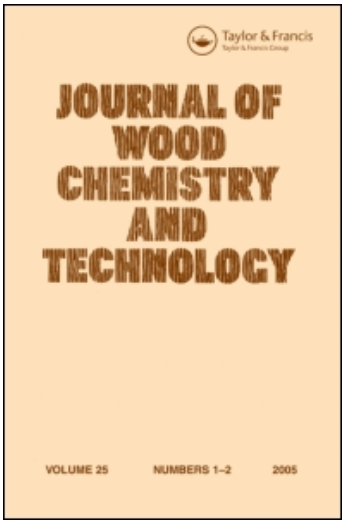

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THE POTENTIAL OF ^{13}C CP/MAS NMR IN THE STUDY OF KRAFT PULPING KINETICS

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ABSTRACT

Solid state ^{13}C CP/MAS nuclear magnetic resonance spectra were obtained for unbleached kraft pulps prepared from white spruce with yields ranging from 47.6 to 96.1%. The observed trends of the relative peak intensities were found to correspond to established facts on kraft kinetics. These results suggest that ^{13}C CP/MAS NMR of wood and pulp could be used to study kinetics in situ.

INTRODUCTION

The kinetics of the degradation of wood components during alkaline pulping has been the subject of numerous studies involving different theoretical approaches[1-8] and many analytical techniques[9-26]. The analysis often involves the isolation of lignin from pulp or cooking liquor. Such isolated lignin may not be representative of the residual lignin in the pulp at various stages of delignification[27,28]. Recently, several studies have illustrated that ^{13}C CP/MAS (cross-polarization/magic angle spin-

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ning) NMR allows the components of wood, pulp and plants to be studied in situ[29-37]. This would therefore circumvent the dependence of the results on the isolation procedure. Results obtained using solid state NMR may thus allow kinetics of pulping to be probed more deeply, by comparing reaction rates in localized areas of the polymers of wood. To the best of our knowledge, this is the first application of CP/MAS NMR to the study of pulping kinetics.

EXPERIMENTAL

Pulp Sample Preparation

Six unbleached kraft pulps were prepared from air dried white spruce (Picea Glauca) chips. These pulps, of 47.6 to 96.1% yield, were produced by cooking 50 g oven dry weight chips in 225 mL of liquor having an effective alkali content of 16%. The temperature of the digester was raised from 25°C to 170°C over a period of 134 min. During this period, four samples were removed from the digester at different times. With the cooking temperature held at 170°C, two more samples were removed, at 15 min and 90 min. The cooking conditions and corresponding H factors[8] are given in Table 1.

After cooking, the chips and pulps were washed with distilled water to remove spent cooking liquor. For the high yield cooks, up to two weeks of leaching were required. Klason lignin contents were determined and holocellulose contents then

TABLE 1

Cooking Conditions and Some Properties of the Wood and Pulp Samples

Sample #	Total Cooking Time (min)	H Factor	Pulp Yield (%)	Lignin[a] (%)	Carbohydrate[b] (%)
1[c]	0	-	100	28.7	71.3
2	50	-	96.1	27.4	68.7
3	95	3	81.9	24.6	57.3
4	115	32	75.8	20.8	55.0
5	130	137	68.4	15.9	52.5
6	147	392	58.2	8.9	49.3
7	224	1549	47.6	1.8	45.8

a - Klason lignin, does not include UV soluble lignin, based on oven dry wood.
b - Hollocellulose content determined by difference, based on oven dry wood.
c - White spruce wood sample.

obtained by difference. These values are also given in Table 1. In preparation for the NMR measurements, the pulps were air dried and ground to pass 40 mesh in a Wiley mill.

NMR Measurements

The experiments were performed on a Bruker CXP 200 MHz NMR spectrometer, operating with resonance frequencies of 200 MHz and 50.3 MHz for the proton and carbon-13 nuclei, respectively. A single contact Hartmann-Hahn condition[38] was established through spin-locked cross polarization, using applied proton and carbon-13 radio frequency fields of 10 G and 40 G, respectively. The

contact time, 5 ms, was carefully determined to maximize the signal-to-noise ratio, with a delay time of 4 s between successive sampling pulses. For each sample, a total of 15,000 scans was accumulated in a 12 kHz spectrum. Phase alternation was used throughout to eliminate baseline and intensity artifacts.

