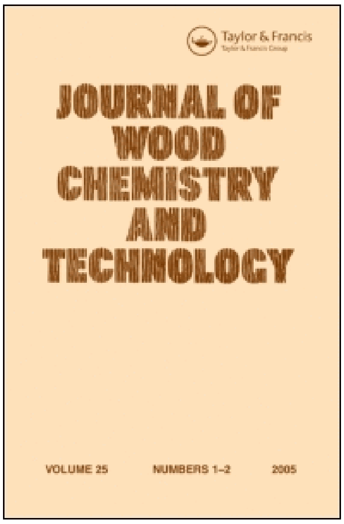

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CROSS POLARIZATION/MAGIC ANGLE SPINNING ^{13}C-NMR CHARACTERIZATION OF STEAM EXPLODED POPLAR WOOD

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ABSTRACT

High resolution solid state ^{13}C CP/MAS NMR has been used to study poplar wood samples before and after steam treatment. The principal structural components of wood have been characterized and the main effects of the rapid steam hydrolysis process (hydrolysis of the hemicelluloses, depolymerization of the lignin) were discussed. Evidence of molecular-level interactions between the principal components have been obtained from $T_{1\rho}^{H}$ relaxation times of protons belonging to the corresponding species.

INTRODUCTION

In the last decade, the combined use of high-power proton decoupling, magic angle spinning (MAS) and cross-polarization (CP) has opened the route to high resolution ^{13}C NMR in the solid state[1-5]. ^{13}C CP/MAS NMR which permits direct observation of carbon nuclei in the solid state gives information on the chemical and physical structure of polymers and coals which are difficult to obtain by other means.

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This technique has also been used for characterization of wood and its components. Many ^{13}C CP/MAS NMR studies of wood's major components have been reported recently[6-19]. The principal component of wood, cellulose, has been characterized with ^{13}C CP/MAS NMR by a number of groups[6-16], the morphology and crystal structure of different celluloses being discussed. The studies of another component of wood, lignin, have also been reported using this technique[17-20] ; they showed that lignin structure is dependent both on the isolation method and on the lignin origin. The wood itself has been analysed by ^{13}C CP/MAS NMR. This technique has been applied to a pine wood sample before and after steam explosion treatment in order to investigate the relative amounts of and interactions between the three major components. The ^{13}C NMR spectra of various preparations of lignin, holocellulose, hemicellulose and <u>alpha</u>-cellulose have been analysed and provide evidence for a lignin-carbohydrate complex[21,22]. Recently it was demonstrated that ^{13}C CP/MAS NMR is a valuable technique for the study of wood pulp[23] or kraft pulping kinetics[24]. The spectra of ash wood and spruce wood have been reported and discussed[17,25,26]. Hatcher et <u>al</u>.[25] have studied the coalification of woody tissue ; Taylor et <u>al</u>.[26] have shown a pronounced narrowing of resonances in the exploded spruce spectrum. This sharpening of resonance signals was interpreted as arising from an increase in the crystallinity of cellulose after the explosion treatment, according to evidence obtained from X-ray studies. ^{13}C CP/MAS NMR analysis and enzymatic hydrolysis were also used to characterize the products of pretreatment procedures designed to enhance the enzymatic conversion of pine wood biomass to sugar[27]. Teejaer et <u>al</u>.[28,29] have applied ^{13}C CP/MAS NMR spectroscopy to the study of spin-lattice relaxation times T_1 of protons in native and steam-exploded birch wood. They showed that the steam-explosion autohydrolysis of the wood resulted in destruction of the super network and differentiation between lignin and cellulose in the spectra.

In the following, the study of structural composition of poplar wood "Populus Tremula" and its components separated after steam explosion treatment are presented using ^{13}C CP/MAS NMR spectroscopy. During the reaction, the hemicelluloses are hydrolysed and the lignin is depolymerised. At the end of the process, the samples are explosively discharged and an extra mechanical defibration is obtained.

