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The Fate of Hexenuronic Acid Groups during Alkaline Pulping

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ABSTRACT

This study conducted detailed characterizations of HexA content in softwood pulps obtained in various alkaline wood pulping processes and conditions. The study found that the maximum HexA formation rate is linearly dependent on hydroxide ion (effective alkali) concentration and the rates of HexA formation and degradation reactions are not affected by the presence of sulfide or AQ. The study also found that the amount of HexA in pulp from one-stage cooking is directly related to the amount of effective alkali (EA) consumed, regardless of the pulping processes and conditions. Furthermore, the same maximum amount of HexA was found in various pulps obtained from different pulping processes for a given wood species. The study demonstrated that the amounts of HexA in the pulps obtained in the early stages of pulping are linearly proportional to the amounts of methanol found in the corresponding pulping liquors with a slope close to unity, which validates the accuracy of the rapid HexA measurement method employed in this study.

Key words: Hexenuronic acid; xylan degradation; kraft; soda; pulping; AQ; kappa number; pulp yield; methanol.

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INTRODUCTION

The formation of hexenuronic acid groups (HexA) during alkaline wood pulping has recently been a concern in the pulp industry because of its detrimental effects on bleaching operations, such as increased bleaching chemical consumption, bounding with transition metals, and reduced pulp brightness ceiling. Thus, research in this area has been very active in the last several years. One area of research is developing analytical methods to determine HexA content [1-5], which will assist the studies on the issues related to HexA that leads to the control of bleaching plant operations. The other two areas are developing HexA-removal processes prior to bleach plant [1] and understanding the impact of HexA on different bleaching stages and sequences [6-8]. However, little research activities have been reported on the effect of various parameters, including alkali charge, temperature, pulping time, wood species, pulp yield, and pulping additives (AQ and polysulfide), on HexA formation during chemical pulping. Such information is critically needed because it can demonstrate whether HexA removal during kraft cooking is possible or not.

Although a number of studies have reported that the HexA content in pulp is a strong function of the pulping process [9-10], limited studies have been reported on the effects of pulping parameters on the formation of HexA [11-12]. Buchert et al. [12] studied the effect of two parameters, cooking time and alkali charge, on HexA formation using a limited amount (12-36%) of pulp xylan peeled by xylanase. They found that the maximum amount of HexA was formed at the end of the heating-up period, and the HexA content was reduced by over 50% when active alkali charge was increased from 18 to 22%. More recently, Gustavsson et al. [13] reported that the HexA content at kappa number of 20 in Scots pine pulp could be predicted as functions of cooking time, initial [HS^-], and [HO^-]. They found that HexA formation is increased with the increase of initial sulfide concentration and the decrease of initial NaOH concentration. Furthermore, they found that the effect of cooking time was negligible, i.e., only to the power of 0.06. These two studies [12, 13] were conducted using high liquor-to-wood ratio, 6:1, and two stage-cooking with fresh liquors in each stage, which has limited applications in conventional pulping process.

Recently, Tenkanen et al. [14] presented a detailed comparison of three HexA measurement methods [1, 3, 5]. In general the three methods can give consistent measurements of HexA. However, all these three methods are tedious and time consuming (all take several hours to complete one measurements), which is probably why a systematic study on HexA formation in various pulping processes has not been conducted. In this study, a detailed characterization of HexA in chemical pulps obtained during various pulping processes was conducted using a simple and rapid method [15]. The effects of effective alkali (EA) charge, EA consumption, pulping process, and addition of AQ on time-dependent HexA content in pulp were investigated. The relationship of HexA content with pulp kappa number and yield was also analyzed. The HexA content is also quantitatively correlated with methanol content in the corresponding pulping liquor.

EXPERIMENTAL

Pulping

All pulping experiments were carried out in 500-mL bomb digesters. Eight bombs were mounted on a rotating drum, and heated with glycol oil. Fifty grams (ODW) of loblolly pine chips were charged in each bomb. Active alkali (AA) charge was varied between 15 and 18% on wood. Sulfidity was changed from 0 to 30%. Liquor-to-wood ratio was 4:1. The cooking temperature was ramped at 2.1°C/min from 23°C in 70 minutes and then maintained at 170°C. Cooking time was varied for a set of digestions in different bombs conducted under the same pulping condition to obtain time-dependent formation data of HexA and methanol. The pulp was completely disintegrated in a laboratory blender and thoroughly washed with tap water in a basket with 200-mesh screen. Pulp pads were then prepared in a handsheet machine for the measurement of pulp yields, kappa numbers, and HexA. The pulp yield, kappa number, and chemical strength of the cooking liquor, such as EA, and sulfidity, were measured according to the standard TAPPI test methods [16].

