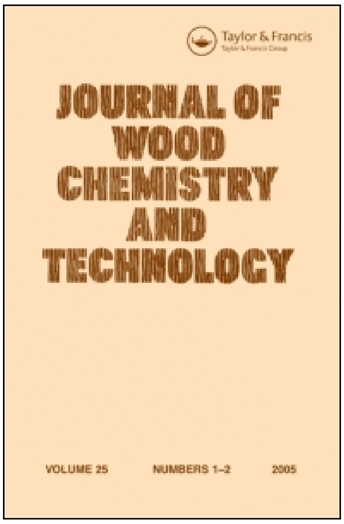

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END-WISE DEGRADATION OF HYDROCELLULOSE IN MILDLY ALKALINE SOLUTIONS AND ITS RETARDATION BY AMMONIA

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ABSTRACT

At pH 11 and 140°C, the rate of end-wise degradation ("peeling") of hydrocellulose is approximately 27 percent of that in 1 N NaOH. As the pH is reduced further, the rate of peeling declines by a factor of 0.34 per pH-unit. This decline is less than expected on the basis of end-group ionization. Consequently end-wise degradation can be a significant reaction even at neutral pH.

The peeling rate is strongly retarded at pH 11 and below by the presence of ammonia and, to a lesser degree, by borate. The retardation is believed to be caused by the formation of Shiff's bases in case of ammonia.

INTRODUCTION

It is well known that the end-wise degradation ("peeling") of polysaccharides proceeds rapidly in alkaline solutions in the temperature range 100° to 130°C. The kinetics of this process have been extensively clarified for hydrocellulose,[3] softwood glucomannan[4] and amylose[5] above pH 12, but no systematic studies have been performed at lower alkalinities. Consequently, a study was undertaken to clarify the kinetic pattern of alkaline peeling

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of hydrocellulose in the pH range 9 to 11. During the course of this study it was found that ammonia exerts retarding influence on the rate of peeling in this pH range. This phenomenon was then subjected to a separate investigation.

EXPERIMENTAL

Buffer Solutions

The buffer solutions used in this study were phosphate (pH 11.1, 0.05 N NaOH and 0.386 N Na_2HPO_4), bicarbonate (pH 10.2, 0.175 N NaOH and 0.250 N $NaHCO_3$), and borax (pH 9.2, 0.16 N $Na_2B_4O_7$ and 0.27 N $CaCl_2$). Bicarbonate buffer solution of pH 9.2 was also prepared by adding solid NaOH to 0.40 N $NaHCO_3$ until the pH reached the said value. These buffer solutions were used without dilution.

Preparation and Alkaline Degradation of Hydrocellulose

Hydrocellulose was prepared by hydrolyzing purified cotton cellulose[6] with 2.5 N HCl (acid/cellulose = 30/1 by weight) at 60°C under N_2 for 2 hours.

Alkaline degradation of hydrocellulose was carried out in 45-ml Parr autoclaves. After blanketing with nitrogen, the autoclaves containing hydrocellulose (0.5 g OD weight) and 25 ml of buffer solution were sealed and inserted in a rocking cylindrical aluminum block preheated to the appropriate temperature. The heating of the block was controlled by a linear temperature programmer and monitored by a thermocouple inserted into the heating block. The temperature inside the autoclave was measured by a separate thermocouple connected with a digital thermometer and remained constant within 0.2°C. The zero reaction time, in each case, was recorded at a point at which the autoclaves had reached the selected reaction temperature indicated by the digital thermometer. In each series of experiments, the heat-up time was controlled to be 8 minutes.

When ammonia was added to the buffer solutions, the pHs were adjusted to the original levels by adding acetic acid. The alkaline degradation was then carried out in the same manner as described above.

After the degradation reaction, the suspension was acidified and filtered, the hydrocellulose was washed with 1% acetic acid, followed by water and air-dried. A moisture determination was made and percent weight loss (L) calculated, as depicted in Figure 1. Figure 2 shows the degradation of hydrocellulose with the presence of ammonia. The complete alkaline peeling of the hydrocellulose by 5% NaOH at 100°C or by buffer solutions at 140°C resulted in an identical weight loss (L_∞) of 31.0% which decreased to 7.3% after $NaBH_4$-reduction.[7] This 7.3% weight loss is probably caused by the dissolution of oligomeric cellulose hydrolysis products in the alkaline medium and was subtracted from the determined weight losses L_∞ and L.