The magic angle was adjusted by monitoring the ^{79}Br spectrum of potassium bromide, a small amount of which was packed into thebottom of the rotor[39]. A Kel-F spinner was used in all experiments, at a spinning rate of 2.5 kHz. The chemical shifts were measured relative to tetramethylsilane (TMS), and all experiments were performed at room temperature.

RESULTS

The NMR spectra obtained for spruce wood and the six pulp samples are illustrated in Figure 1. Peak assignments were made using variable contact time and dipolar dephasing experiments and are in agreement with literature values reported for lignin and carbohydrates[27,28,40-42].

In general, peak areas are more quantitative than peak heights in routine NMR experiments. However, the degree of convolution observed for the spectra and the nature of the CP/MAS experiment make the determination and comparison of peak areas very difficult[27,30-32,34,43]. Such analysis of the spectra would introduce large errors in the results. In order to minimize such errors, results presented in this paper are based on peak height

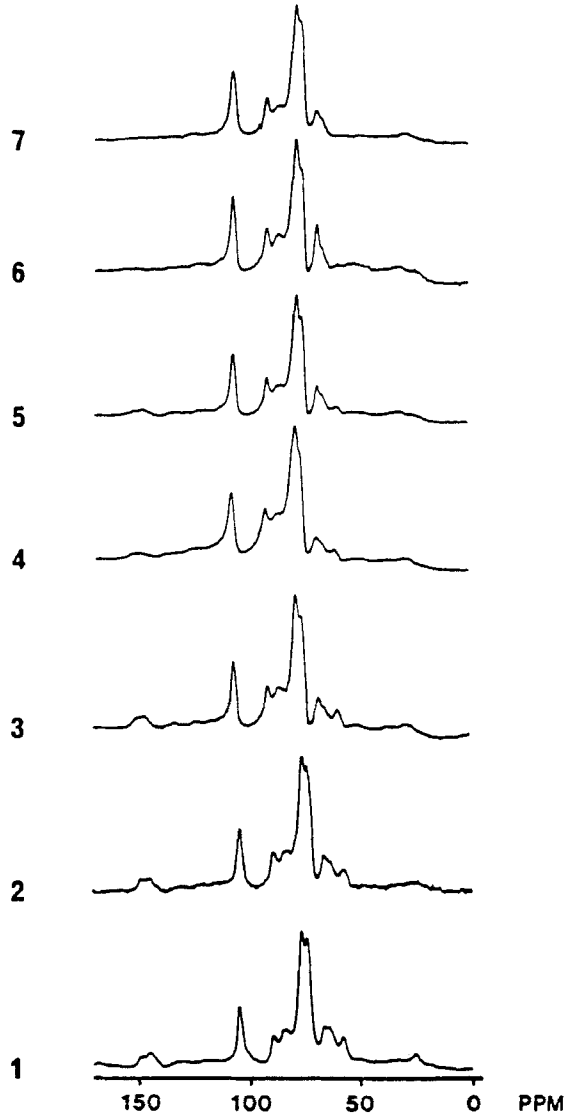
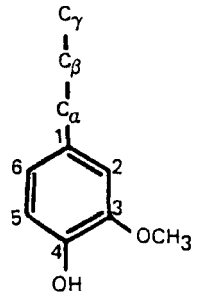


FIGURE 1. The ^{13}C CP/MAS NMR spectra of white spruce wood and kraft pulps of different yields prepared from spruce.



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measurements. A straight baseline was drawn on all spectra before determining the heights (taken proportional to the intensities) of the peaks. To minimize differences between spectra due to slight variations in the spectrometric conditions, all peak heights were normalized with respect to the peak at 105 ppm, the intensity of which remained almost constant throughout. The experimental error was estimated to be within 10%.

