Organic Composition of a Pulp and Paper Mill Sludge Determined by FTIR, ^{13}C CP MAS NMR, and Chemical Extraction Techniques

Mark J. Jackson* and Martin A. Line

Department of Agricultural Science, University of Tasmania, G.P.O. Box 252-54, Hobart, 7001 Australia

The organic composition of a primary pulp and paper mill sludge (PMS) was determined by carbon-13 cross polarization nuclear magnetic resonance spectroscopy with magic angle spinning (^{13}C CP MAS NMR), Fourier-transformed infrared spectroscopy (FTIR), and chemical extraction methods. Spectroscopic studies showed that the PMS consisted of cellulose type I, which is present in ordinary pulp, with a minor uronic acid and lignin contribution. Minor to large structural changes occurred during extraction of lignin, holocellulose, and cellulose. The standard chemical techniques used to extract these components resulted in sample degradation as well as changes in functionality and structural organization. Chemical extraction techniques were therefore unsuitable to accurately quantitate the organic composition of PMS, and the spectroscopic techniques used provided a more reliable, semiquantitative assessment of actual organic composition.

Keywords: *Holocellulose; cellulose; hemicellulose; Klason lignin*

INTRODUCTION

PMSs (pulp and paper mill sludges) produced by the paper manufacturing process are currently the subject of many recycling studies, particularly by composting. Composted PMS may then be used in horticulture or agriculture, thereby eliminating the need for landfilling. PMSs contain chemically modified wood fibers in association with a number of chemical contaminants, the latter depending on the nature of the wood material entering the mill, the chemical treatment processes used to manufacture paper, and the type of waste-handling practices in operation within the mill (Scott and Smith, 1995). Thus the chemical composition of a PMS produced by one mill is often significantly different from another (McGovern *et al.*, 1982).

A detailed knowledge of the chemical composition of a PMS is required to follow the sequential steps in its breakdown during composting. Chemical extraction procedures have been used to selectively isolate organic components, but result in considerable modification of covalent bonding, which changes the chemical nature of the sample (Worobey and Barrie Webster, 1981), leading to uncertainty of conclusions drawn. To characterize the organic composition of PMS, a direct nondestructive analysis of an intact sample is preferable. A technique that has demonstrated potential for reliable structural characterization of soil organic matter, wood, composts, and herbages is ^{13}C CP MAS NMR (Hatcher *et al.*, 1981; Kolodziejski *et al.*, 1982; Piotrowski *et al.*, 1984; McBride, 1991). Another nondestructive method, FTIR, is capable of characterizing principal chemical groups in organic substances. When ^{13}C CP MAS NMR and FTIR are used in a complementary manner, detailed structural information can be obtained (Gerasimowicz and Byler, 1985).

The aim of this study was to determine the structural composition of PMS produced by Australian Newsprint Mills (ANM) with ^{13}C CP MAS NMR and FTIR spectroscopy. Structural modifications of lignin, holocellulose, and cellulose present in PMS imposed by chemical extraction methods were also identified by ^{13}C CP MAS NMR and FTIR.

MATERIALS AND METHODS

Origin of PMS. The PMS analyzed in this study was produced by a totally chlorine free bleached newsprint mill consisting of a thermomechanical pulping mill (TMP), a chemimechanical pulping mill (CMP), a kraft slushing plant, a bleaching tower (hydrogen peroxide and caustic soda based), and two newsprint/speciality grade paper machines. *Pinus radiata* (softwood) comprises approximately 66% of total wood used in the mill, whereas the remainder consists of *Eucalyptus* spp. (hardwood) (*E. regnans, E. delegatensis, and E. obliqua*) (30% in total) and kraft (4%). *Pinus radiata* chips are pulped in the TMP mill, whereas the *Eucalyptus* spp. chips are pulped in the CMP mill with cold caustic soda. Effluents produced by the TMP mill, CMP mill, bleaching tower, and waste waters generated by the paper machines are directed to the primary clarifiers. Following primary clarification, the sludge is dewatered to between 25 and 30% solids (not subject to biological treatment), resulting in the production of a fibrous cake (PMS) with a low ash (2.1%) and a high carbon content (48.0%) (Jackson and Line, 1997). The pulp yields obtained from the CMP and TMP mills vary, usually being approximately 85 and 95%, respectively.