RESULTS AND DISCUSSION

Effect of pH on the Rate of Peeling

For the purpose of evaluating the rates of peeling in the pH range 9 to 11, weight losses of hydrocellulose were determined after heating in appropriate buffer solutions for varying periods of time. The data obtained are shown in Figure 1 and demonstrate that although decreasing pH does clearly retard the peeling reaction, the process occurs rapidly even at pH 9 at 140°C. Generally, the kinetics of peeling of hydrocellulose follow equation (1).[3,5]

$$k_p t = \bar{X}_n \ln \frac{L_\infty}{L_\infty - L} \qquad (1)$$

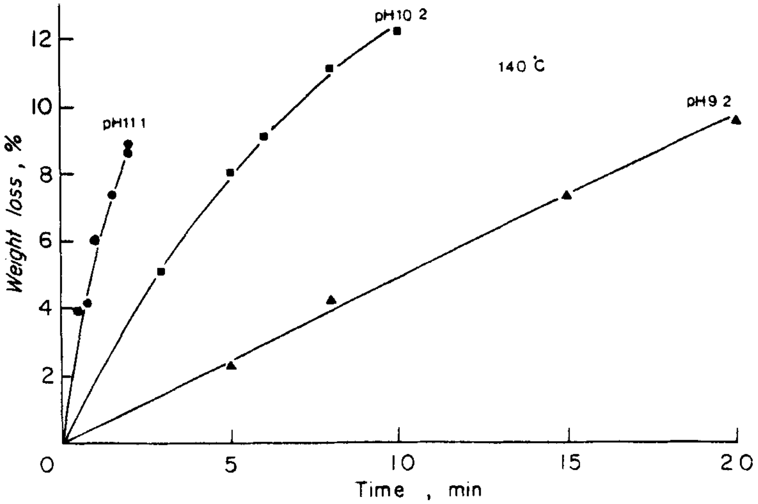


Figure 1. Peeling loss of hydrocellulose as a function of time in three buffer solutions at 140°C.

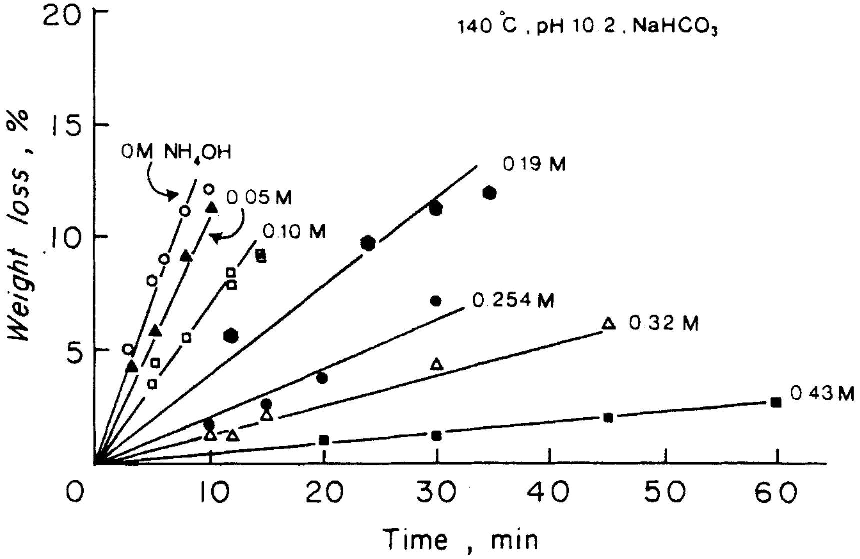


Figure 2. Effect of ammonia on the peeling loss of hydrocellulose at pH 10.2 and 140°C.

where k_p is the rate constant for propagation, $\bar{X}_n$ is the number average degradable chain length (appr. 68 for hydrocellulose[8,9,10]) and L_∞ and L are the percent weight fractions lost due to peeling after prolonged reaction time and time t, respectively.