Measurement of HexA in Chemical Pulps

In a previous study [15], we developed a reliable, simple, and rapid technique for HexA measurements in chemical pulps; therefore, it is particularly suitable for the present systematic

study. In this method, 22 mM (0.6 %) mercuric chloride and 0.7 % sodium acetate are used to make a hydrolysis solution. The mercuric chloride ($HgCl_2$) and sodium acetate trihydrate ($CH_3COONa{\cdot}3H_2O$) of analytical grade were from commercial sources. Accurately weigh about 0.05 gram of air-dried pulp handsheet with known moisture content and put it into a 20 mL vial with 10 mL of hydrolysis solution. The mixture is sealed in the vial by a septum. To obtain good mixing of the pulp with the hydrolysis solution, we shake the vial and then heat the mixture for 30 minutes in a water bath with a temperature range of 60-70°C. After the solution is cooled to room temperature, we conducted UV absorption measurements of the filtered solution in a 10 mm path length silica cell using a by spectrophotometer (UV-8453, Hewlett-Packard) at a wavelength range of 260 to 290 nm. Detailed description on the measurement procedure can be found in our previous publication [15].

Measurement of methanol concentration in pulping liquors.

Accurate quantification of methanol concentration in pulping liquor is not trivial because of the complex sample matrix and the presence of inorganic salts in the liquor. In this study, methanol measurements in pulping liquors were conducted using an indirect headspace GC method that we developed [17] using a commercial gas chromatograph (HP-6890, Hewlett-Packard) and an automatic headspace sampler (HP-7694, Hewlett-Packard). The method uses the standard addition approach but relies on methanol material balance and liquid/vapor phase equilibrium in the sampling vials. Through the sampling of the vapor phase in the headspaces of two sampling vials (one with the standard addition of known amount of methanol), the method calculates the methanol concentration in the liquor from the ratio of the peak areas of the two headspace measurements. Therefore, calibration and direct sampling of the liquor are not required. It has been demonstrated that the method is reliable for determining methanol concentration in various kraft mill streams, including black liquors [17].

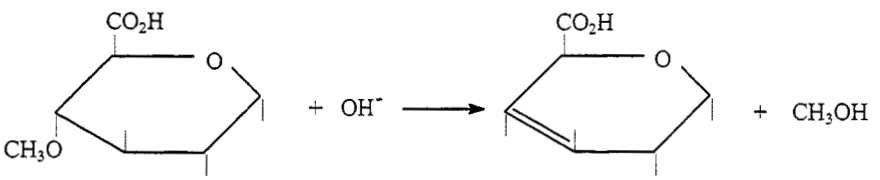
RESULTS AND DISCUSSIONS

Time-dependent Formation and Degradation of HexA

Figure 1 shows the HexA content in pulp as a function of cooking time for conventional kraft cooking with a sulfidity of 30%. The HexA content in pulp increased very rapidly as the

digester temperature linearly ramped to the final cooking temperature of 170°C. Shortly after the temperature reached the final cooking temperature, it started to decrease continuously. Similar results were reported by Buchert et al. [12].

The fundamental chemistry of HexA formation in pulp has well been established [18]. During alkaline pulping, hydroxide ions in the cooking liquor attack the methoxyl groups in the xylan chain through the following rapid hydrolysis reaction, leading to formation of HexA in pulp and methanol in the pulping liquor:



(1)

As the temperature increases, the HexA content in pulp increases until all the methoxyl groups in xylan chains are completely eliminated. Meanwhile, the degradation of xylan also takes place, leading to the reduction of HexA content in pulp. The HexA degradation from pulp will outpace HexA formation after the temperature reaches the final cooking temperature. Thus, HexA content in pulp begins to decline.

According to reaction (1), the same molar amount of methanol and HexA will be formed during the hemicellulose hydrolysis reaction. Figure 2 shows the amounts of methanol found in the pulping liquors and of HexA found in the corresponding pulps for cooks that were terminated at the different early stages of the cooking, i.e., before final pulping temperature of 170°C was reached. A linear relationship between methanol and HexA was obtained as shown. Furthermore, the slope of the linear relationship is 1.1, very close to unity, suggesting that almost all the methanol is formed from the hydrolysis of 4-O-methylglucuronoxylan, leading to the formation of the same amount of HexA. The close-to-unity slope of the methanol and HexA linear relationship also validates the accuracy of the HexA measurement method we developed [15]. The slightly higher than unity slope of 1.1, could be due to the small systematic errors in the measurements of methanol and (or) HexA, and could also be due to the dissolution (degradation) of HexA-containing xylan in the cooking liquor. Nevertheless, the result indicates that the degradation of xylan is not significant during the early stage of the cooking. The positive

intercept of 32.3 mmol/kg-ODW of the linear relationship indicates that methanol can also be released in the early stage of the pulping through mechanisms other than xylan hydrolysis.

Effect of Effective Alkali Charge on HexA Formation

Figure 3 shows the time-dependent HexA formation in different pulping processes. The data clearly show that the addition of AQ does not affect the formation and degradation of HexA. Although the profiles for HexA in various pulps obtained in different pulping conditions (soda and kraft with low and high active alkali charge and different sulfidities) are quite different, the same maximum amount of about 65 mmol/kg-OD pulp) of HexA was yielded during all the pulping processes immediately after the the pulping temperature reached 170°C. This indicates that the hydrolysis reaction is rapid [18] and perhaps results in a 100% conversion of 4-O-methylglucuronoxylan to methanol and HexA. Therefore, the final amount of HexA formed does not vary with pulping process for a given wood species.

