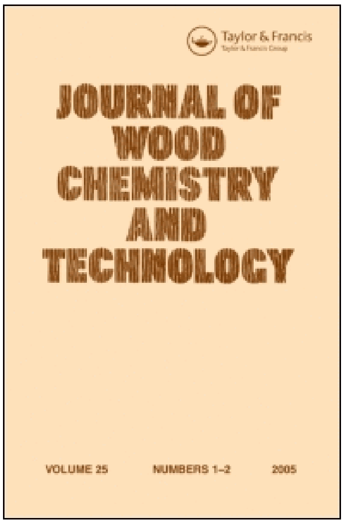
This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Wood Chemistry and Technology

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

Modification of Alkaline Pulping to Facilitate the Isolation of Aliphatic Acids Part 1. Sodium hydroxide pretreatment of pine wood

Raimo Alén[a]; Klaus Niemelä[a]; Eero Sjöström[a]
[a] Laboratory of Wood Chemistry, Helsinki University of Technology, Espoo, Finland

To cite this Article Alén, Raimo , Niemelä, Klaus and Sjöström, Eero(1984) 'Modification of Alkaline Pulping to Facilitate the Isolation of Aliphatic Acids Part 1. Sodium hydroxide pretreatment of pine wood', Journal of Wood Chemistry and Technology, 4: 4, 405 — 419

To link to this Article: DOI: 10.1080/02773818408070658

URL: http://dx.doi.org/10.1080/02773818408070658

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 4(4), 405-419 (1984)

MODIFICATION OF ALKALINE PULPING TO FACILITATE THE ISOLATION OF ALIPHATIC ACIDS

Part 1. Sodium hydroxide pretreatment of pine wood

Raimo Alén, Klaus Niemelä, and Eero Sjöström
Laboratory of Wood Chemistry, Helsinki University
of Technology, SF-02150 Espoo 15, Finland

ABSTRACT

Pretreating pine chips (*Pinus sylvestris*) with sodium hydroxide prior to the alkaline delignification (kraft, kraft-anthraquinone, and soda-anthraquinone) can facilitate the recovery of the carbohydrate degradation products from alkaline pulping liquors. Under suitable pretreatment conditions large amounts of carbohydrate degradation products (aliphatic acids) were formed relative to lignin. The lignin fraction was composed of comparatively low-molecular-weight fragments. Although the delignification was considerably retarded and the yield (based on wood) was decreased by 1 - 3 %, the properties of the resulting pulp were essentially maintained despite pretreatment. Finally, data are given for the composition of aliphatic acids in liquors resulting from pretreatments.

INTRODUCTION

In addition to the degraded lignin, kraft black liquors contain another large fraction composed of a variety of aliphatic acids formed as degradation products of polysaccharides[1]. Because of several factors (including the low heat values), interest has been directed at the possibility of recovering these acids[2]. The main obstacle is the lack of reasonably simple methods of separating

0277-3813/84/0404-0405$3.50/0

them from lignin and other constituents, and the need to recover inorganic chemicals[3].

To circumvent separation problems, process streams containing less lignin than is present in black liquors could be used, for example liquor withdrawn from the digester at early stages of the cook because the most extensive degradation of carbohydrates takes place during the heating-up period[1]. Another way to obtain fractions of low lignin content would be to modify the cooking procedure, for example by pretreating the chips with sodium hydroxide alone prior to the delignification stage. Besides carbohydrate degradation products, extractives easily soluble in alkali[4] could possibly be recovered after pretreatment. Because results could not be predicted from the literature, a study was made into the effects of such a pretreatment on delignification and pulp yield and pulp properties.

The object was to define pretreatment conditions that maximize the formation of carbohydrate degradation products and minimize the dissolution of lignin. After pretreatment the chips were delignified. In addition to ordinary kraft pulping, kraft and soda pulping in the presence of anthraquinone were applied.

RESULTS AND DISCUSSION

Pretreatments

A number of pretreatments was made (alkali charge from 8 to 14 % NaOH on wood, temperature 140 - 160 °C, and time 30 - 120 min) and only the most useful results are collected in Table 1. No striking differences were found either in the dissolution of lignin or in the formation of aliphatic acids. Most of the dissolution of lignin had occurred after 30 minutes' treatment, whereas the formation of hydroxy acids continued and

TABLE 1

Results from Alkaline Pretreatments at 150 °C

Alkali charge, % NaOH on wood	8			10		
Pretreatment time, min	30	60	90	30	60	90
Material dissolved[a], % of wood	15.6	19.4	19.8	21.4	21.9	22.8
Lignin dissolved, % of wood	3.7	4.3	4.3	4.6	5.8	6.4
Hydroxy acids formed[b], % of wood	4.7	6.4	6.7	6.6	7.0	7.5
Weight ratio hydroxy acids/lignin	1.3	1.5	1.6	1.4	1.2	1.2
Residual alkali, g/L	1.8	1.3	1.1	2.8	2.3	2.0
pH after treatment	11.0	10.3	9.7	11.9	11.5	11.3

[a] The total amount of extractives dissolved was approximately 3.6 % on wood.