EXPERIMENTAL

Material

Freshly cut poplar wood chips "Populus tremula", supplied by the Centre Technique du Papier, Grenoble, France, were treated with superheated steam (40 bars, 249°C) for different times. At the end of the steaming the wood chips were explosively discharged.

Extractions

Exploded wood samples were fractionated according to Figure 1. The hemicelluloses were dissolved in distilled water at room temperature (2 x 500 ml when starting with 50 g equivalent dry weight of wood chips). The water extracts were concentrated to 200 ml and freeze-dried. During concentration an insoluble fraction appeared which was removed by centrifugation. This insoluble fraction was called lignin-carbohydrate complex (L.C.C.)

Water-extracted steam exploded material was continuously extracted in a Soxhlet by refluxing dioxan-water during 48 hours, in order to remove the depolymerized lignin which was solubilized (azeotropic composition : 82/18, dioxan/water respectively).

NMR Spectroscopy

^{13}C CP/MAS NMR experiments were performed at 50.328 MHz on a modified Bruker spectrometer interfaced with a Nicolet 1180 and an Oxford cryomagnet (4.7 T). Quadrature detection was employed and a single RF coil which is doubly tuned for both ^{13}C and ^{1}H. A common

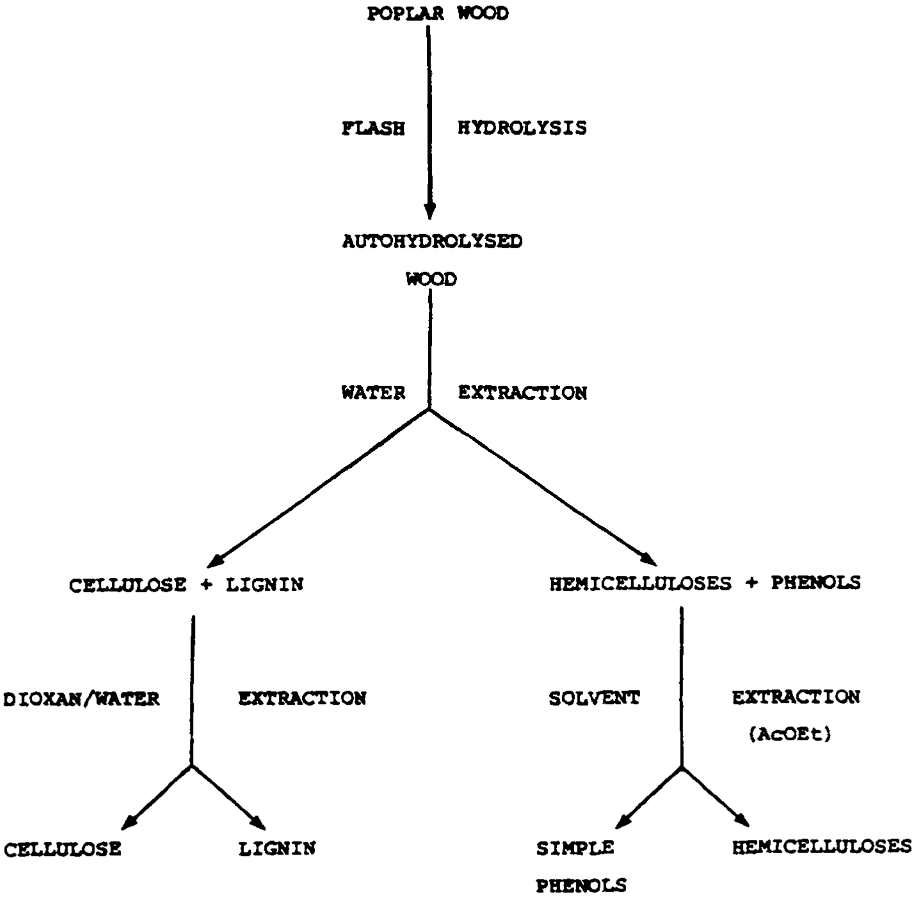

Figure 1. Fractionation scheme of autohydrolysed poplar wood.