According to reaction (1), the HexA formation rate can be written as follows:

$$\frac{d[HexA]}{dt} = k \cdot Exp(-E_a / RT) \cdot [(OCH_3^+)_{-xylan}][OH^-] \qquad (2)$$

Therefore, the effective alkali (EA or OH^- concentration) is a key factor controlling the formation of HexA for a given cooking temperature and wood species. Figure 4 shows that the maximum HexA formation rate is linearly proportional to the initial EA concentration in the cooking liquors or the first order in hydroxide ion concentration. Data also clearly show that a higher initial EA does lead to a fast HexA formation.

An interesting phenomenon was found when we plotted the HexA content vs the consumption of EA. As shown in Fig. 5, HexA profiles for different pulping processes fall to a single curve. Although a quantitative interpretation of this result is not presently possible, a few implications can be drawn from it. Firstly, the fate of HexA in pulp, formation and degradation, is only a function of hydroxide ion. Secondly, all the reactions during pulping that consume a major part of the hydroxide proceed to the same degree as that of reactions associated with HexA in all pulping processes. It is known that the hydroxide is mainly consumed in the neutralization of organic acid groups in original wood components, and that the acids are generated during

degradation of carbohydrates and lignin. Because depolymerization of lignin is strongly accelerated by the presence of sulfide and AQ in kraft cooking, the data shown in Fig. 5 suggest that lignin degradation by sulfide and AQ does not generate a large amount of acid groups, which otherwise would consume a measurable amount of alkali. Finally, the results shown in Fig. 5 and Fig. 1 also suggest that the xylan redeposited onto the fiber surface during the final cooking stage when residual alkali concentration becomes very low does not contain, or at least not a measurable amount of HexA. Otherwise, we should see increased HexA content during the end of cooking. Buchert et al. [12] measured the total xylan content in pulps based on O.D. weight of wood and found that these pulps contained higher xylan, but less HexA.

The results in Fig. 5 can be used to estimate the amount of HexA content in pulp with EA data without conducting HexA measurements. If one can determine the amount of EA consumed for any type of one-stage cook, e.g., kraft with different sulfidity, soda, with and without AQ, one can determine the amount of HexA in pulp using the data shown in Figure 5 without conducting HexA measurements. To facilitate this estimation, we conducted a least-square fit of the data to obtain the following equation for HexA determination,

$$HexA = \frac{a \cdot w}{5(EA_{consum} - 0.42)^2 + w^2} + b(EA_{consum})^2 \qquad (3)$$

where $a = 9.1$, $w = 0.15$, and $b = 43$. Eqn (3) is purely a mathematical fit of the data and specific for southern pine. Eqn. (3) fits the data well, in particular at large EA consumption as shown in Fig. 5. But the accuracy of Eqn. (3) decreases outside the region where there are no experimental data points.

The data shown in Fig. 5 were obtained in the pulping of southern pine. The profile of HexA vs EA-consumed may be different for different wood species. The validity of the results in Fig. 5 and Eqn. (3) for other wood species will have to be investigated in the future. Furthermore, the results in Fig. 5 were obtained in one-stage pulping processes, i.e., no liquor exchange or addition during cooking. The validity of the results in Fig. 5 and Eqn. (3) for complex pulping processes, such as EMCC and RDH, will also be investigated in the future. In these complex processes, determination of EA consumption may require a lot more effort than

just simply determining HexA in pulp. Therefore, the practical importance of Fig. 5 may be limited as the measurement of HexA will be easier than the determination of EA consumption.

Relationship of HexA Content in Pulp with Kappa Number and Yield

Because HexA formation through hydrolysis and degradation reactions proceed simultaneously with delignification, correlating HexA with pulp number may have some practical applications. We plotted the HexA formation as functions of pulp kappa number and yield for both soda and kraft cooks with or without AQ as shown in Figs. 6 and 7, respectively. HexA content in pulps with AQ addition is slightly higher than that in pulp without AQ addition. These results do not contradict the findings presented in the previous section, i.e., HexA formation is mainly affected by hydroxide ion concentrations, not by the presence of AQ or sulfide. However, the addition of AQ facilitates delignification and thus reduces the required pulping time, which results in high yield of HexA. The results shown in Figs. 6 and 7 clearly demonstrate that sulfidity has no effect on HexA formation and degradation.

For a given pulp kappa number or yield, HexA in kraft pulp is much higher than that in soda pulp as shown in Figs. 6 and 7. The difference in HexA content between soda and kraft pulp at a given yield cannot be explained by the negative effect of higher hydroxide concentration on pulp yield, and can only be attributed to that fact that hydroxide concentration has a much stronger effect on HexA degradation than on pulp yield. The difference between HexA content in soda and kraft pulps at a given kappa number is due to the difference in delignification selectivity. Kraft cooking not only has lower EA concentration at the same active alkali charge, but also requires much lower H factor to reach a given kappa number. Both lower H factor and EA concentration will result in less HexA degradation.

