also comparing at a same temperature, the extent of delignification in kraft

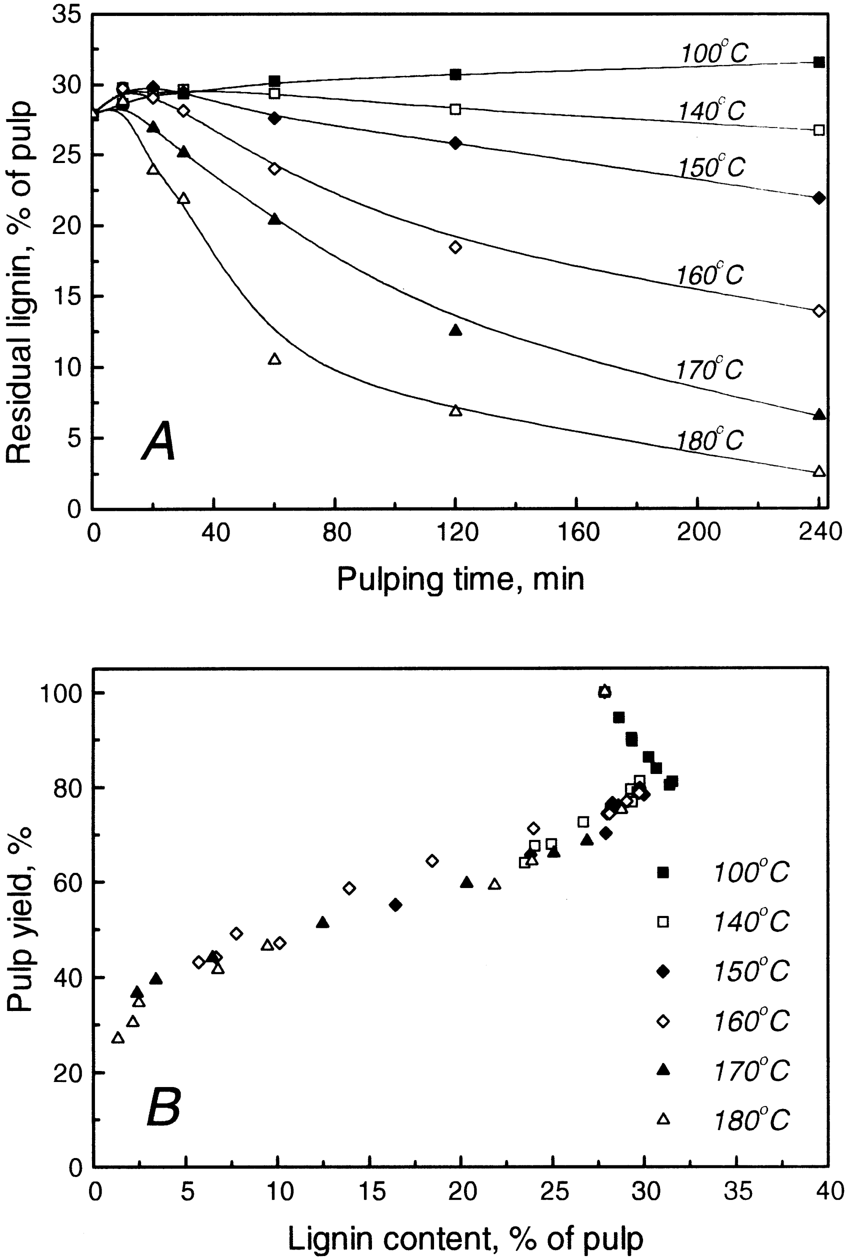


Figure 2. The influence of temperature in soda delignification process (A) and selectivity (B) of Norway spruce.