When data from peeling experiments conducted in the pH range 9 to 11 were applied to equation 1, it was found that L_∞ values were nearly unaffected by the pH of the experiment and satisfactory straight-line relationships corresponding to equation 1 were obtained (Figure 3). On this basis, the propagation rate constants were computed and are given in Table 1 together with the estimated value for the rate constant at pH 14, extrapolated from runs at lower temperatures.[3] Corresponding rate constants for the alkaline degradation of amylose were likewise extrapolated from previously published data at 100°C[5] and are included in Table 1. The observed rate constants are shown in Figure 4, curve 1, as percentages of the value at pH 14.

In the same diagram, data points from earlier studies on hydrocellulose[3] and amylose[5] have been included. It can be seen that all experimental points conform with a common sigmoidal curve.

The observed decline in peeling rate at lower pH levels is in conformity with the proposition that the reactive species in peeling is the anion of the reducing end-group, as has been proposed.[5] This anion is probably generated through the dissociation of the hemi-acetalic hydroxyl group attached to carbon-1. The inflection point in the sigmoidal curve in Figure 4 is positioned at pH 11.7 corresponding to the pK-value for the ionization of the reducing end-group. The observed pH is of the correct order of magnitude for the ionization of a hemiacetalic hydroxyl but would be low for the direct formation of an enolate ion _via_ C-H-ionization at carbon-2.[10,11] Overall, the results

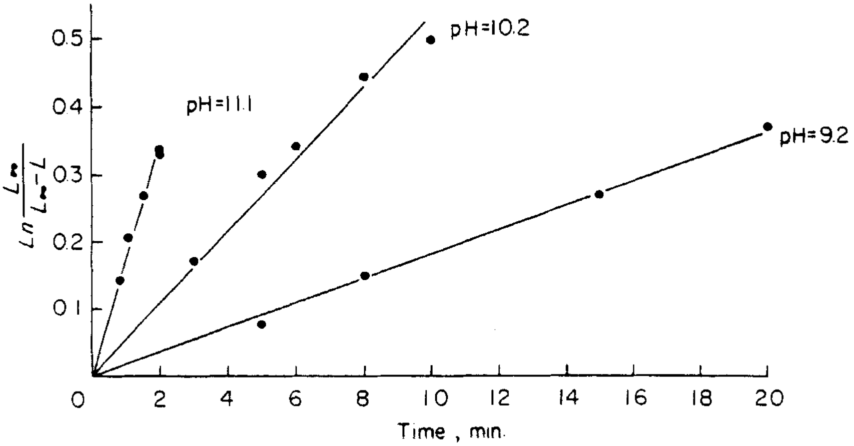


Figure 3. Rate plots, based on equation 1, for the peeling of hydrocellulose in three buffer solutions at 140°C.

TABLE 1

Rate Constants for the Alkaline Degradation of Hydrocellulose and Amylose at 140°C

Substrate	pH'	k_p (min^{-1})
Hydrocellulose	14 (NaOH)	56.8[a]
	11.6 (Na_2CO_3)	21.4[a]
	11.1 (Na_2HPO_4)	15.64
	10.2 ($NaHCO_3$)	5.09
	9.2 ($NaHCO_3$)	1.76
	9.2 ($Na_2B_4O_7$)	0.15
Amylose	14 (NaOH)	79.7[b]
	13.5 (NaOH)	74.3[b]
	12 (NaOH)	58.4[b]

a: Rate constants extrapolated using the activation energy of 103 kJ mol^{-1} and experimental k_p values at 130°C.[3]

b: Rate constants extrapolated using the activation energy of 88.7 kJ mol^{-1} and experimental k_p values at 100°C.[5]

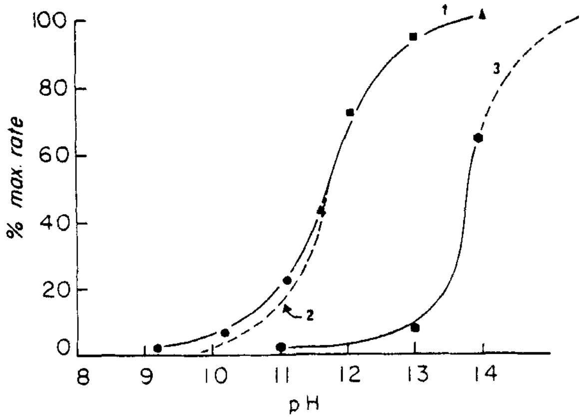


Figure 4. Curve 1: Propagation rate constants, expressed as percentages of the extrapolated constant at pH 14, shown as a function of pH. ■: Results based on earlier study by Haas *et al.*[3] ●: Present data. ▲[5]: Data extrapolated to 140°C for the peeling of amylose. Curve 2: Theoretical curve based on the observed inflection point of Curve 1. Curve 3: Data for the peeling of hydrocellulose in the presence of 0.8 M ammonia.