[b] In these data formic and acetic acids are not included. Their formation varied within the limits 1.6 - 2.4 and 1.8 - 2.2 % on wood, respectively. See Table 3 for the hydroxy acid composition.

levelled off after 60 minutes. Extractives were also dissolved almost completely (90 - 95 %) during the early stage of pretreatments. The average molecular weights of the lignin fractions were very low (Table 2).

The highest ratio of the total amount of hydroxy acids to lignin in liquors after pretreatment was 1.5 - 1.6, which is much higher than for kraft black liquors (about 0.6)[3]. No attempts, however, were made to isolate the aliphatic acids. The spent liquor obtained after pretreatment at 150 °C for 60 minutes with an alkali charge of 8 % act. alkali (as NaOH) on wood was selected for further processing.

About 35 different aliphatic acids were identified in the liquors after pretreatment. All are known alkaline degradation products of polysaccharides analyzed earlier in black liquors[5-8]. The major components are presented in Table 3. Possibly because the varying conditions direct the degradation routes, larger

TABLE 2

Average Molecular Weight of Alkali Lignins Dissolved at 150 °C

Pretreatment time, min	Alkali charge, % NaOH on wood	Lignin dissolved, % of total lignin	$\bar{M}_w$
30	8	13.7	1046
60	8	15.9	1266
60	10	19.6	1215
60	12	22.1	1214
60	14	23.2	1770
90	8	15.5	1173
120	8	16.6	1099

amounts of 2,5-dihydroxypentanoic acid and less glucoisosaccharinic acid were present than in black liquors from pulping. Acetic acid was formed early because of the deacetylation of galactoglucomannans[1], whereas the amount of formic acid increased continuously during pretreatment.

Delignification

The pretreated chips were delignified more slowly than the untreated chips (Fig. 1, where the cooking time is plotted

TABLE 3

Relative Composition of Aliphatic Acids in the Spent Liquor from Pretreatment (150 °C, 60 min, 8 % act. alkali on wood)

Acid	Content, % of aliphatic acids
Formic	18.6
Acetic	19.4
Glycolic	5.2
Lactic	7.9
2-Hydroxybutanoic	1.9
2-Deoxytetronic	1.7
3-Deoxytetronic	1.9
2,5-Dihydroxypentanoic	10.4
3-Deoxypentonic	2.2
Xyloisosaccharinic	1.1
3,6-Dideoxyhexonic	0.6
Anhydroisosaccharinic	1.2
α-Glucoisosaccharinic	6.6
β-Glucoisosaccharinic	11.7
Miscellaneous	9.6

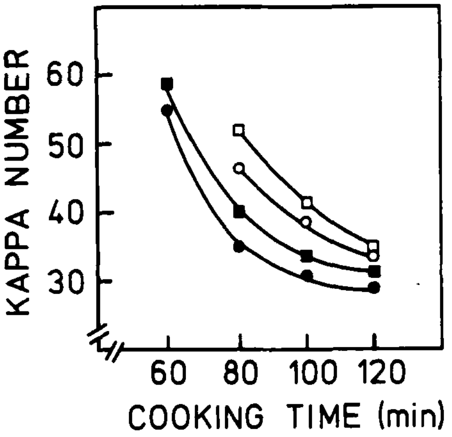


FIGURE 1. Kappa number *vs*. cooking time for the kraft cooks. Open symbols: cooks after pretreatment. Solid symbols: reference cooks (without pretreatment). □ , ■ 20 % and ○ , ● 22 % act. alkali (as NaOH) on wood.

against kappa number after kraft pulping). Fig. 2 shows that pretreating the chips resulted in a lower pulp yield, the difference being about 1 % at a kappa number level of 35 - 40. Similar, or somewhat more pronounced, effects for both the rate of delignification (Fig. 3) and pulp yield (Fig. 4) were observed when the pretreated chips were delignified with sodium hydroxide in the presence of anthraquinone. The effect of pretreatment was most striking after kraft-anthraquinone pulping (Figs. 5 and 6).