The sensitivity of the CP/MAS NMR technique to the determination of lignin was estimated from the plot of the Klason lignin content of the samples versus the normalized heights of the peak at 150 ppm, which corresponds to the C_3, C_4 aromatic carbons of lignin (1). As shown in Figure 2, the line had a correlation coefficient of 99% and an intercept of 5.6% lignin based on oven dry wood. This indicates that the NMR spectrum of pulp having a lignin content below 5% will not have measurable

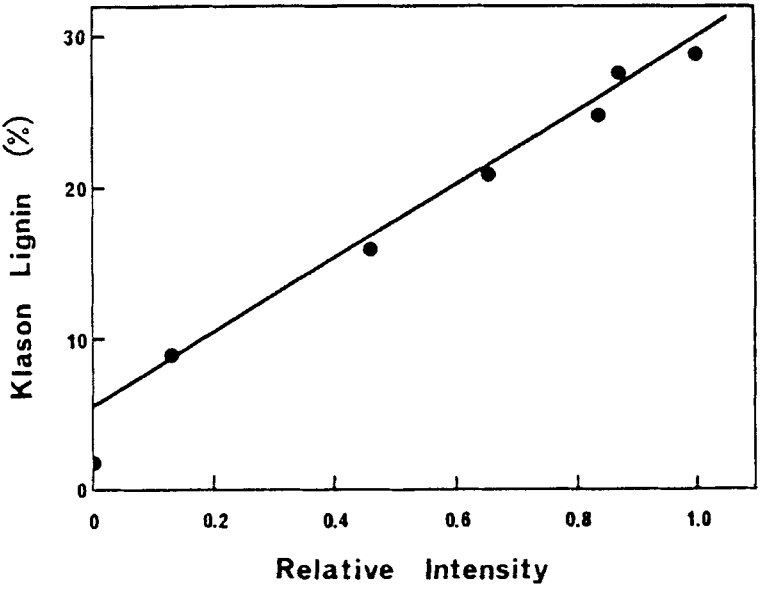


FIGURE 2. The plot of the percent Klason lignin content of the pulp samples and wood versus the normalized intensity of the aromatic carbons signal of lignin at 150 ppm from the CP/MAS NMR spectra.

lignin resonances, under the experimental conditions used in this study.

The percentages of lignin and carbohydrate dissolved during cooking were calculated from the values of the Klason lignin content of the pulps and the corresponding pulp yields, and are shown in Figure 3. The transition from the initial stage of delignification (samples 1 and 2) to bulk delignification (samples 3-7) can readily be seen. The weight percent lignin values of all the samples were determined by the use of the method described by Hemmingson and Newman[30], using peak heights

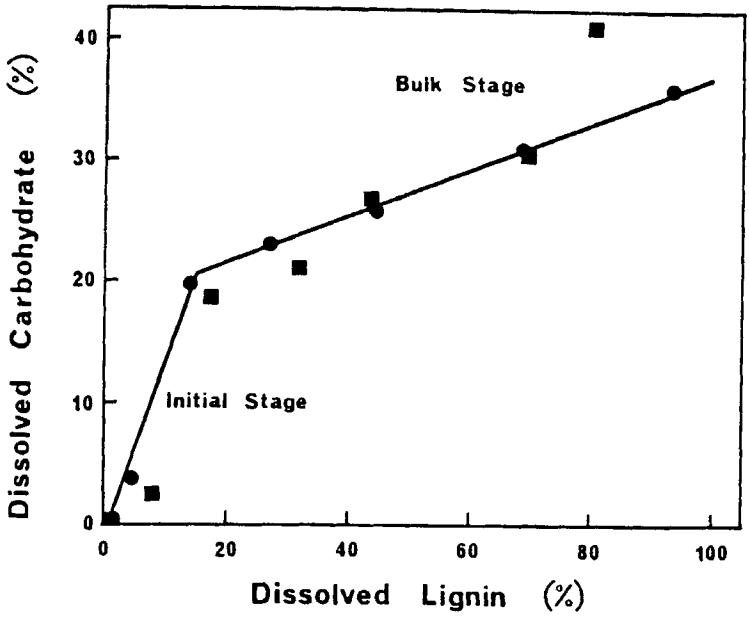


FIGURE 3. The comparison between the percent carbohydrate and percent lignin dissolved during cooking determined chemically (●) and those values determined from the NMR spectra (■).