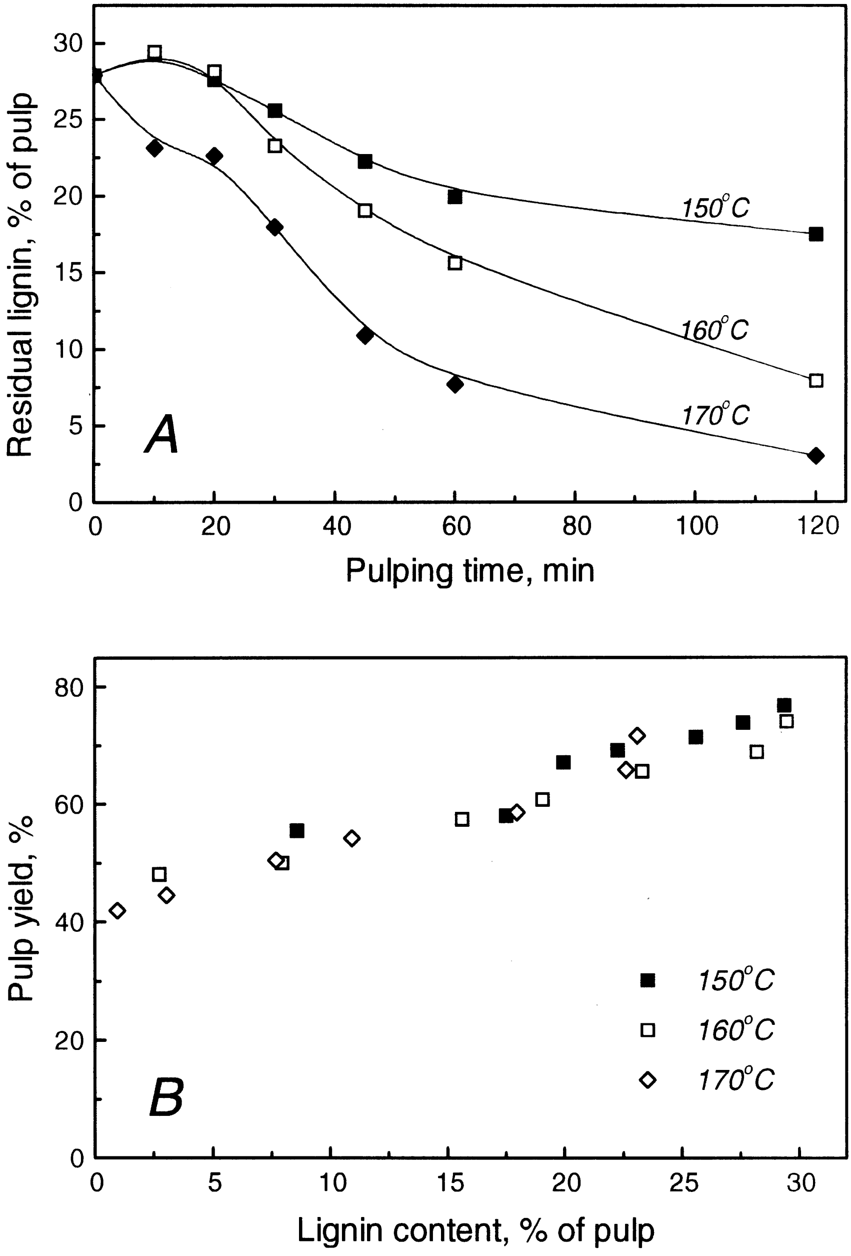


Figure 3. The influence of temperature in kraft delignification process (A) and selectivity (B) of Norway spruce.

cooks (0.8 M $NaOH + 0.2$ M Na_2S) (Fig. 3A) was significantly higher than that of soda cooks conducted at a higher alkali (1 M NaOH) (Fig. 2A). This finding is in line with the well-known role of sodium sulfide in promoting the delignification process.