Finally, Table 4 shows the results from the cooking experiments on a larger scale after which pulp enough for bleaching and testing was obtained. As can be seen the effect of pretreatment on the delignification rate and yield was similar as before. It was further observed that the reference pulp was bleached somewhat more easily than the pulp from the modified cook, but practically no differences were found as regards the pulp properties.

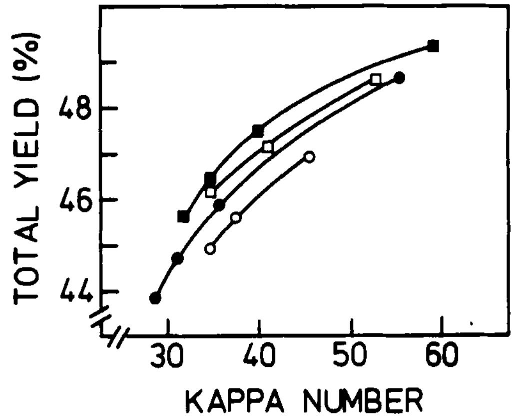


FIGURE 2. Yield *vs.* kappa number for the kraft cooks. See Fig. 1 for explanation of symbols.

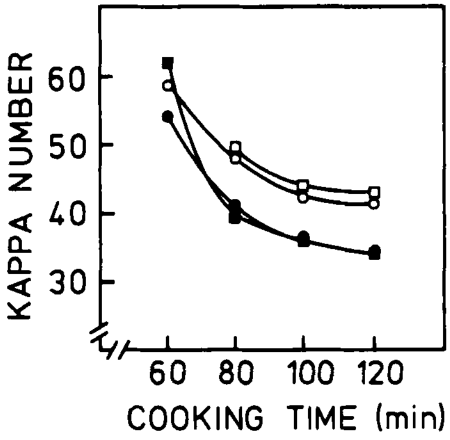


FIGURE 3. Kappa number *vs.* cooking time for the soda-AQ cooks. See Fig. 1 for explanation of symbols.

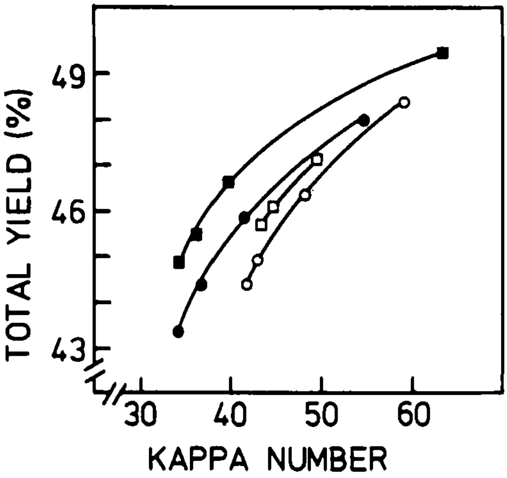


FIGURE 4. Yield *vs*. kappa number for the soda-AQ cooks. See Fig. 1 for explanation of symbols.

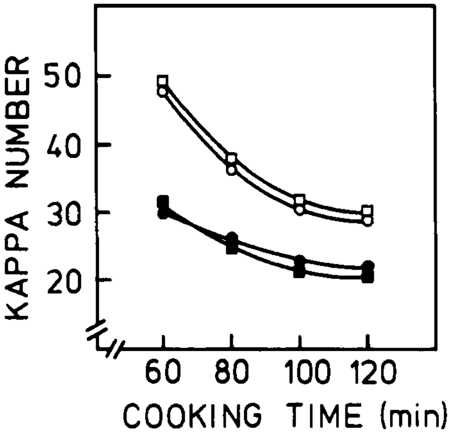


FIGURE 5. Kappa number *vs*. cooking time for the kraft-AQ cooks. See Fig. 1 for explanation of symbols.

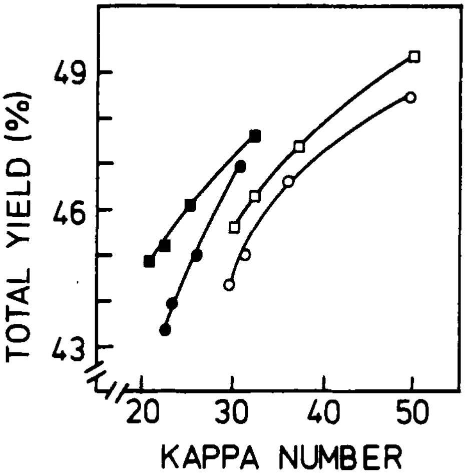


FIGURE 6. Yield *vs.* kappa number for the kraft-AQ cooks. See Fig. 1 for explanation of symbols.