CONCLUSIONS

We conducted detailed characterizations of HexA content in softwood pulps obtained in various alkaline wood pulping processes and conditions. Our study found that the maximum HexA formation rate is linearly dependent on (first order) hydroxide ion (effective alkali) concentration and the rates of HexA formation and degradation reactions are not affected by the presence of sulfide or AQ. The study also found that the amount of HexA in pulp from one-

stage cooking is directly related to the amount of EA consumed, regardless of the pulping processes and conditions. Furthermore, the same maximum amount of HexA was found in various pulps obtained from different pulping processes for a given wood species, regardless of the pulping processes and conditions. HexA content as a given yield or kappa number was different at different sulfidity or AQ addition, which is a result of the increased delignification rate by these additives. Finally, the study demonstrates a linear relationship with unity slope between the amounts of HexA in the pulps obtained in the early stages of pulping and the amounts of methanol found in the corresponding pulping liquors, which validates the hydrolysis reaction theory [18] as well as the accuracy of the technique for rapid HexA measurements that we developed [15].

PRACTICAL IMPLICATIONS

Two possible practical implications could be derived from the information generated from this study. The first one is that the HexA content in pulp could be estimated by knowing the EA consumption of the cooking process for one-stage cooking. For multi-stage cooking processes, e.g., EMCC and RDH, the existence of the relationship has to be investigated in the future. The second implication is that it is unlikely to find suitable procedures or conditions to reduce HexA content during pulping process. This is because the amount of HexA removal is directly proportional to the EA consumption, and not by any other conditions. The amount of EA consumption is basically linked to the amount of carbohydrate degradation. Therefore, any attempts to reduce HexA during pulping will likely result in higher carbohydrate degradation, leading to lower yield or/and lower strength. Any improvement in delignification selectivity will lead to higher HexA content in pulp as is shown by the presence of sulfide and AQ. Finally, the HexA measurement method we developed [15] is not only simple and rapid (it only takes 30 minutes to obtain one measurement), but also accurate. Therefore, the method [15] has significant advantages over most of the existing techniques [1-5, 14] (all take several hours to obtain one measurement) in practical applications.

ACKNOWLEDGEMENT

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REFERENCES

1. Vuorinen, T., Buchert, J., Teleman, A., Tenkanen, M., and Fagerstrom, P., "Selective hydrolysis of hexenuronic acid groups and its application in ECF and TCF bleaching of kraft pulps", *Proc. 1996 Int. Pulp Bleaching Conf.,* TAPPI Press, Atlanta, p.43.

2. Teleman, A., Harjunpaa, V., Tenkanen, M., Buchert, J., Hausalo, T., Drakenberg T., and Vuorinen, T., "Characterisation of 4-deoxy-β-L-threo-hex-4-enopyranosyluronic acid attached to xylan in pine kraft pulp and pulping liquor by ^{1}H and ^{13}C NMR spectroscopy", *Carbohydr. Res.*, 272, 55-71, 1995.

3. Tenkanen, M., Hausalo, T., Siika-aho, M., Buchert, J., and Viikari, L., "Use of enzymes in combination with anion exchange chromatography in the analysis of carbohydrate composition of kraft pulp", *Int. Symp. Wood Pulping Chem. 8th*, Proceedings, Vol. 3, p. 189-194, 1995.

4. Dahlman, O., Rydlund, A., and Lindquist, A., "Characterization of carbohydrates from chemical pulp using capillary electrophoresis and MALDI-TOF-MS", *Carbohydr. Res.*, 294:41, 1996.

5. Gellerstedt, G. and Li, J., "An HPLC method for the quantitative determination of hexenuronic acid groups in chemical pulp", *Carbohydr. Res.*, 41-51, 1996.

6. Ikeda, T., Hosoya, S., Tomimura, Y., Magara, K., Ishihara, M., "Contribution of LCC Bond Cleavage to the Kappa Number Reductionof Kraft Pulp", *Proc. 9th Intl. Symp. Wood Pulping Chem.,* Tech. Sect., CPPA, Montreal, p.J1-1, 1997.

7. Hososya, S., Tomimura Y., and Shimada, K., "Acid treatment as one stage of non-chlorine bleaching", *Proc. 7th Intl. Symp. Wood Pulping Chem.,* CTAPI, Beijing, Vol 1:206, 1993.

8. Ratnieks, S., Foelkel, C., Sacon, V., and Sauer, M., "Improved eucalyptus pulp bleachability via high temperature acid treatment', *Proc. 1997 Intl. Emerging Technol. Conf.*, Miller Freeman, San Francisco, Section 5-3, 1997.

9. Gellerstedt, G., and Al-Dajani, W.W., "On the bleachability of kraft pulp", *Proc. 9th Intl. Symp. Wood Pulping Chem.,* Tech. Sect., CPPA, Montreal, p.A1-1, 1997.