suggest that the rate of peeling at lower pH range should be governed by the following expression:

$$\text{Rate of propagation} = k_p \times [\text{End group anion}] \qquad (2)$$

If the validity of equation 2 extends to pH values lower than 10, the anticipated rate of peeling can be estimated as a function of pH from the rate observed at pH 11.0 and from the pK-value 11.7. On this basis, expected values for log k_p as a function of pH should conform with the straight line 1 in Figure 5. It can be seen that the experimentally determined log k_p-values are significantly higher than those predicted by line 1. The results indicate that the peeling rate, for some unknown reason, declines less than anticipated with a decrease in alkalinity and may still be significant in a neutral solution.

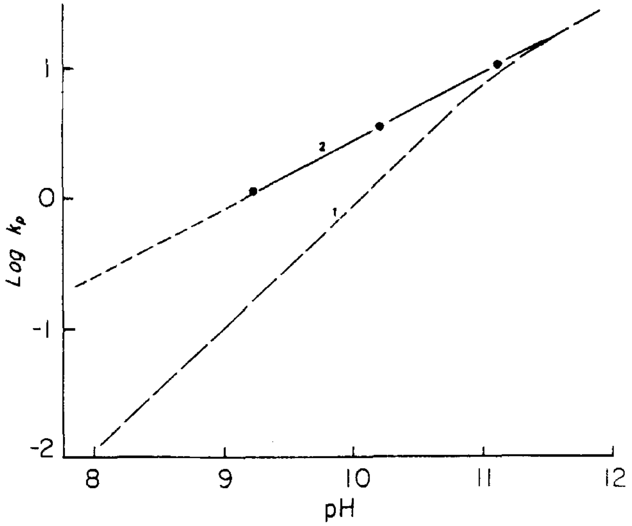


Figure 5. Log k_p as a function of pH. Curve 1: Theoretical curve. Curve 2: Experimental values.

This possibility prompted us to investigate the peeling process at pH 7. Two runs were conducted in a buffered solution at temperatures at 140° and 170°C. The results are illustrated in Figure 6 and demonstrate that the initial rate of the peeling reaction is indeed significant at 140°C and becomes quite rapid at 170°C. However, the peeling process levels off, in both cases, at lower L_∞ values than in runs at pH 9 and above, making the comparison of respective propagation rate constants difficult.

Effect of Ammonia on the Rate of Peeling

It was observed that the presence of ammonium salts in mildly alkaline solutions retarded strongly the rate of peeling as illustrated in Figure 2. This observation was totally unexpected and was therefore subjected to a detailed study. When partially peeled hydrocellulose samples were recovered after