CONCLUSIONS

The degradation of wood polysaccharides to aliphatic acids proceeds much faster than delignification when pine chips are treated at moderate temperatures with sodium hydroxide alone. To aid separation, therefore, it might be advantageous to perform the cook in two stages and isolate the aliphatic acids from the liquor after pretreatment instead from the final black liquor which contains high amounts of lignin in addition to sodium sulfide and other sulfur compounds. However, the decreased delignification rate seems to be unavoidable and this modified pulping system results in prolonged cooking times and somewhat lower pulp yields.

EXPERIMENTAL

Wood Material

The wood consisted of air-dried industrial chips of Scots pine (*Pinus sylvestris*) which were subjected to further screening.

TABLE 4

Comparison between Conventional (A) and Modified (Two-Stage) (B) Kraft Pulping[a]

	A[b]	B[c]
Time at max. temperature (170 °C), min	90	150
Total yield, % of wood	45.1	45.6
Kappa number	36	47
Reject, % of wood	1.6	1.0
Beating time (20° SR), min	3.1 (19)	3.4 (19)
Tensile index (20° SR), Nm/g	110 (84)	101 (85)
Tear index (20° SR), Nm^2/kg	11.4 (6.8)	11.6 (7.1)
Bleaching yield, %	93.9	94.1
ISO brightness, %	91.0	89.2

[a] The values in parentheses refer to bleached pulps.

[b] Cooking conditions: 23.3 % act. alkali (as NaOH) on wood, sulfidity 30 %, liquor-to-wood ratio 4 L/kg, time to max. temp. 120 min.

[c] After pretreatment (8 % NaOH on wood, 150 °C, 60 min) 40 % of the liquor was withdrawn. Temperature was then raised from 150 °C to 170 °C (20 min) and white liquor (30 % sulfidity) was added (13.9 % act. alkali as NaOH). The liquor-to-wood ratio was kept constant (4 L/kg) during the pretreatment and delignification stages.

The fraction passing the 4 mm screen and retained on the 2 mm screen was used. The lignin and extractives content of the wood material was 27.6 % and 3.9 %, respectively.

Alkaline Pretreatments

Alkaline pretreatments of air-dried chips were carried out in rotating stainless steel autoclaves of about 1.8 L capacity and were heated in a polyglycol bath. The heating of the liquor in the autoclaves up to maximum temperature took less than 10 minutes. The liquor-to-wood ratio was 4 L/kg; the other conditions employed are given in Table 1. Additional pretreatments (not given in the table) were made using either lower temperature (140 °C) or more drastic conditions (longer times (120 min), higher temperatures (160 °C), and alkali charges up to 14 % on wood). After sample pretreatment the autoclaves were cooled in cold water and the pretreated chips were washed with water and air-dried to a constant weight.

Delignification after Pretreatment

The pretreated chips (air-dried) were charged into autoclaves (the same as used for pretreatments) and pulped under the following conditions (see also Fig. 1):

Total alkali charge	20 or 22 % act. alkali (as NaOH) on wood
Sulfidity	30 %
AQ-charge	0.2 % on wood
Liquor-to-wood ratio	4 L/kg
Time to max. temperature (170 °C)	85 min

To obtain pulp for testing the fiber properties, a stainless steel digester of about 25-liter capacity, fitted for liquor circulation and indirect heating, was used. After pretreatment with sodium hydroxide, about 40 % of the liquor was withdrawn from the digester and, following the charge of sodium hydroxide and sodium sulfide, the pretreated chips were pulped. The conditions employed both for pretreatment and pulping are given in Table 4.

Analytical Determinations

Wood, Pretreated Chips, and Pulps

The extractives contents were determined according to SCAN-C 7:62 and the lignin determinations for untreated chips were made as described by Jayme *et al.*[9]. The lignin content of pretreated chips was calculated from the chlorine number (determined according to SCAN-C 29:72), which was multiplied by a factor of 0.86. This correlation coefficient was obtained from separate experiments on pretreated chips (9 samples), for which the total lignin content was determined gravimetrically in the same way as for untreated chips[9] and the values were corrected for acid-soluble lignin (UV determinations at 203 nm, absorptivity 128 L/gcm). The samples for chlorine number determinations were first ground to a particle size less than 40 mesh in a Wiley mill.

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

The tear and tensile strengths were determined on handsheets after beating in a PFI mill by standard methods (SCAN-P 11:73 and SCAN-P 16:76).