^{13}C and ^{1}H RF field strength of 50 KHz was employed to fulfill the Hartmann-Hahn condition. Spinning rates using a boron nitride rotor were in most cases 2.5 KHz. The proton spin-lattice relaxation times in the rotating frame $T_{1\rho}^{H}$ were obtained from a plot of the magnitude of the carbon magnetization as a function of the carbon-proton contact time.

All spectra presented in Figures 2-3 were recorded with a contact time of 1 ms, 25 ms of data acquisition (1 K data points zerofilled to 8 K) and a pulse delay of 5 s.

RESULTS AND DISCUSSION

Untreated wood

The ^{13}C CP/MAS NMR spectrum of poplar wood is presented in Figure 2a. It is dominated by cellulose resonance signals. Chemical shifts for specific carbons in the cellulose, as indicated in Figure 2a, were attributed to resonances at approximately 65, 72-74, 83-89 and 105 ppm. In addition to cellulose signals, the spectrum of poplar wood has less intense but distinct peaks at 7, 21, 56, 120-145, 153 and 172 ppm. The acetyl groups from hemicellulose components dominate the peak at 21 ppm (methyls) and that at 172 ppm (carbonyls).

The presence of hemicelluloses is also confirmed by the upfield shoulder at about 103 ppm (C-1) and a background between 50 and 90 ppm (C-2,3,4,5,6)[21]. This is confirmed in Figure 3b where the ^{13}C CP/MAS spectrum of freeze-dried water soluble hemicellulose extract is shown.

As in the spectra of pine, ash and spruce wood reported earlier[17,20,21,23,24], distinct resonance signals are observed for the lignin component. The peak at 56 ppm most likely corresponds to Ar-OCH_3 methyl carbons[17]. The peaks at about 122 and 135 ppm correspond to unsubstituted and alkylated aromatic carbon resonances, respectively. The peak at 153 ppm is that of oxygen-substituted aromatic carbons. Phenolic and methoxyl substituted aromatic structures that are part of the lignin structure contribute to this peak.

Finally, the small signal at about 7 ppm may arise from the terminal CH_3 groups of the aliphatic chains.

Exploded poplar wood samples

The steam explosion treatment is one of the methods leading to separation of wood in its three major components[30]. This treatment involves brief contact of wood chips (generally 60 s) with superheated steam (30-40 bars, 230-250°C) in a reactor,