Sample Preparation for Spectroscopic Analysis and Chemical Extraction. A 10 kg sample of PMS was collected from the sludge dewatering plant at ANM when the mill was operating under normal conditions. After collection, the PMS was oven dried at 70 °C for 12 h. Samples of PMS were prepared for FTIR, for ^{13}C CP MAS NMR, and for chemical extraction by grinding to <2 mm particle size. Sample homogeneity was ensured by mixing the ground PMS. FTIR samples were prepared by combining *ca.* 100 mg of KBr with *ca.* 2 mg of dry PMS, which was compressed under vacuum to disks. Extracted lignin, holocellulose, and cellulose from PMS were dried at 70 °C for 1 h prior to spectroscopic analysis.

Chemical Extraction of PMS. Lignin, holocellulose, cellulose, and hemicellulose were extracted from PMS (extractives-free) according to established procedures (Browning, 1967; 1975). Briefly, lignin was isolated with the Klason method by selectively removing cellulose and hemicelluloses in 72% sulfuric acid, followed by boiling in 3% sulfuric acid. Percentage lignin was also determined indirectly by the Kappa number procedure (TAPPI Standard Method, 1993). Holocellulose was isolated by removal of lignin with sodium chlorite in dilute acetic acid. Cellulose was further isolated from the holocellulose fraction by selectively removing hemicelluloses with 24% potassium hydroxide. Hemicellulose was precipitated from the filtrate obtained during cellulose extraction of holocellulose by addition of acetic acid. ^{13}C CP MAS NMR and

S0021-8561(96)00946-6 CCC: $14.00

FTIR were performed on Klason lignin, holocellulose, and cellulose as detailed below. Each analysis was replicated three times, and yield data were expressed as a mean of the three analyses.

Spectroscopic Analysis of Samples. High-resolution solid state ^{13}C CP MAS NMR spectra were acquired with a Bruker MSL 400 spectrometer at a ^{1}H frequency of 90.1 MHz, ^{13}C frequency of 22.6 MHz, spinning rate of 7 kHz, contact time of 1 ms, spinning angle of 54.7° to the magnetic field, cycle time of 1 s, acquisition time of 1024 ms, sweep width of 531.11 ppm, line broadening of 40 Hz, and a scan number of 2−3000. FTIR spectra were obtained at a wavenumber range of 4800−400 cm^{-1} on a Bruker IFS 66 FTIR spectrophotometer. A linear baseline correction function was applied to spectra using 4780, 3780, 2300, 1890, and 843 cm^{-1} as zero-baseline points. The FTIR absorbance spectra presented here possess a wavenumber range of 2000−750 cm^{-1}.

^{13}C CP MAS NMR spectra were rescaled at 74 ppm in order to obtain difference spectra. The magnitude of the 74 ppm signal was unaffected by the chemical extraction procedures, and all signals were rescaled accordingly following peak standardization. After baseline correction of FTIR spectra, all spectra were rescaled at 3300 cm^{-1} (OH region) to obtain difference spectra, since absorbances at this frequency were not affected by the chemical extraction procedures, and all peaks were found to rescale accordingly.

