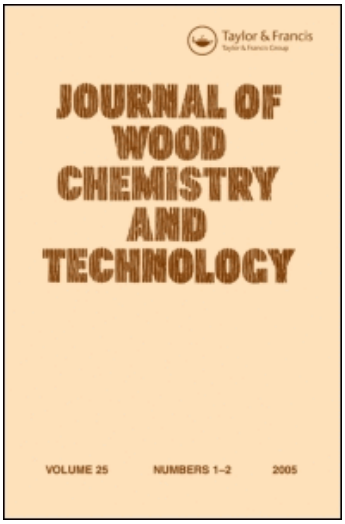

Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

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To cite this Article Alén, Raimo , Niemelä, Klaus and Sjöström, Eero(1985) 'Modification of Alkaline Pulping to Facilitate the Isolation of Aliphatic Acids Part 2. Sodium Hydroxide Pretreatment of Birch Wood', Journal of Wood Chemistry and Technology, 5: 3, 335 — 345
To link to this Article: DOI: 10.1080/02773818508085197
URL: http://dx.doi.org/10.1080/02773818508085197

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 5(3), 335-345 (1985)

MODIFICATION OF ALKALINE PULPING TO FACILITATE THE ISOLATION OF ALIPHATIC ACIDS
Part 2. Sodium hydroxide pretreatment of birch wood

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ABSTRACT

A modified pulping system of birch wood (*Betula verrucosa / Betula pubescens*) involving alkaline pretreatment of the chips was studied as a possibility for a facilitated recovery of the carbohydrate degradation products (aliphatic acids). Although a proper pretreatment resulted in a fairly extensive formation of aliphatic acids compared with the lignin dissolution, delignification was retarded in the pulping stage (kraft or soda-anthraquinone) and the pulp yield was somewhat lower (0.5 - 1 % of wood). Data are reported for the composition of aliphatic acids in liquors after pretreatments.

INTRODUCTION

Pretreatment of pine chips with sodium hydroxide prior to ordinary delignification in order to facilitate the recovery of aliphatic acids was studied earlier[1]. Although the liquor after pretreatment contained high amounts of aliphatic acids in relation to lignin, the delignification rate in the pulping stage was decreased and the pulp yield was somewhat lower compared with cooks without pretreatment.

A fairly extensive removal of xylan and glucomannan in the initial stage of birch kraft pulping[2] indicates that in this case

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too a two-stage cooking may be favorable for the recovery of aliphatic acids, although not enough information is available on the degradation of birch wood carbohydrates by mild alkali. This work was undertaken to evaluate suitable pretreatment conditions in which a reasonably extensive formation of aliphatic acids takes place, and to study how this pretreatment affects the rate of delignification and the pulp yield. In addition to ordinary kraft pulping, the soda cooking method in the presence of anthraquinone was applied.

EXPERIMENTAL

Wood Material

The wood material was air-dried industrial chips of birch wood (*Betula verrucosa / Betula pubescens*). The chips were screened on a William screen and the fraction of 2 - 4 mm size was accepted. The content of lignin and extractives of the wood material was 22.0 % and 4.6 %, respectively.

Alkaline Pretreatments

Alkaline pretreatments were performed using air-dried chips according to the procedure described earlier[1]. Additional pretreatments (not given in Table 1) were made using either lower temperatures (80 - 140 °C) or more drastic conditions (higher temperature, 170 °C, and alkali charges, 12 and 14 % NaOH on wood).

Delignification after Pretreatment

The pretreated chips (air-dried) were charged into autoclaves (the same as used for pretreatments) and pulped under the following conditions:

TABLE 1

Results from Alkaline Pretreatments at 160 °C

Alkali charge, % of NaOH on wood[a]	8			10		
Pretreatment time, minutes	30	60	90	30	60	90
Material dissolved[b], % of wood	15.9	17.4	17.9	20.4	20.4	20.4
Lignin dissolved, % of wood	3.9	4.4	4.7	5.1	5.5	5.5
Hydroxy acids formed[c], % of wood	4.0	5.3	5.6	4.2	6.0	6.3
Weight ratio hydroxy acids/lignin	1.0	1.2	1.2	0.8	1.1	1.1
Residual alkali, g/L	0.4	0.2	0.2	2.0	1.4	0.8
pH after treatment	10.0	9.3	9.3	11.0	10.5	9.7

[a]The liquor-to-wood ratio was 4 L/kg.

[b]Total amount of extractives dissolved was approximately 2 - 3 % of wood.

[c]In these data formic and acetic acids are not included. Their formation varied within the limits 0.7 - 1.4 and 4.0 - 4.6 % of wood, respectively. See Table 2 for the hydroxy acid composition.

Total alkali charge	20 or 22 % act. alkali
Sulfidity	30 %
Anthraquinone charge	0.1 % on wood
Liquor-to-wood ratio	4 L/kg
Time to max. temperature (168 °C)	85 min

The corresponding single-stage kraft and soda-AQ cooks were made for reference.

Analytical Determinations

Liquor Analysis

The hydroxy acids were determined as trimethylsilyl derivatives by gas-liquid chromatography (GLC) as described previously[1, 3].