Phenolic Hydroxyl Groups

Figure 4A shows that the influence of temperature in soda cooks on the overall formation of phenolic hydroxyl groups (PHOH) in the residual lignin. All the curves display a similar pattern containing an initial rapid phase followed by a slower process. As indicated, the reaction rate and the maximum formation of this functional group increased appreciably with a rise in reaction temperature. Also, a significant portion of these units was rather stable in soda cooks at low temperatures. This finding supports the contention that different aryl ether units present in wood lignin vary considerably in reactivity. Accordingly, the *erythro* β-aryl ether unit is known to be more reactive than the corresponding *threo* form.[9,13,14]

A similar pattern on the formation of PHOH in the residual lignin was observed in kraft cook (Fig. 4B), and the rate was appreciably higher than that of soda cooks. This enhancement is likely attributed to the fact that the cleavage of phenolic β-aryl ether units is more significant in kraft than in soda cooks.

Impacts of Aryl Ether Cleavages

Figure 5 illustrates the dependence of alkaline delignification on the aryl ether cleavages, as indicated by the PHOH formation in the residual lignin. Both soda and kraft cooks displayed a similar pattern, and pulping temperatures were shown having noticeable influence on the apparent impact of aryl ether cleavages in delignification.

In soda delignification, the data of 160-180°C cooks can be fitted with a single curve reasonably well, and clearly displayed a two-stage process. The initial 10% delignification was associated with a very small increase of PHOH in the residual lignin, whereas the generation of this functional group was shown having a direct impact on the bulk phase extending to the 90-95% delignification. For the lower temperature cooks (100-150°C), distinctly different lines were obtained, and the initial delignification phase became hardly discernible. Also, the data of 140-150°C cooks began to deviate from the initial regression line at about 40 and 60% delignification,