instead of areas. These quantities were then normalized with respect to wood and the 5% sensitivity level of the technique taken into account. From these quantities, the percentages of dissolved lignin and carbohydrate were calculated and also plotted in Figure 3. The point corresponding to sample 7 deviated from the line because it was below the sensitivity of the NMR technique.

For samples 3 to 7, the normalized peak heights, relative to the intensities measured for the spruce wood sample, were plotted against log H factor and are shown in Figures 4 and 5 for bulk

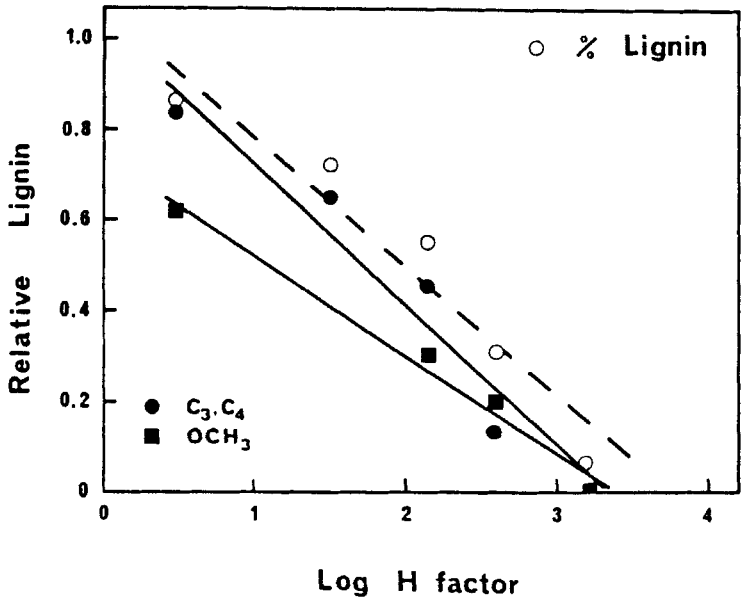


FIGURE 4. The comparison between the decrease in the relative intensity of the lignin signals determined by NMR and the decrease in the relative Klason lignin content of the pulps, as a function of H factor.

delignification and bulk carbohydrate removal, respectively. The change in the Klason lignin content of the pulps, relative to the Klason lignin content of the wood, was also included in Figure 4. Similarly, the relative change in the holocellulose content was included in Figure 5. In this way, the bulk delignification and bulk carbohydrate removal determined by chemical means could be compared with that determined by spectrometric (NMR) means. The lines represent the linear regression analysis of the data. Values of the linear correlation coefficients and the slopes of these lines are given in Table 2.