Formic and acetic acid were converted to benzyl esters before GLC determination, as described elsewhere[4, 5]. A Hewlett-Packard 5880 A gas chromatograph equipped with a flame ionization detector and a Silar 10 C glass capillary column (0.32 mm i.d. x 25 m) was used. The temperature program was 4 min at 100 °C and 10 °C/min to 130 °C. The injection port and manifold were kept at 260 °C. The flow rate of carrier gas (H_2) was 7 mL/min. The injection volume was 0.5 µL and the split ratio 20:1. The relative molar response factors (benzyl propionate = 1) used for benzyl formate and benzyl acetate were 0.75 and 0.89, respectively.

Methanol was analysed by injecting a diluted spent liquor sample (1 µL) directly to a GLC column (3.175 mm x 2 m) packed with 12 % Carbowax 20 M on Chromosorb W-HMDS (80 - 100 mesh). A Perkin-Elmer 900 gas chromatograph equipped with a flame ionisation detector was used. Oven temperature was kept at 50 °C. The temperatures of the injection port and manifold were 140 °C and 200 °C, respectively. The flow rate of carrier gas (N_2) was 30 mL/min. Methanol contents were determined by using reference solutions of known methanol concentrations.

The lignin concentrations were measured by UV spectrophotometry using a Zeiss PMQ II Spectrophotometer (1-cm silica cells). The sample solutions were diluted with water to give a UV absorbance

of 0.3 - 0.5 at 278 nm. The lignin concentrations were calculated using an absorptivity value of 15.0 L/g cm[6].

The molecular-weight distribution of the lignin fractions was determined by gel permeation chromatography as described previously[1].

Residual alkali was titrated with 0.1 N HCl and the final pH values were measured with a Metrohm-Herisau E 436 potentiograph.

Wood and Pulps

The extractives contents were determined according to SCAN-C 7:62. The lignin determinations for untreated chips were made gravimetrically as described by Jayme *et al.*[7] and the values were corrected for acid-soluble lignin (UV determinations at 203 nm, absorptivity 128 L/g cm).

The kappa numbers of pulps were determined according to SCAN-C 1:77.

RESULTS AND DISCUSSION

Pretreatments

Although no striking changes were observed in the total amount of material dissolved during pretreatments, a prominent formation of hydroxy acids was obtained only at temperatures above 150 °C (Fig. 1 and Table 1). The rapid increase in hydroxy acid contents was probably due to the degradation of xylan, which obviously appears at lower temperatures (80 - 140 °C) in the pretreatment solutions mostly in the form of polysaccharides[8, 9].

In agreement with the results from the alkaline pretreatment of pine chips[1], the dissolution of lignin occured mainly during the first 30 minutes' treatment and the average molecular weights of the lignin fractions were very low ($\bar{M}_w$ approximately 1500 in the pretreatments performed at 150 and 160 °C). At temperatures of 150 - 160 °C most hydroxy acids were formed after 60 minutes, whereas under these conditions only 50 - 70 % of extractives were dissolved. Based on the weight ratio of the total amount of hydroxy

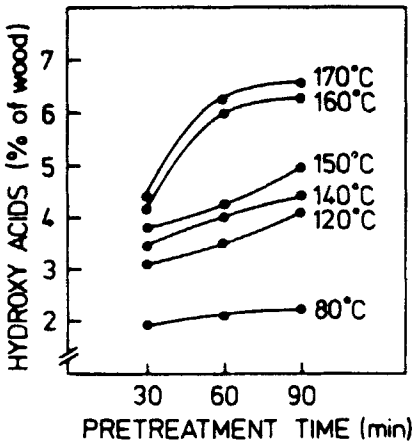

FIGURE 1. Formation of hydroxy acids during alkaline pretreatments (10 % NaOH on wood).

acids to lignin, generally varying within the limits of 0.8 - 1.2 (*cf.* Table 1), the liquor obtained after pretreatment at 160 °C for 60 minutes with an alkali charge of 8 - 10 % NaOH on wood was considered to be most suitable for isolation of hydroxy acids. Although these values were clearly lower than those obtained from the pretreatments of pine wood, the corresponding weight ratios of aliphatic acids (formic, acetic, and hydroxy acids) to lignin were, however, almost equal (1.8 - 2.5).

Almost 40 different aliphatic acids were identified in the liquors after pretreatment. Most of the components (Table 2) have been previously detected in the spent liquors from the alkaline pulping of birch wood[10 - 12]. The high acetic acid content (4.0 - 4.6 % of wood) originates from the acetyl groups of xylan, which are easily saponified during these pretreatment conditions. The formic acid and methanol contents were, respectively, 0.7 - 1.4 % and 0.2 - 0.3 % on wood.