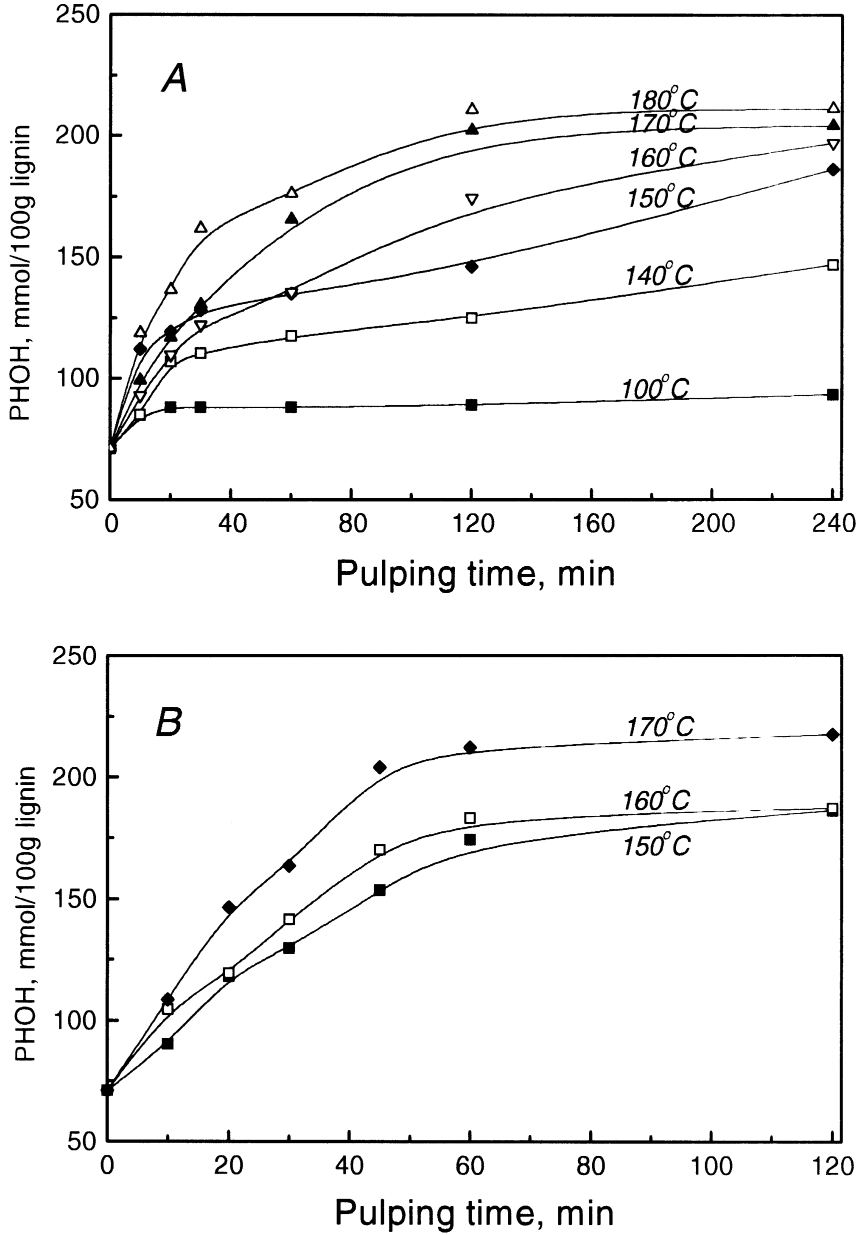


Figure 4. The influence of temperature in soda (A) and kraft (B) cooking of Norway spruce on the formation of phenolic hydroxyl groups (PHOH) in the residual lignin.