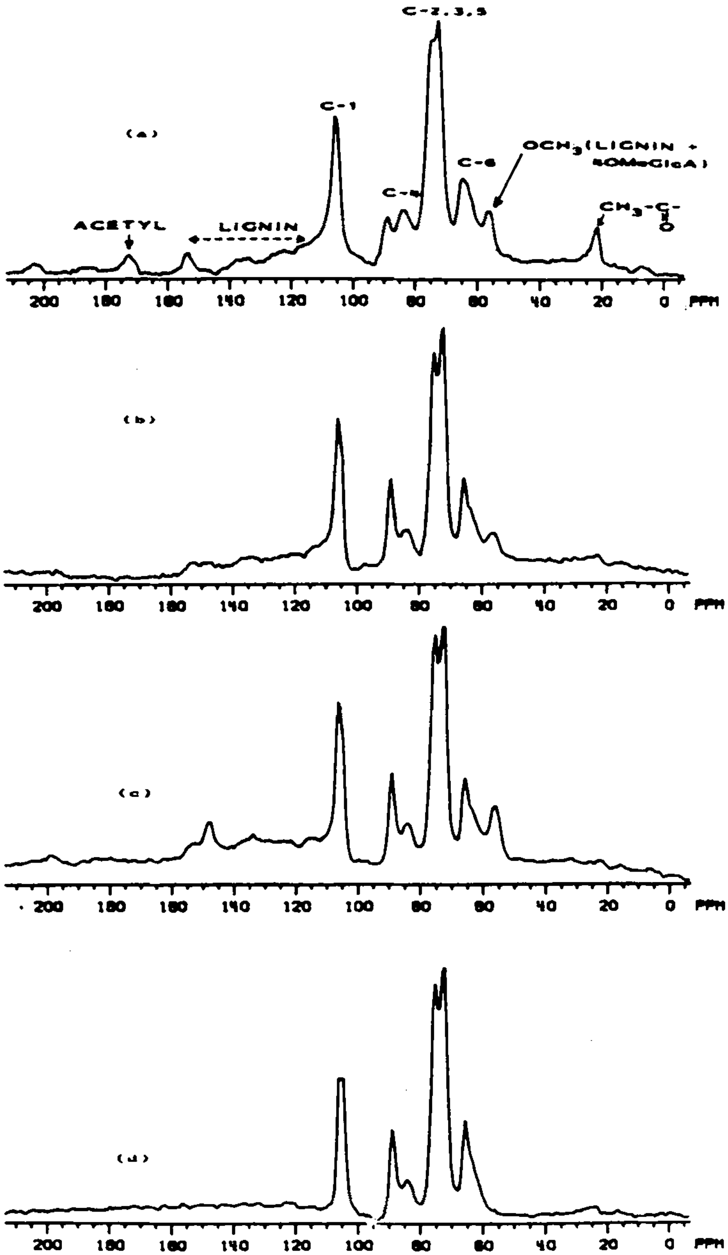

Figure 2. ^{13}C CP/MAS NMR spectra of poplar wood recorded for (a) coarsely divided untreated chips, (b) and (c) water extracted exploded samples pretreated at 40 bars during 90 and 165 s, respectively, (d) water extracted samples pretreated at 40 bars during 165 s with additional chlorite bleaching.

followed by explosion due to a rapid decompression. Such a treatment leads to physical and chemical modifications permitting greater accessibility of the different components to solvents and to chemical or enzymatic hydrolysis. A diagram of poplar wood composition and separation by selective dissolution after the steam hydrolysis process is shown in Figure 1.

The following samples were examined :
untreated wood ; water extracted exploded wood samples (treated for 90 s and 165 s at 40 bars) ; water soluble hemicelluloses after removal of phenolic compounds ; dioxan/ water soluble lignin ; lignin-carbohydrate fraction (L.C.C.) ; insoluble cellulosic material after chlorite bleaching.

The effect of steam explosion is easily observed on Figure 2; the disappearance of signals at 21 and 172 ppm as well as line sharpening show that after 90 s of treatment at 40 bars, most of the hemicelluloses are removed during water washings. This is confirmed by acid hydrolysis and conventional sugar determination[31]. After 165 s of treatment under the same conditions (40 bars), the ^{13}C CP/MAS spectrum (Figure 2c) shows a more pronounced signals at 56 and 143 ppm which could be explained by recondensation of degradation products (i.e. furfural or hydroxymethylfurfural) on the lignin.

If we compare the carbohydrate signals of spectra reported in Figure 2 we can notice that the steam treatment induces important intensity changes in C-4 signals which occur between 80-90 ppm, due to the removal of the hemicelluloses (C-4 of 4-OMe glucuronic residue) and to a small extent to the preferential hydrolysis of amorphous cellulose, whereas crystalline cellulose is more resistant.

Smaller changes in the region 60-65 ppm can also be explained by the removal of the hemicelluloses and disappearance of C-5 xylose signal.

The modification of the lignin is easily observed on spectra of Figure 2. First of all the lignin is partly removed as it can be seen on Figure 2a and 2b. After 165 s treatment time, there is an increase of methoxyl signals (56 ppm) and a signal around 146 ppm appeared which could be explained by recondensation reactions (Figure 2c). The removal of the lignin is clearly confirmed by comparing spectra of Figure 2c and 2d. An exploded sample (40 bars, 165 s) has been bleached according to Wise et al. procedure[32] and the disappearance of characteristic signals at 56 ppm and in the 110-160 ppm region confirmed that all the lignin has been oxidized.