10. Buchert, J., Tenkanen, M., Ek, M., Teleman, A., Viikari, L., and Vuorinen, T., "Effect of pulping and bleaching on carbohydrates and technical properties", *Proc. 1996 Intl. Pulp Bleaching Conf.,* Tappi Press, Atlanta, p.39, 1996.

11. Buchert, J., Laine, J., Tenkanen, M., Vuorinen, T., Viikari, L., "Characterization of Hexenuronic Acids during Kraft and Superbatch Pulping", *Proc. 9th Intl. Symp. Wood Pulping Chem.,* Tech. Sect., CPPA, Montreal, p.M3-1, 1997.

12. Buchert, J., Teleman, A., Harjunpaa, Tenkanen, V.M., Viikari, L., and Vuorinen, T., "Effect of Cooking and Bleaching on the Structure of Xylan in Conventional Pine Kraft Pulping" *Tappi J.,* **78**(11): 125-130, 1995.

13. Gustavsson, C., Sjostrom, K., Al-Dajani, W.W., "The Influence of Cooking Conditions on the Bleachability and Chemical Structure of Kraft Pulps," Nordic Pulp & Pap. Res. J., **14**(1):71-81, 1999.

14. Tenkanen M.,, Gellerstedt, G., Vuorinen, T., Teleman, A., Perttula, M., Li, J., and Buchert, J., "Determination of Hexenuronic Acid in Softwood Kraft Pulps by Three Different Methods," *J. Pulp and Paper Sci.*, **25**(9):306, 1999.

15. Chai, X.S., Zhu, J.Y., and Li, J., "A Simple and Rapid Method to Determine Hexenuronic Acid Groups in Chemical Pulp", Proceedings of the 10th ISWPC, Yokohama, Japan, June 1999, also submitted to *J. Pulp & Paper Sci.*, 1999.

16. Tappi Test Methods, ISBN 0-89852-334-6, 1996.

17. Chai, X.S., Dhasmana, B., and Zhu, J.Y., "Determination of Volatile Organic Compound Contents in Kraft-Mill Streams Using Headspace Gas Chromatography," *J. Pulp & Paper Sci.*, **24**(2): 50(1998).

18. Clayton, D.W., "The Alkaline Degradation of Some Hardwood 4-O-Methyl-D-Glucuronoxylans", *Svensk Papperstidning*, **66**(4):115 (1963).

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Fig. 3 Time-dependent HexA in pulps during various pulping processes with and without AQ addition.

Fig. 4 Effect of initial EA concentration on the maximum formation rate of HexA in various pulping processes.

Fig. 5 The relationship between HexA content in pulp and the corresponding EA consumption.

Fig. 6 The relationship between HexA content in pulp and the corresponding kappa number.

Fig. 7 The relationship between HexA content in pulp and the corresponding pulp yield.

Fig. 1

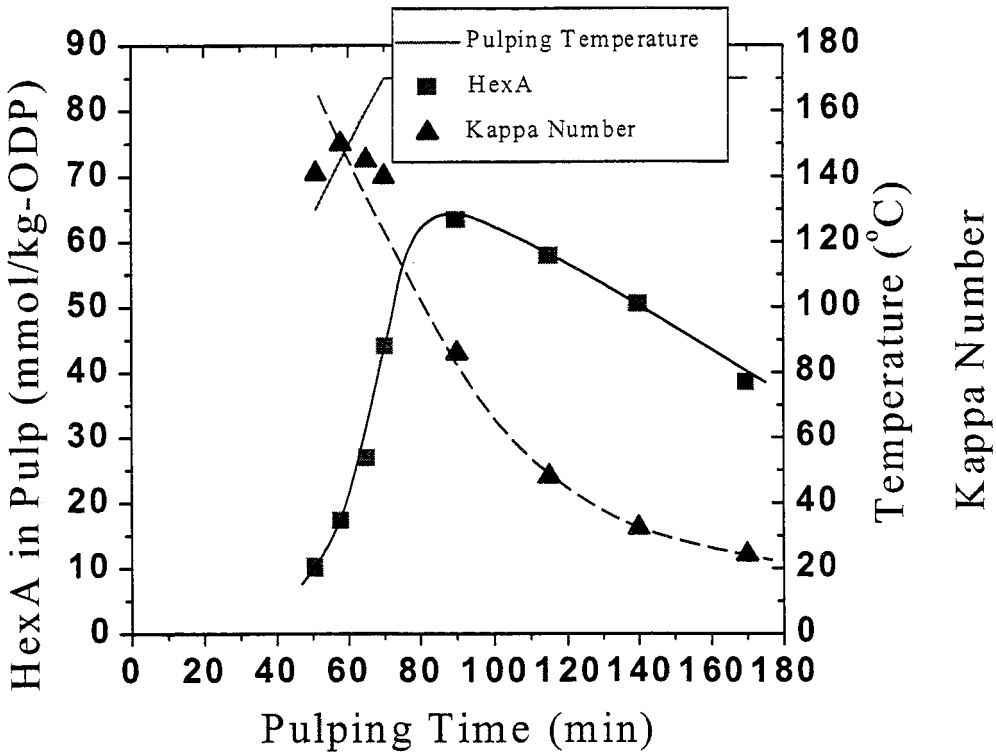

Pulping Temperature
HexA
Kappa Number
HexA in Pulp (mmol/kg-ODP)
Temperature (°C)
Kappa Number
Pulping Time (min)
0
10
20
30
40
50
60
70
80
90
0
20
40
60
80
100
120
140
160
180
0
20
40
60
80
100
120
140
160
180