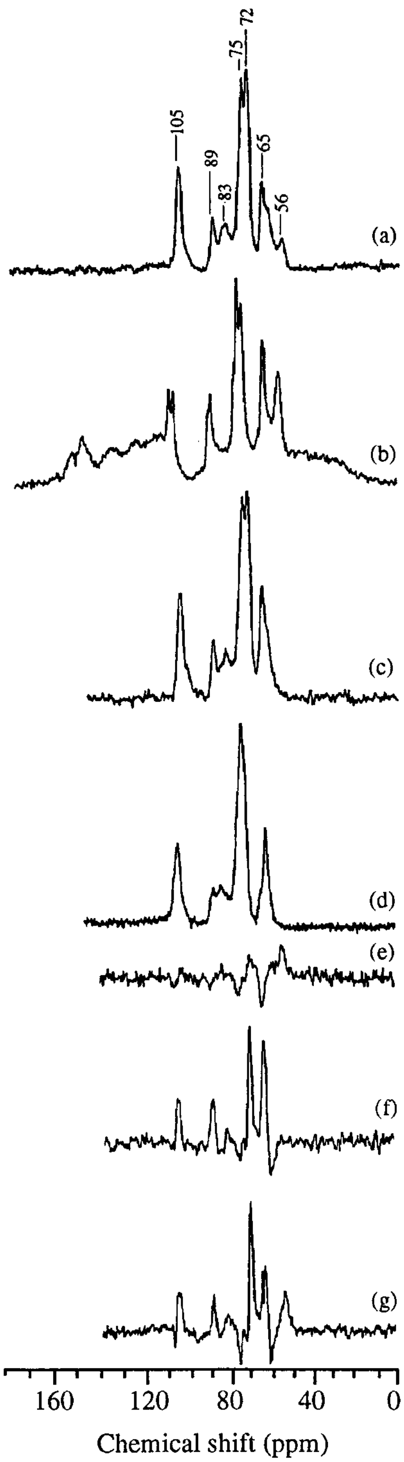

Figure 1. ^{13}C CP MAS NMR spectra of (a) PMS; (b) extracted Klason lignin; (c) extracted holocellulose; (d) extracted cellulose; (e) difference spectrum a − c; (f) difference spectrum c − d; (g) difference spectrum a − d.

RESULTS AND DISCUSSION

A ^{13}C CP MAS NMR spectrum of the PMS is shown in Figure 1a. The spectrum strongly resembles published spectra of chemically isolated cellulose polymorph type I by Dudley *et al.* (1983) and contains little lignin or hemicellulose-like material. Since no aromatic signals were present in the spectrum (143−160 ppm), the PMS could be assumed to contain little or no lignin. The only signal that may indicate the presence of lignin was at 56 ppm, attributable to methoxyl carbons. Signals characteristic of hemicellulose however were difficult to resolve, since many of the spectral features tend to be similar to cellulose (Haw *et al.*, 1984). The lack of hemicellulose in PMS was confirmed by the absence of a shoulder on the higher shielding side of the 105 ppm peak, normally characteristic of hemicellulose carbons of xylose, mannose, and arabinose that are structurally analogous to cellulose carbon C-1 (Haw *et al.*, 1984). This contention was further supported by an absence of signals at 22 and 174 ppm, characteristic of carbonyl and methyl carbons of acetate groups present in 4-*O*-methyl-α-D-glucuronic acids of arabinoglucuronoxylan and glucuronoxylan in hemicellulose (Browning, 1975; Kolodziejski *et al.*, 1982). However, signals representing carbonyl and methyl carbons of acetyl groups are poor indicators of hemicellulose content since they are difficult to resolve (Kolodziejski *et al.*, 1982) and are susceptible to hydrolysis during the early stages of pulping (Haw *et al.*, 1984). The remainder of the spectrum was dominated by signals characteristic of the C-1 to C-6 carbon atoms of cellulose. The large doublet between 72 and 75 ppm was due to the C-2, C-3, and C-5 carbons of cellulose, and the peak at 65 ppm was due to the cellulose carbon C-6, whereas on the higher shielding region of the 65 ppm shoulder (61 ppm) lie methoxyl signals of 4-*O*-methyl-α-D-glucuronic acid groups of hemicellulose and possibly lignin (Haw *et al.*, 1984). The signal at 89 ppm and the broader high-shielding shoulder at 83 ppm was due to the cellulose carbon C-4, while the sharp signal at 105 ppm was due to cellulose carbon C-1. The strong resemblance between the ^{13}C CP MAS NMR spectrum obtained in this study and that obtained from bisulfite and kraft pulp (Haw *et al.*, 1984) suggested that the PMS consisted mainly of cellulose type I present in ordinary pulp, possibly in combination with a small quantity of lignin and uronic acid groups present in hemicellulose.