In Figure 3 are shown solid state ^{13}C CP/MAS spectra of soluble fractions which were freeze-dried. The spectra are less resolved than the corresponding ones obtained by high resolution n.m.r. in solution, but we can nevertheless recognize some of the specific hemicellulose or lignin carbons. For example, Figure 3a shows the ^{13}C spectrum of extracted lignin with characteristic signals at 56 ppm (OMe carbon signals) and 149 ppm (methoxy-substituted C-3 carbon atoms) ; poorly resolved broad signals between 110 and 140 ppm could be also detected.

Figure 3b shows the ^{13}C spectrum of the water soluble hemicellulose fraction. We can easily recognize the acetyl carbon signals at 21 ppm (methyls) and 172 ppm (carbonyls). Moreover, characteristic anomeric carbons could be visualized with $C-1_{\alpha}$ at 93 ppm and $C-1_{\beta}$ at 98 ppm corresponding to the reducing xylose, and a broad signal at 100-105 ppm which corresponds to the anomeric carbons involved in a glycosidic linkage but in different environment, with or without acetyl group in the C-2 or C-3 position, with or without 4-OMe glucuronic acid residue linked in C-2 position.

Figure 3c shows the ^{13}C CP/MAS spectrum of a lignin-carbohydrate complex fraction. This LCC has not been characterized but we can recognize in the ^{13}C spectrum some specific signals corresponding either to lignin or hemicellulose carbon atoms.

Wood is a complicated blend of cellulose, hemicelluloses and lignin. In order to obtain more information about molecular level