Fig. 2

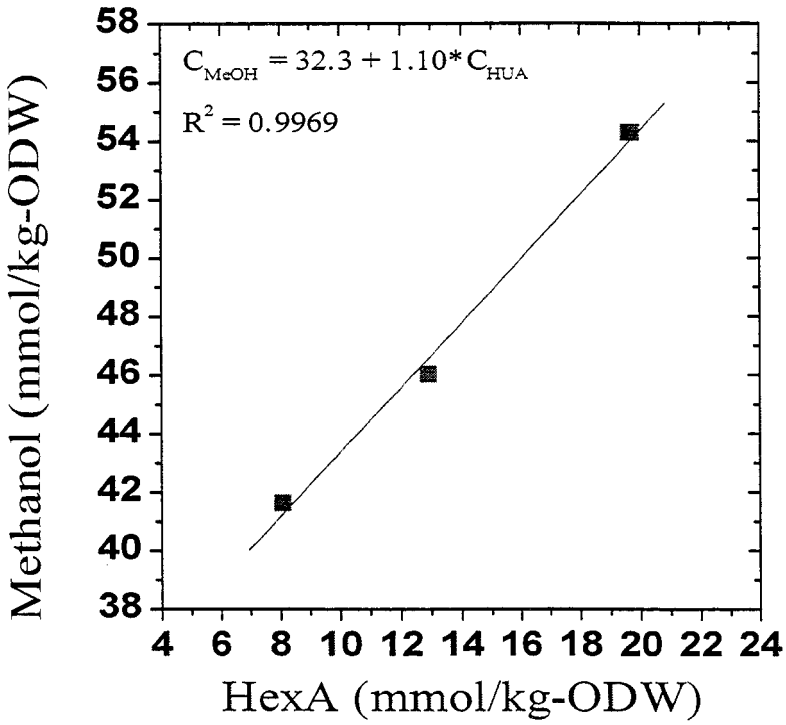

$C_{MeOH} = 32.3 + 1.10 * C_{HUA}$
$R^2 = 0.9969$
Methanol (mmol/kg-ODW)
HexA (mmol/kg-ODW)
38
40
42
44
46
48
50
52
54
56
58
4
6
8
10
12
14
16
18
20
22
24

Fig. 3

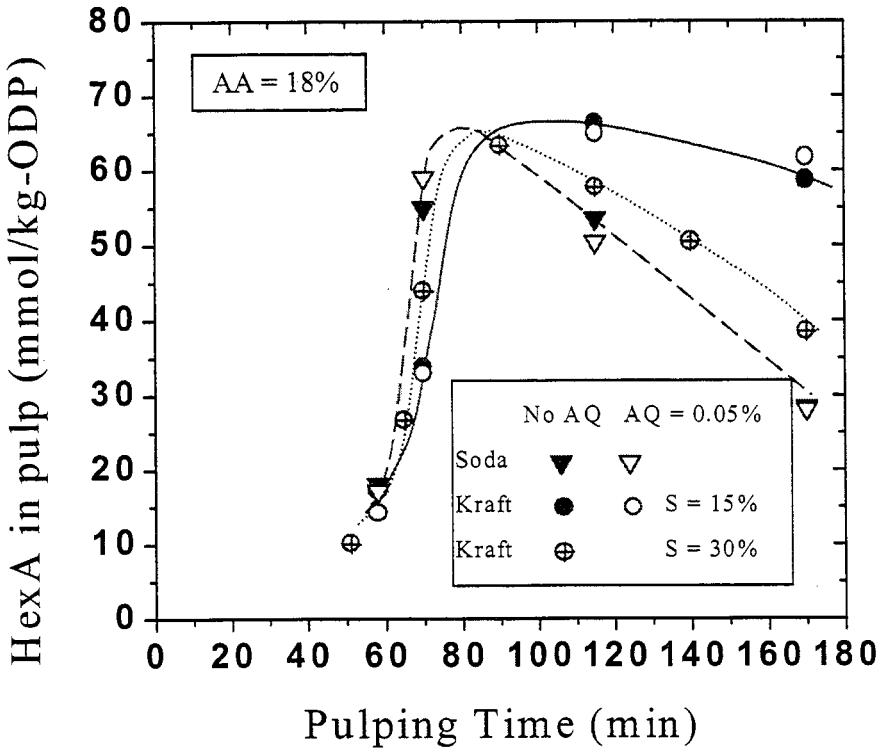

AA = 18%
No AQ
AQ = 0.05%
Soda
Kraft
S = 15%
Kraft
S = 30%
HexA in pulp (mmol/kg-ODP)
Pulping Time (min)
0
10
20
30
40
50
60
70
80
0
20
40
60
80
100
120
140
160
180