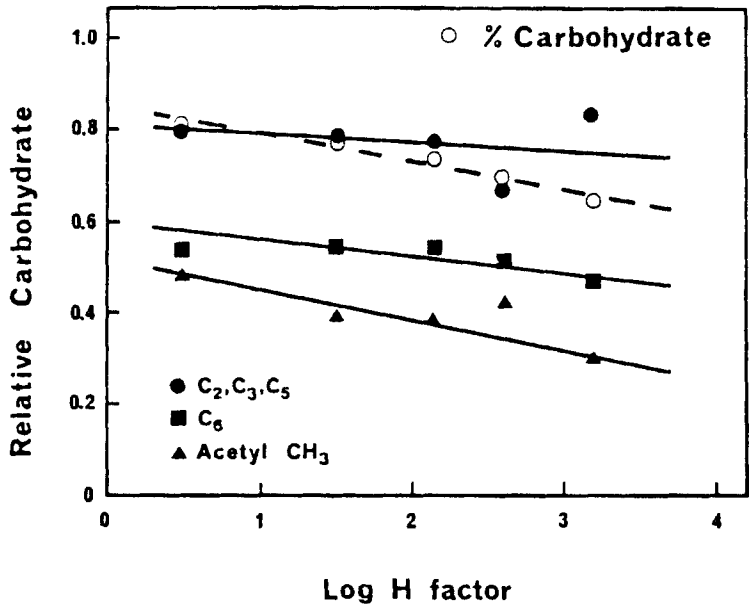


FIGURE 5. The comparison between the decrease in the relative intensity of the carbohydrate signals determined by NMR and the decrease in the relative carbohydrate content of the pulps (determined by difference from the Klason lignin values), as a function of H factor.

TABLE 2

The Slopes and Correlation Coefficients Obtained for the Linear Plots of Relative Intensity Versus Log H Factor.

		Slope×10[1]	Correlation Coefficient (%)
LIGNIN:			
	% Lignin	3.0	98
	C_3, C_4	3.2	97
	OCH_3	2.2	99
CARBOHYDRATE:			
	% Carbohydrate	0.60	97
	C_2, C_3, C_5	0.21	98
	C_6	0.46	96
	Acetyl CH_3	0.67	99

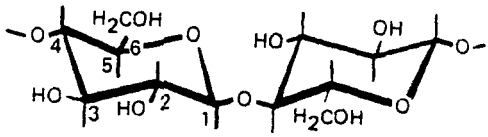
DISCUSSION

As shown in Figure 1, the intensities of the peaks corresponding to lignin, at 150 ppm and 56 ppm, decreased rapidly with the yield of the pulp as the degradation of the macromolecular network of lignin progressed. At the same time, the intensities of the peaks corresponding to carbohydrate macromolecules, at 25 ppm and from 65 ppm to 105 ppm, decreased at a much slower rate than was found for lignin and agree well with known kraft kinetics[1-26].

A fairly good correlation was found between the values of the dissolved lignin and carbohydrate contents determined chemically and those determined by the NMR technique. This is illustrated in Figure 3. It is possible to claim, therefore, that the NMR technique is a reliable one to use in following relative changes in wood and pulp composition, at lignin contents above the sensitivity of the NMR experiment.

Initial Dissolution

The data presented in Figures 4 and 5 illustrate how the relative peak intensities, determined by NMR, change in comparison to the relative Klason lignin content (% lignin line) and the relative carbohydrate content (% carbohydrate line). It is interesting to note that the plot corresponding to the methoxyl group (56 ppm) of lignin (1) is displaced to lower relative values from the % lignin line. Likewise, the plots corresponding to the C_6 methyl alcohol (56 ppm) of cellulose (2) and acetyl



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methyl (25 ppm) of hemicellulose are displaced from the % carbohydrate line. This suggests that these groups are associated with the rapid dissolution which occurs during the initial stages of pulping.

Recently, it has been shown that a large proportion of the acetyl groups of hemicellulose are cleaved within the first hour of pulping and that the residual acetyl groups undergo cleavage at a much slower rate[11,18]. This supports the trend observed for the acetyl group, as shown in Figure 5. Similarly, the alkaline peeling reaction may account for the initial rapid loss of the methyl alcohol groups of the carbohydrate[11,44].

Gierer[16,18,45,46] and others[11,15,47] have suggested that the reactions which occur during the initial stage of delignification, where up to 23% of the lignin originally present in wood is removed[11,24], involve the α- and β-aryl ether cleavage of phenolic lignin units. Perhaps this would give rise to the displacement observed for the methoxyl group of lignin, as shown in Figure 4.

In contrast, the data obtained for the C_3, C_4 resonances of lignin (150 ppm) and the cyclic carbons of the carbohydrates (80-105 ppm) are not significantly displaced from the % lignin and % carbohydrate lines. This suggests that the initial degradation reactions which occur at these sites proceed at about the same rate as that observed for the bulk delignification or bulk carbohydrate removal.