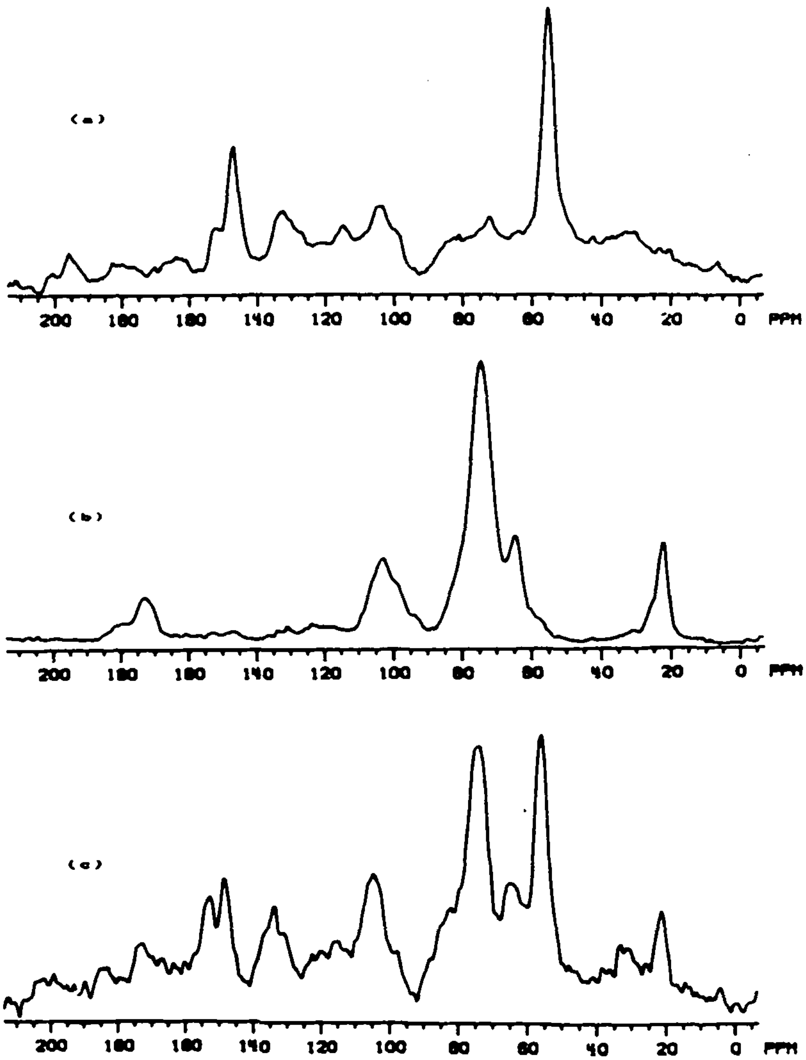

Figure 3. ^{13}C CP/MAS NMR spectra of (a) dioxan-water soluble lignin, (b) water soluble hemicelluloses and (c) lignin carbohydrate complex (L.C.C.).

TABLE I : $T_{1\rho}$ relaxation times[•] of protons of principal poplar wood components and of different samples composition

	Cellulose	Hemicellulose	Lignin
Untreated wood	8.1	6.8	8.0
Cellulose + Lignin (40 bars ; 90 s)	7.9	-	8.2
Cellulose + Lignin (40 bars ; 165 s)	9.5	-	8.0
Hemicellulose + Lignin (L.C.C.) (40 bars ; 90 s)	-	6.3	8.4
Hemicellulose (40 bars ; 90 s)	-	5.0	-
Lignin (40 bars ; 90 s)	-	-	9.5
Cellulose ; bleached (40 bars ; 165 s)	10.0	-	-

[•] All relaxation times in ms (experimental error is ± 10%).

interactions of these three major constituants, we measured the spin lattice relaxation times in rotating frame (T^{H}_{1}) of the protons attached to the corresponding polymers.

As shown by Schaefer and al.[33], high resolution solid-state ^{13}C NMR experiments can be employed to measure individual spin-lattice relaxation times in the rotating frame for protons attached to different kinds of carbons. This is possible because the final evolution of the carbon signal intensity, as a function of the contact time in a cross-polarization experiment, is governed

governed by the proton spin-lattice relaxation time in the rotating frame $T_{1\rho}^{H}$.

Through the spin-diffusion relaxation mechanism[34], proton spin-lattice relaxation times $T_{1\rho}^{H}$ are strongly dependent on short-range spatial proximity of the interacting dipole moments of protons and thus are very sensitive to the homogeneity of the blend. As can be seen from Table I, the $T_{1\rho}^{H}$ values of major wood components in different environments are altered with respect to these values observed for isolated components. This fact indicates either that mixing is intimate enough so that relaxation of one component is aided by interaction with other nearby components or that molecular motions are altered by blending. In both cases, one is drawn to the conclusion of a significant intimate mixing on the molecular level.

The molecular-level mixing seems to be substantially reduced for the cellulose component in a sample treated for 165 s, as indicated by the increase of $T_{1\rho}^{H}$ value. This value approaches that observed for pure cellulose. However, the effect of such a demixing phenomenon is not manifested in the $T_{1\rho}^{H}$ value of the lignin component. This fact can be explained by recondensation of lignin during treatment which in turn leads to a change of molecular mobility. The change of molecular mobility may lead to a decrease of the $T_{1\rho}^{H}$ value and to compensation of the effect of demixing phenomena. The increase of the $T_{1\rho}^{H}$ of cellulose could also be explained by removal of either non crystalline cellulose during pretreatment or hemicelluloses (acetyl containing components) leading finally to a more homogeneous polymer.

CONCLUSION

^{13}C CP/MAS NMR spectroscopy appears to be a powerful and promising technique for the control of steam exploded biomass materials, as it provides information on the yield of hemicellulose hydrolysis, on the amount of delignification, and can give valuable details on the polymer interactions and on possible recondensation occuring during the treatment.

The apparent increase in crystallinity already observed on exploded samples could be due to faster hydrolysis of amorphous cellulose and increased degree of order in its amorphous component compared to more resistant crystalline cellulose.

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