Liquor Analyses

The hydroxy acids were separated from the liquors after pretreatment by anion exchange[10]. A liquor sample (0.5 mL) was passed through a 20x100 mm column filled with anion exchange resin (Dowex 1x8, 50 - 100 mesh, acetate form). The neutral components were first displaced from the column with water (200 mL) and then the hydroxy acid fraction was eluted with 3 M acetic acid (100 mL). An internal standard (1 mg D-mannono-1,4-lactone) was added to the resulting effluent and the solution was evaporated to dryness in vacuum at 35 °C. To the hydroxy acid residue was added 0.5 mL pyridine and 0.25 mL trifluorobis(trimethylsilyl)acetamide (BSTFA) containing 5 % of chlorotrimethylsilane (TMCS), and the mixture was shaken for approximately 30 min at room temperature[11].

GLC separations were performed after trimethylsilylation on a Hewlett-Packard 5880 A instrument equipped with a differential flame ionisation detector and an OV-101 fused-silica capillary column (0.32 mm i.d. x 25 m). The temperature program was 2 min at 100 °C, 20 °C/min to 200 °C, and 5 min at 200 °C. The temperature of both the injection port and manifold was 260 °C. The flow rate of carrier gas (H_2) was 2 mL/min. The injection volume was 0.1 - 0.5 μL.

A Hewlett-Packard 5992 instrument (70 eV) fitted with the same column as before was used for GLC-MS identification of the trimethylsilylated samples. The temperature program was 4 min at 100 °C, 8 °C/min to 200 °C, and 10 min at 200 °C. Interpretation of the mass spectra was based on the data published by Petersson[12, 13]. The corresponding retention time data[14] were used to identify diastereomeric compounds.

Formic and acetic acids were determined as benzyl esters[15] by GLC[16].

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

The molecular-weight distribution of the lignin fraction was determined by gel permeation chromatography[17] in a column (1x122 cm) packed with Sephadex G-50 and using 0.5 M sodium hydroxide as eluent (flow-rate 0.4 mL/min). The peaks were detected by UV measurements at 280 nm (Pharmacia dual path monitor UV-2). The column was calibrated using a kraft lignin sample of known molecular-weight distribution as a reference, and the relative retention volume scale was obtained by measuring the retention volume of sodium chloride (Metrohm-Herisau E 365 B conductivity detector).

ACKNOWLEDGEMENTS

The financial support of the Academy of Finland (Research Council for Technical Sciences) and the Ministry of Trade and Industry is gratefully acknowledged. We are also grateful to Dr. Jan Janson, the Finnish Pulp and Paper Research Institute, for the two-stage cooking experiments. The mass spectra were recorded at the Technical Research Center of Finland.

REFERENCES

1. E. Sjöström, Wood Chemistry, Fundamentals and Applications, Academic Press, Inc., New York, 1981.
2. E. Sjöström, Production of Chemicals from Wood as an Integrated Part of the Pulping Process, In 1983 International Symposium on Wood and Pulping Chemistry, Vol. III, p. 57-62, Tsukuba Science City, Japan, 1983.
3. R. Alén, Isolation of Aliphatic Acids from Pine and Birch Kraft Black Liquors, Doctor Thesis, Helsinki University of Technology, Espoo, Finland, 1981.
4. L. Olm and G. Tistad, Sven. Papperstidn. 82(15), 458 (1979).
5. R. Malinen and E. Sjöström, Paperi Puu 57(11), 728 (1975).
6. N.A. Ivanov, Yu.I. Chernousov, V.N. Piyalkin, and L.G. Popova, Khim. Drev. (2), 96 (1975).
7. L. Löwendahl, G. Petersson, and O. Samuelson, Tappi 59(6), 118 (1976).
8. O. Samuelson and L.-A. Sjöberg, Cellulose Chem. Technol. 12(4), 463 (1978).

9. G. Jayme, W. Schempp, and S. Mahmud, Cellulose Chem. Technol. 1(1), 77 (1967).

10. B. Alfredsson, S. Bergdahl, and O. Samuelson, Anal. Chim. Acta 28, 371 (1963).

11. T. Hyppänen, E. Sjöström, and T. Vuorinen, J. Chromatogr. 261, 320 (1983).

12. G. Petersson, Tetrahedron, 26(13), 3413 (1970).

13. G. Petersson, Org. Mass Spectrom. 6(5), 565 (1972).

14. G. Petersson, J. Chrom. Sci. 15, 245 (1977).

15. P.O. Bethge and K. Lindström, Analyst 99(1175), 137 (1974).

16. R. Alén and E. Sjöström, Paperi Puu 62(5), 328 (1980).

17. K. Forss, B. Stenlund, and P.-E. Sågfors, Appl. Polym. Symp. (28), 1185 (1976).