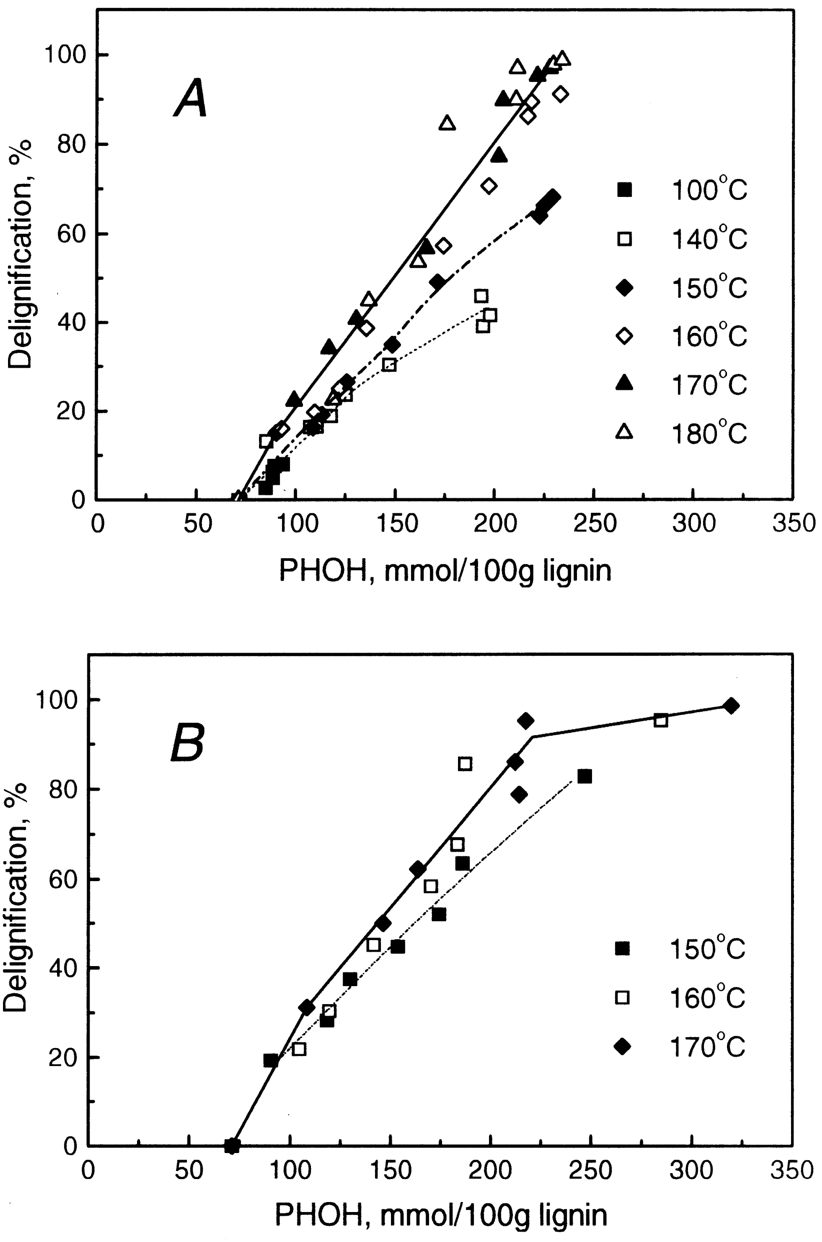


Figure 5. The influence of temperature in soda (A) and kraft (B) delignification of Norway spruce as related to the phenolic hydroxyl group (PHOH) content of residual lignin.

respectively. It follows that the impact of aryl ether cleavage in soda delignification was considerably reduced at pulping temperatures below 160°C.

A similar temperature effect was observed in the kraft cooks. As shown in Fig. 5B, the impact of aryl ether hydrolysis in kraft delignification was noticeably less at 150°C than at 160 and 170°C. Also, data of the latter two temperatures like in soda cooks can be represented by a single curve. It is not entirely clear on the causes of this temperature effect in delignification. However, it may be partly attributed to the relative stability of aryl ether units of the condensed type, which probably are more resistant to hydrolysis than the uncondensed type under low temperature cooking conditions. On the other hand, the reduced impact of aryl ether cleavages in delignification may be partly attributed to being counteracted by other chemical factors such as lignin condensations.

It is clearly shown for the kraft cooks at 160 and 170°C that the impact of aryl ether cleavages in delignification displayed three distinct phases. The initial delignification up to about 20% level was accompanied by a very small increase in the PHOH content. The bulk phase extending to approximately 90% delignification had a direct correlation with the aryl ether hydrolysis, whereas this hydrolysis reaction has only a slight effect on the residual delignification process.

A further comparison of the results of kraft and soda cooks at 170°C reveals several interesting features. As indicated in Fig. 5, the extent of the initial delignification was considerably higher in kraft than in soda cooks (10 *vs* 20%) by a factor of two. This finding further supports the contention that the initial delignification was mainly associated with degradation of the existing phenolic aryl ether units, which are facilitated by the presence of sodium sulfide in kraft cooks. Also, the dependence of bulk phase delignification on the aryl ether hydrolysis was very similar for both soda and kraft cooks. It thus appears that the alkaline hydrolysis of both phenolic and etherified aryl ether structures has comparable impact on the overall delignification process.

Nature of Residual Lignin

The extent to which cooking temperatures may affect the nature of residual lignin was further examined by the alkaline nitrobenzene oxidation method. This oxidation converts the uncondensed guaiacyl units to mainly vanillin plus some vanillic acid. The yield of these monomeric products (NOP) may also serve as an indication on the amount of condensed units.

Figure 6 illustrates that the temperature of soda cooks has a significant effect on the NOP (vanillin plus vanillic acid) yield of residual lignin as