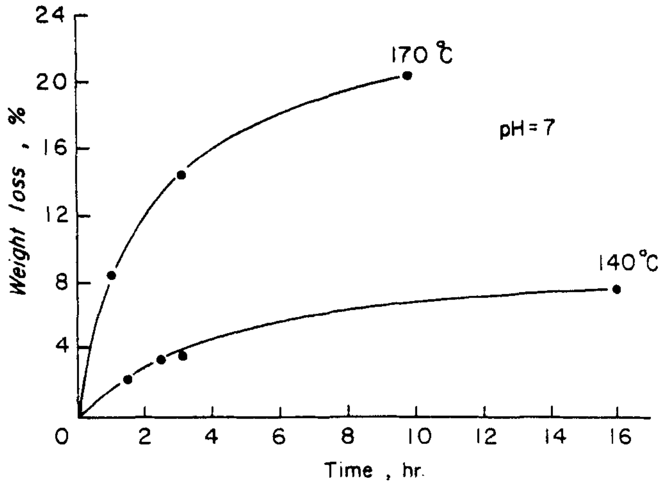


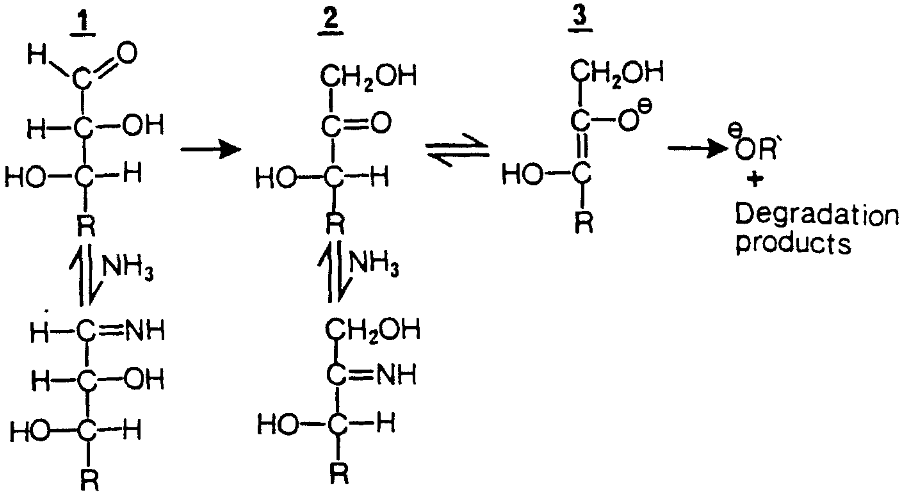
Figure 6. Peeling loss of hydrocellulose as a function of time in a pH 7 buffer at 140° and 170°C.

experiments illustrated in Figure 2 and subjected to a standard alkaline degradation, complete peeling was observed. Consequently, the presence of ammonia does not generate stabilized end-groups but must nevertheless modify them in such a manner as to reduce the rate of peeling.

The results from systematic studies on the retardation of peeling by ammonia are shown in Figure 7. In the pH range 9 to 13, more than 95 percent reduction in peeling rate can be achieved by the addition of sufficient amounts of ammonium salts. In contrast, even large concentrations of NH_4^+ have relatively minor effect at pH 14. The relative peeling rates in solutions (0.8 M in NH_4^+) are shown as a function of pH in Figure 4 (curve 3). The sigmoidal form of curve 3 does not necessarily mean that the ionization constant of the reducing end groups has been modified. It is equally probable that ammonia may retard the peeling process in the pH range 11.0 to approximately 13.5.

The underlying chemical reaction is probably the conversion of carbonyl groups in reducing end-groups and in peeling reaction intermediates to the corresponding Schiff's bases.[12,13]

It should be noted that the formation of Schiff's bases not only retards the initial reaction step (1 → 2) in peeling but also is likely to delay the conversion of 2 → 3:



R, R' = The remaining portion of the glucan

Consequently, the relationship between the rate constant for peeling and the NH_4^+- concentration is complex. However, reasonably good empirical straight-line correlations were found to exist between the logarithm of the ratio of normal over retarded peeling rate constant and ammonia concentration at individual pH levels, as shown in Figure 8. These correlations may be useful in predicting the effect of ammonia on peeling especially since data for pH 11 suggest the correlations to be reasonably independent of the reaction temperature.

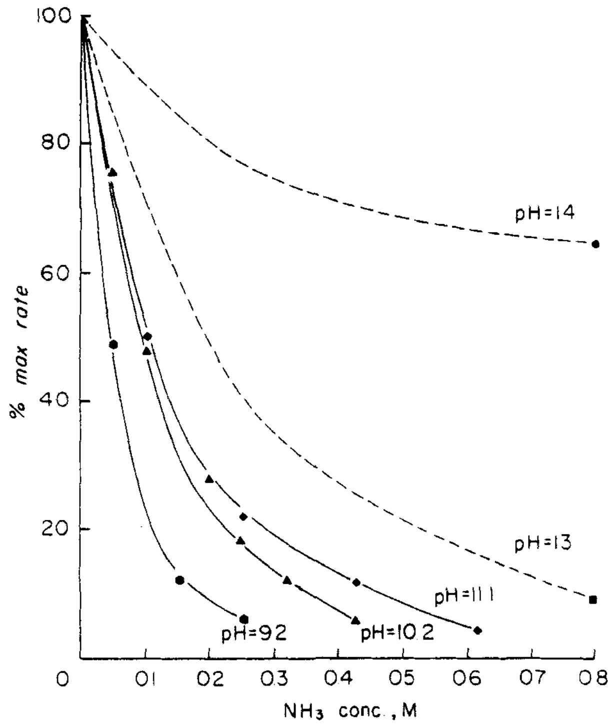


Figure 7. Retardation of peeling of hydrocellulose by ammonia in the pH range 9-14.