The FTIR spectrum of PMS (Figure 2a) complemented the structural information obtained in the ^{13}C CP MAS NMR spectrum (Figure 1a). The FTIR spectrum was dominated with carbonyl ($C{=}O$) (1630−1660, 1720 cm^{-1}), carboxylic (COOH) (1350 cm^{-1}), aliphatic (C−H) (1420, 1470 cm^{-1}), alcoholic (C−OH), and hydroxyl (O−H) (1050, 1110, 1185, 1250 cm^{-1}) functional group stretches, which are characteristic of polysaccharide

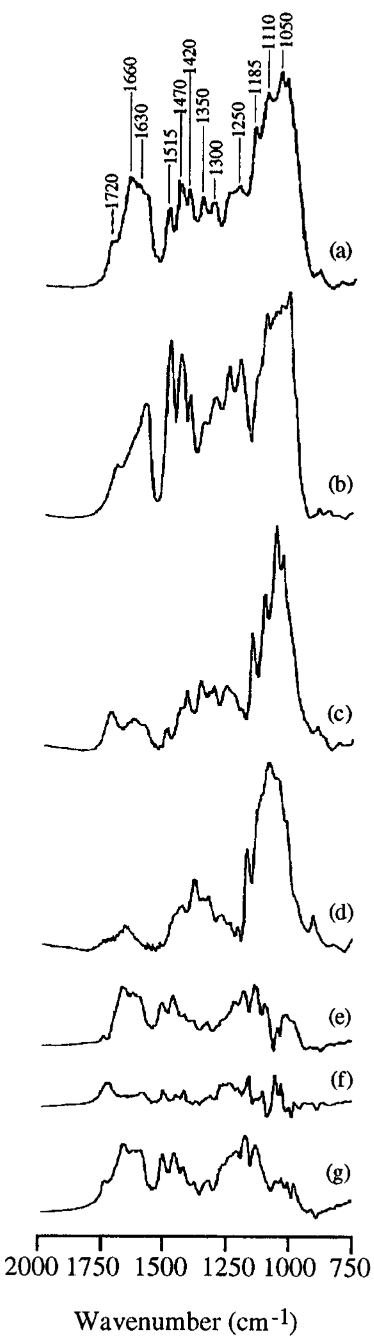

Figure 2. FTIR spectra of (a) PMS; (b) extracted Klason lignin; (c) extracted holocellulose; (d) extracted cellulose; (e) difference spectrum a − c; (f) difference spectrum c − d; (g) difference spectrum a − d.

materials (Stevenson, 1982). Aromatic ring stretches were detected at 1515 and 1300 cm^{-1}, although small in intensity relative to those of the polysaccharide functional group stretches. The peak at 1515 cm^{-1} may have indicated the presence of lignin (Johnston, 1964). A weak absorption peak characteristic of xylose, 4-*O*-methyl-α-D-glucuronic acid, or arabinose present in hemicellulose was located at 1720 cm^{-1} (Marchessault, 1961). Given the absence of xylose, mannose, and arabinose polymer signals (as in hemicellulose) as determined previously, evidence suggested that the hemicellulose fraction present in the PMS consisted primarily of uronic acid groups. Selective hydrolysis and dissolution of hemicellulosic polysaccharides into mono- and oligosaccharide units during the early stages of cooking/alkaline treatment in the TMP and CMP mill may explain the absence of the latter in the PMS. The PMS analyzed therefore consisted primarily of polysaccharide material, specifically cellulose possibly in combination with a small quantity of lignin and uronic acid groups present in hemicellulose.