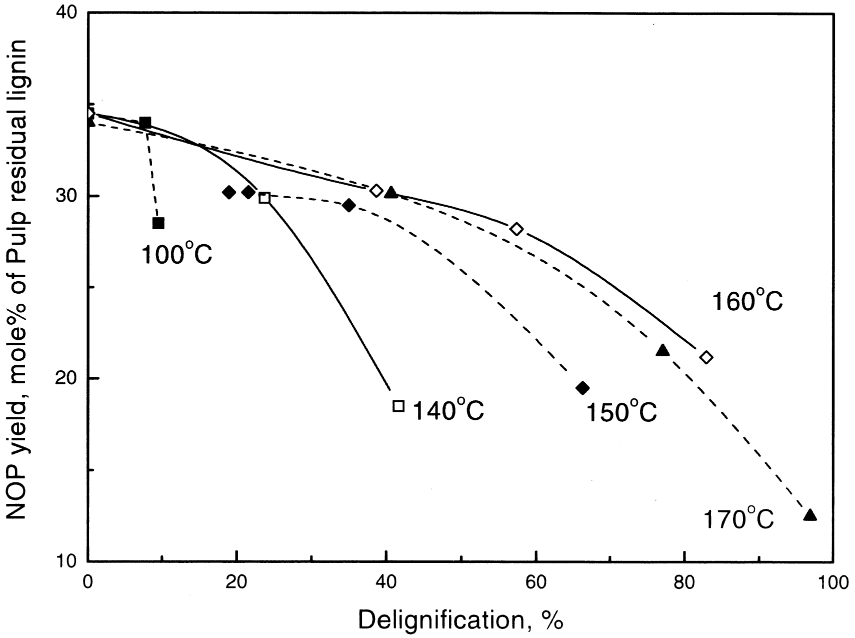


Figure 6. The influence of temperatures in soda cooking of Norway spruce on the yield of vanillin plus vanillic acid form alkaline nitrobenzene oxidation of pulp residual lignin as related to percent delignification.

related to the percentage of delignification. Compared at a given delignification level, the NOP yield decreased considerably with decreasing the pulping temperature. Thus, the residual lignin of low-temperature cooks contained a substantially higher content of C-5 condensed units than that of the high-temperature cooks. This finding may partly account for the observed reduced impact of aryl ether cleavages in alkaline delignification when cooking at low temperatures.

Additionally, it is of interest to note that the residual delignification phase is accompanied by a significant increase in the formation of PHOH in the residual lignin. Since a high content of this functional group would facilitate lignin dissolution in alkali, the observed increasing resistance of residual lignin to alkaline delignification is likely related to its structures being more condensed (Fig. 6) or partially linked to the fiber matrix. The extent to which these chemical factors may retard the reactivity of residual lignin in alkaline delignification, however, requires a further evaluation.

CONCLUSIONS

The cleavage of aryl ether units has been shown having a proud impact on the alkaline delignification of softwood. The overall impacts like delignification also displayed three distinct phases. Initial delignification was associated with the hydrolysis of some very reactive aryl ether units, whereas the bulk phase was related directly to the aryl ether cleavage reaction. On the other hand, the residual delignification was relatively unaffected by the hydrolysis reaction.

It appears that the aryl ether structures present in wood lignin vary significantly in reactivity under alkaline pulping conditions. Some of these units were fairly resistant to hydrolysis at temperatures below 160°C. Thus, pulping temperature has a significant influence on the chemical nature of residual lignin.

EXPERIMENTAL

Materials

Extractive-free Norway spruce wood-meal samples (40-60mesh) were prepared by extraction with a mixture of benzene and ethanol (2:1 by volume) for 48 h. The air-dried samples were used in all the experiments.

Cooking Procedures

The cooking experiments were conducted in small stainless-steel autoclaves (100 mL) using approximately 4 g sample and a liquor-to-wood ratio of 20. Soda cooks were conducted in 1 M NaOH solution while kraft liquor used a mixture of 0.8 M NaOH and 0.2 M Na_2S. The autoclaves were sealed under N_2 atmosphere and heated isothermally in oil bath for a prescribed period. In order to reduce heating time for samples to reach at a desired temperature, the bath was preheated to a higher temperature (10°C) than prescribed prior to insert the autoclaves.

After reaction, the autoclaves were cooled rapidly in cold water. The cooked mixture was filtered on a sintered glass crucible and washed thoroughly with distilled water. The washed samples, after being air-dried for about 24 h, were analyzed for pulp yield, lignin, and PHOH contents.

Analytical Methods

Lignin (Klason plus acid-soluble lignin) contents were determined by Tappi Standard Methods. The PHOH content was determined by the periodiate oxidation procedure[24,25] based on methanol formation (Eq. 1).

ACKNOWLEDGEMENTS

The financial support of this study by the Empire State Paper Research Institute (ESPRI), a USDA NRI competitive grant (No. 93-37103-9318), and the U.S. Department of Energy (No. DE-FCO-96-ID-13443) is gratefully acknowledged.

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