Bulk Delignification

The decrease in the intensity of the peak at 150 ppm agrees with the decrease in the Klason lignin content of the pulps, within experimental error as shown in Figure 4. Since this peak corresponds to the C_3 and C_4 aromatic carbons of lignin, the decrease in the intensity of this peak could be due to the loss of lignin units. Model compound studies have shown that lignin is degraded during pulping primarily as a result of the alkaline cleavage of the β-O-4 aryl ether linkages[46]. During bulk delignification, where a further 70% of the lignin originally in wood is removed[11,24], these cleavages involve non-phenolic lignin units and are important in determining the rate of bulk delignification[12,15,16,47,48]. In the present study, the close agreement of the slopes of these two lines suggests that the peak at 150 ppm can be used to give a good indication of the rate of bulk delignification.

In contrast, the intensity of the peak at 56 ppm, corresponding to the methoxyl carbons of lignin, does not decrease as

rapidly as that of the Klason lignin content of the pulps. In this case, the slopes of the lines differ by 30%, which is significantly larger than the experimental error of 10%. Since a large proportion of methoxyl groups, as well as phenolic lignin units, is removed during the initial stage of pulping[11,15,16,18,45], the slower decrease could be due to the fact that the rate of cleavage of the residual aromatic methoxyl groups is slower than the rate of bulk delignification. Another explanation could be the interference of the carbohydrate in this region of the NMR spectrum. Work is currently underway to elucidate this point.

Bulk Carbohydrate Removal

As shown in Figure 5, the peak corresponding to the acetyl methyl groups of the hemicelluloses, at 25 ppm, decreased at a rate which agreed with the decrease in the carbohydrate content of the pulps, within experimental error. During the initial stage of cooking, acetyl groups are lost rapidly, whereas later in the bulk stage, the removal of these groups occurs more slowly. Therefore, the results shown in Figure 5 suggest that for the pulps under study, the alkaline hydrolysis of residual acetyl groups corresponds to bulk carbohydrate removal.

The resonances corresponding to the cyclic carbons of cellulose, C_1 at 105 ppm, C_4 at 90 and 65 ppm, and C_2, C_3 and C_5 between 70 and 80 ppm, decreased very slightly with yield indi-

cating that little cellulose was lost in the yield range studied. In fact, the observed decrease may in part be due to contributions to these peaks by the hemicellulose resonances.

The peaks corresponding to C_6 at 65 ppm decreased at twice the rate of the cyclic carbons. This may correspond to cleavages which occur during residual peeling reactions, or during stopping reactions, involving both cellulose and hemicellulose reducing end groups. It may also be the result of a more significant contribution by the hemicellulose resonances to this peak, in comparison to that which may be occuring for the C_1-C_5 cyclic carbons.

CONCLUDING REMARKS

The results reported here by the use of solid state ^{13}C CP/MAS NMR of wood and pulp have shown that the degradation of lignin and carbohydrate can be studied in situ. Since the results obtained are in agreement with the general trends previously observed for kraft pulping[1-26], CP/MAS NMR may be a potentially powerful method of investigating pulping kinetics. At this stage however, it is at best a semiquantitative technique. One serious impediment to the quantitative determination of the individual components of wood and pulp is the degree of overlap of resonances in the carbohydrate region of the NMR spectra. The only resonances which are distinct correspond to the acetyl methyl of the hemicelluloses at 25 ppm, and the aromatic carbons of lignin at 150 ppm. Both hemicellulose and cellulose contrib-

ute to the peaks between 65 ppm and 105 ppm. In addition, the lignin methoxyl group resonance at 56 ppm may also overlap some weak C_6 resonances of the carbohydrate macromolecules.

Further studies involving isothermal pulping kinetics of different wood species and comparison between the kraft and sulphite processes using ^{13}C CP/MAS NMR are in progress. An attempt is also being made to quantify the contribution of hemicellulose and lignin to the carbohydrate region of the NMR spectrum of wood and pulp and the results will be published in due course.

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