Retardation by Borate

When the peeling of hydrocellulose was carried out at pH 9.2, abnormally low rates were observed when the reaction was conducted in a borate buffer (Figure 9). The propagation rate constant was actually reduced to 8% of the value obtained in a bicarbonate buffer. The retarding effect at pH 9 is probably caused by the reversible conversion of the reducing end-groups to their borate complexes.

CONCLUSION

Exploratory studies carried out in this laboratory[14] suggest strongly that the peeling of glucomannans in softwood parallels

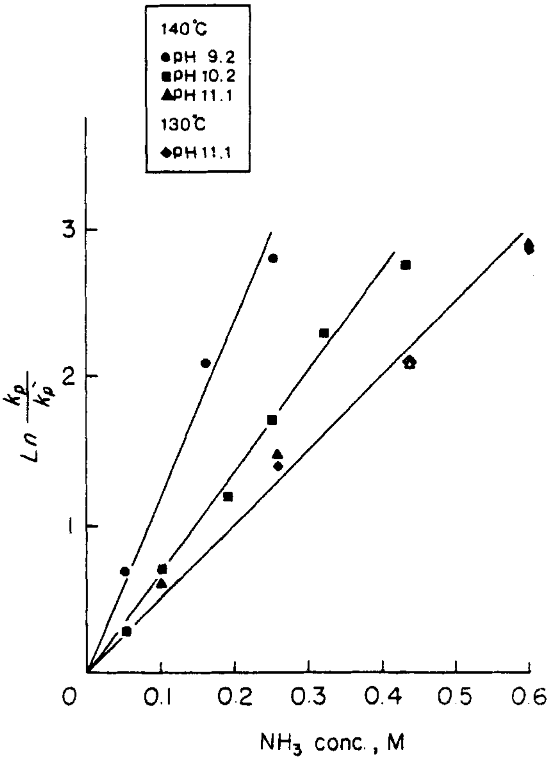


Figure 8. Empirical relationship between ($Ln(k_p/k_p')$) and the concentration of ammonia. k_p' and k_p are the rate constants of peeling reaction with and without the presence of ammonia, respectively.

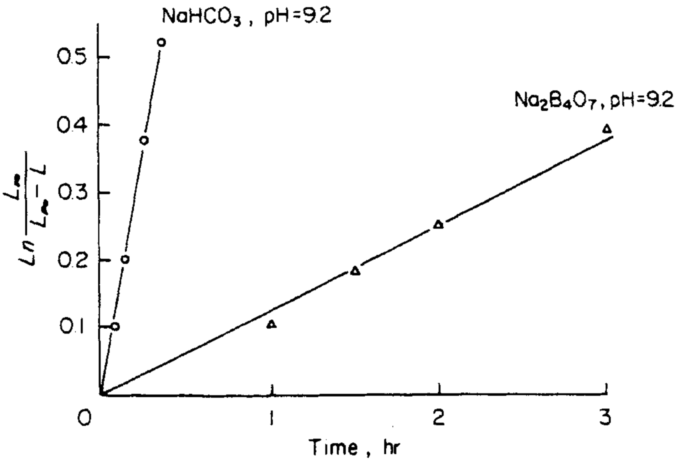


Figure 9. Effect of 0.215 M $Na_2B_4O_7$ on the rate of peeling of hydrocellulose at 140°C.

that of hydrocellulose. Therefore significant hemicellulose losses can be expected to occur whenever wood is pulped under near-neutral conditions. It was also observed that both ammonia and borate retarded the peeling of glucomannan as they did that of hydrocellulose.

Some of the observations reported in the literature can probably be credited to these retardation effects. For example, when DeHaas and Lang[15] pulped softwood chips at 200°C, using a combination of ammonia and aqueous acetone, nearly 90 percent of the original glucomannan was recovered undegraded in the pulp.

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1. Work performed by Vincent L. Chiang at the University of Washington as part of his Ph.D. thesis. Financial support provided by a grant from the Crown Zellerbach Company. The authors thank J. S. Barton and J. S. Fujii for valuable discussions.

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