Fig. 4

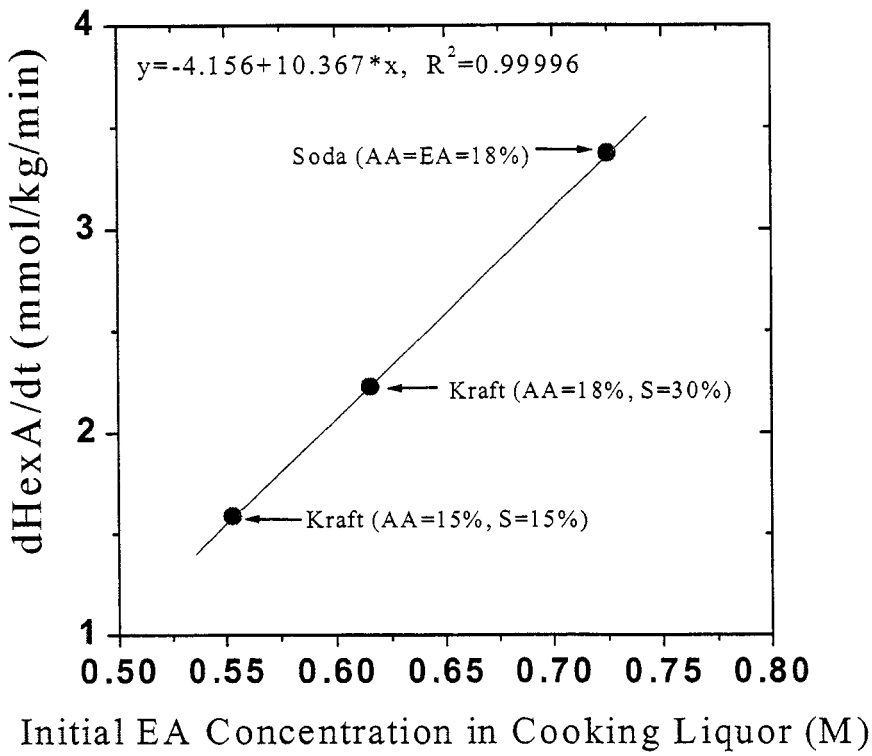

y=-4.156+10.367*x, R2=0.99996
Soda (AA=EA=18%)
Kraft (AA=18%, S=30%)
Kraft (AA=15%, S=15%)
dHexA/dt (mmol/kg/min)
Initial EA Concentration in Cooking Liquor (M)
1
2
3
4
0.50
0.55
0.60
0.65
0.70
0.75
0.80

Fig. 5

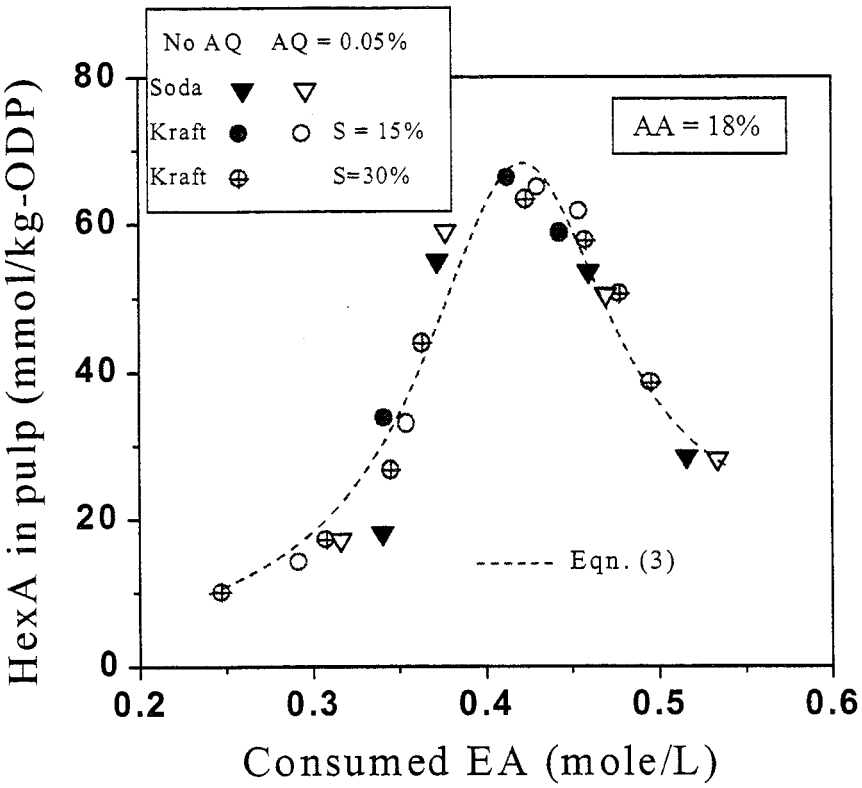

No AQ AQ = 0.05%
Soda
Kraft S = 15%
Kraft S=30%
AA = 18%
------ Eqn. (3)
HexA in pulp (mmol/kg-ODP)
Consumed EA (mole/L)
0
20
40
60
80
0.2
0.3
0.4
0.5
0.6