Delignification

The results from the single-stage reference and two-stage kraft cooks show that the pretreatment resulted in a retarded

TABLE 2

Relative Composition of Aliphatic Acids in the Spent Liquor from Pretreatment (160 °C, 60 min, 10 % of NaOH on wood)

Acid	Content, % of aliphatic acids
Formic	8.8
Acetic	38.1
Glycolic	5.9
Lactic	7.7
2-Hydroxybutanoic	9.1
2-Deoxytetronic	0.9
3-Deoxytetronic	2.0
2,5-Dihydroxypentanoic	3.6
3-Deoxypentonic	2.1
2,3-Dideoxypentaric	1.0
Xyloisosaccharinic	3.8
3,6-Dideoxyhexonic	1.9
Anhydroisosaccharinic	0.7
α-Glucoisosaccharinic	1.8
β-Glucoisosaccharinic	3.1
3-Deoxy-2-C-hydroxymethylpentaric	1.2
Miscellaneous	8.3

delignification and lower pulp yields (0.5 % at a kappa number level of 20 - 35; Figs. 2 and 3). However, the yield losses in two-stage cooks compared with conventional kraft cooks were somewhat lower than those observed in the corresponding pulping of pine chips[1]. Finally, similar results were obtained when the pretreated chips were delignified with anthraquinone as additive (Figs. 4 - 5).

CONCLUSIONS

Most of the hydroxy acids from birch wood are derived from the xylan. The acetyl groups are readily removed by alkali from

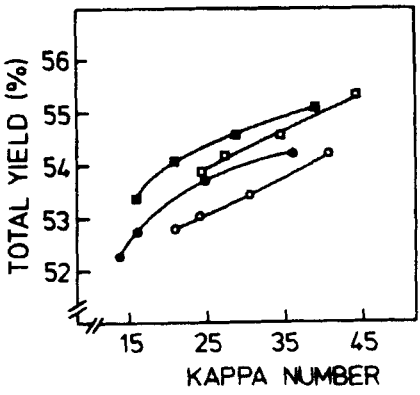

FIGURE 2. Yield *vs.* kappa number for the kraft cooks. Open symbols: cooks after pretreatment. Solid symbols: reference cooks (without pretreatment). □ , ■ 20 % and ○ , ● 22 % act. alkali (as NaOH) on wood.

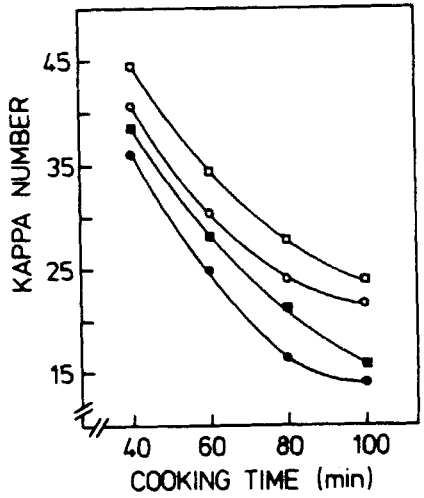

FIGURE 3. Kappa number *vs.* cooking time for the kraft cooks. See Fig. 2 for explanation of symbols.

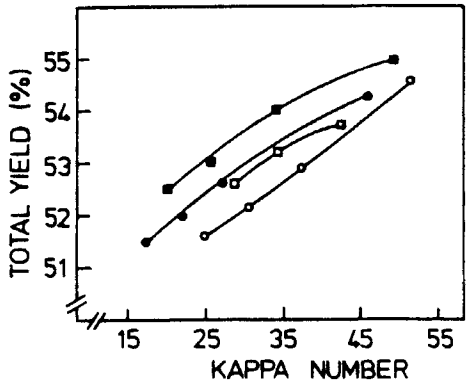

FIGURE 4. Yield *vs.* kappa number for the soda-AQ cooks. See Fig. 2 for explanation of symbols.

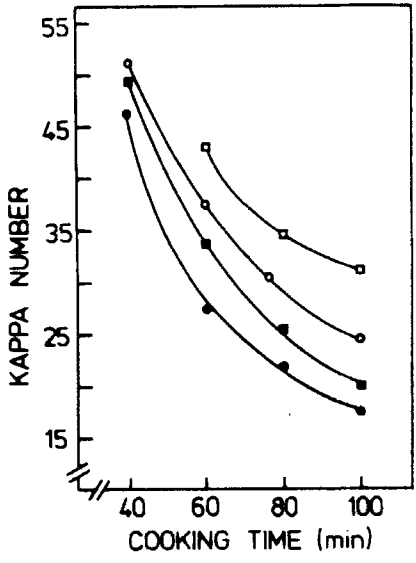

FIGURE 5. Kappa number *vs.* cooking time for the soda-AQ cooks. See Fig. 2 for explanation of symbols.

the xylan, whereas its further degradation to hydroxy acids requires more drastic pretreatment conditions than is needed for the galactoglucomannans in pine wood[1]. Nevertheless, comparatively low amounts of lignin were present in the solutions after pretreatment. Although the alkaline pretreatment is favorable when considering the recovery of the carbohydrate degradation products, a drawback is that the delignification in the following pulping stage proceeds more slowly and results in somewhat lower pulp yields.

ACKNOWLEDGEMENTS

The financial support of the Ministry of Trade and Industry is gratefully acknowledged. Thanks are due to Miss Arja Siirto for her assistance with the experimental work and Mr Kari Kajander for determining the molecular-weight distributions.

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