Fig. 6

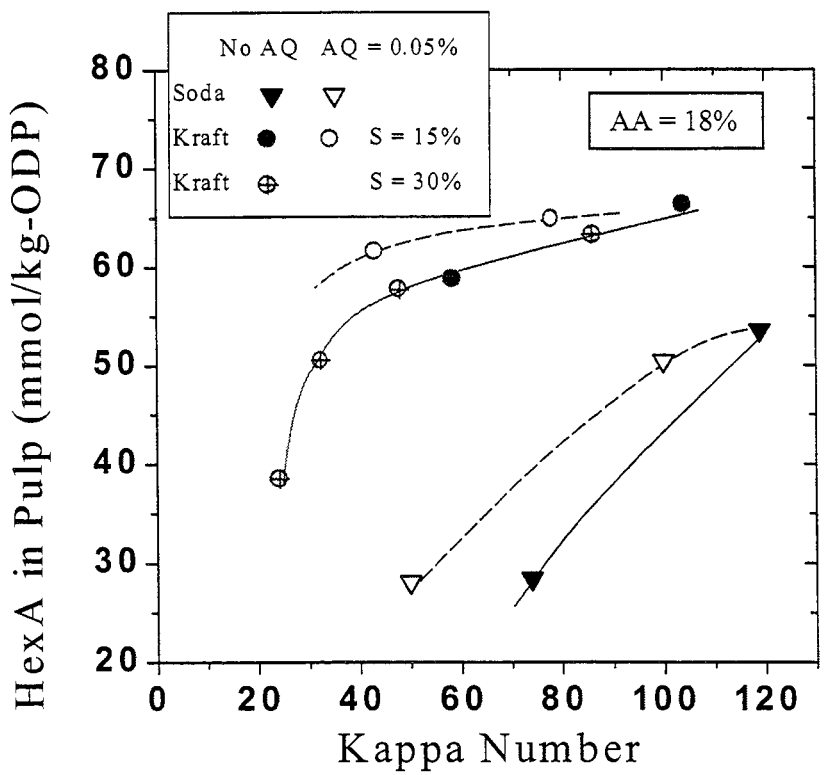
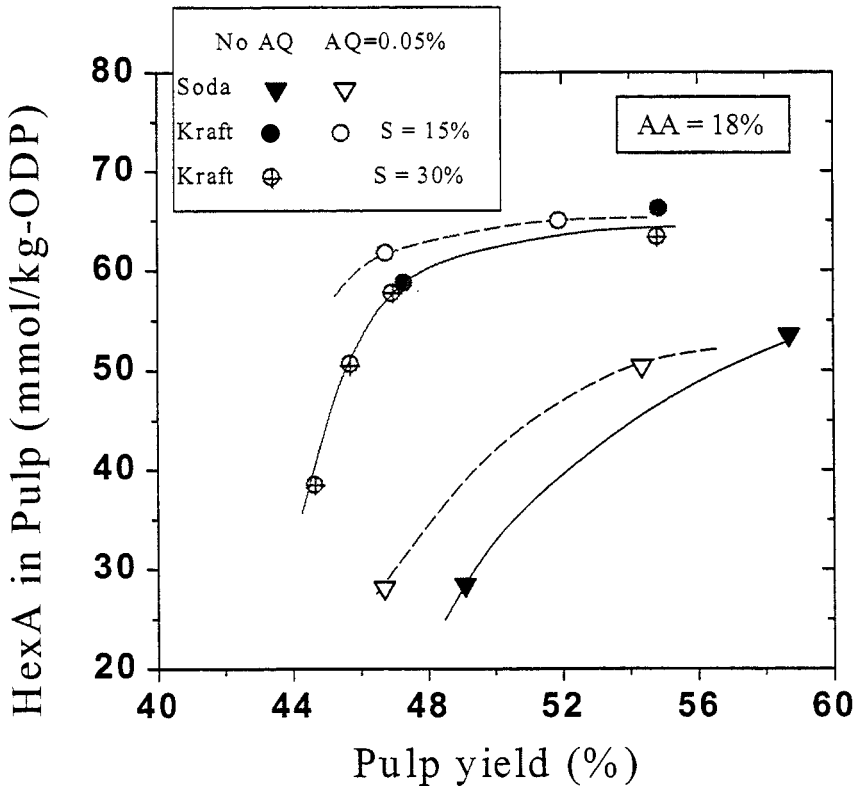

No AQ AQ = 0.05%
Soda
Kraft S = 15%
Kraft S = 30%
AA = 18%
HexA in Pulp (mmol/kg-ODP)
Kappa Number
20
30
40
50
60
70
80
0
20
40
60
80
100
120

Fig. 7


No AQ
AQ=0.05%
Soda
Kraft
Kraft
S = 15%
S = 30%
AA = 18%
HexA in Pulp (mmol/kg-ODP)
Pulp yield (%)
80
70
60
50
40
30
20
40
44
48
52
56
60