The high cellulose content in the PMS may be accounted for in part by mechanical and chemical degradation of wood polysaccharides during TMP and CMP pulping, paper manufacture, and bleaching. The low lignin content in the PMS may be due to the fact that the pulping and bleaching processes used tend to be lignin-preserving, and of the lignin removed from the chips, little is precipitated onto the flocs during primary clarification. Mechanical defibration of softwood chips during TMP pulping is the main source of fiber loss at ANM, as such mechanical processes contribute to polysaccharide degradation through the production of divided fiber fragments (fines). CMP pulping with cold caustic soda also contributes to polysaccharide degradation, since such processes usually exhibit a low degree of lignin selectivity and cause considerable glycosidic bond hydrolysis and polysaccharide degradation relative to sulfate (kraft) delignification processes (Sjöström, 1993). Another source of fiber loss from the pulp is through the action of hydroxyl radicals which are formed after decomposition of peroxide during bleaching. Hydroxyl radicals contribute to polysaccharide degradation since they are only moderately selective for lignin in comparison to other bleaching chemicals (Sjöström, 1993). The lack of lignin removal and low level of lignin selectivity exhibited by the pulping and bleaching processes, together with the mechanical degradation of polysaccharides during TMP pulping and paper manufacture may be responsible for the production of a PMS with a high cellulose and low lignin content at ANM.

Significant structural changes occurred during chemical extraction of lignin with sulfuric acid according to ^{13}C CP MAS NMR and FTIR spectra (Figure 1b and Figure 2b). The Klason method for lignin extraction did not isolate lignin, but resulted in a dimensionally disordered (amorphous) cellulosic product with an increased methoxyl content (56 ppm, Figure 1b) as revealed by the ^{13}C CP MAS NMR spectrum. Neither spectra displayed any similarities with previously published spectra of lignin (Bartuska *et al.*, 1980; Maciel *et al.*, 1981). The amorphous product was in fact the cellulose type II polymorph and not lignin, identified by the C-1 doublet at 108 ppm, which is usually obtained by mercerization of cellulose from solution (Dudley *et al.*, 1983). All functional groups were affected by lignin extraction according to the FTIR spectrum. Aromatic (1515 cm^{-1}), aliphatic (1420 and 1470 cm^{-1}), and alcoholic groups (1250−1350 cm^{-1}) all increased in intensity following extraction, whereas the carbonyl stretch at 1660 cm^{-1} was completely removed. The Klason lignin yield of 27.42% was clearly incorrect, whereas the lignin yield of 2.87% by the Kappa number procedure may better represent the actual lignin content in PMS (Table 1). Neutralizing agents, such as large quantities of ash, may reduce the efficiency of cellulose and hemicellulose removal from Klason lignin during extraction with sulfuric acid and may result in an overestimation of actual lignin content. Since the PMS possessed a low ash content (2.1%) and a low pH (4.38) (Jackson and Line, 1997), the conditions for Klason lignin extraction would have been optimal. Haw *et al.* (1984) similarly reported that the lignin content determined by quantitative ^{13}C CP MAS NMR spectroscopy

Table 1. Yields of Lignin, Holocellulose, Cellulose, and Hemicellulose Isolated from PMS by the Standard Chemical Extraction Techniques

component	%, w/w[a]
Klason lignin[b]	27.42
Kappa no. lignin[c]	2.87
holocellulose[b]	72.65
cellulose[b]	57.08
hemicellulose[b]	11.23

[a] The data reported are a mean of three replicate analyses on a dry weight basis. [b] Browning (1967). [c] TAPPI Standard Method (1993).

was in good agreement with the lignin content of pulps as determined by the Kappa number method. The findings reported here on PMS are in agreement with Lai and Sarkanen (1971), who reported that the Klason lignin method was unsuitable for the estimation of lignin content in pulps that had been treated with agents such as chlorine, hypochlorites, chlorites, and chlorine dioxide. However at ANM the pulp is not delignified or bleached with chlorine-based chemicals, although the imported kraft (comprising 4% of total wood used), which is utilized as a strengthening agent in the pulp, is. Thus the Klason lignin method is also unsuitable for estimation of lignin in pulps that have been partially treated with chlorine-based chemicals, or caustic soda and hydrogen peroxide, which are used at ANM for the purpose of delignification and bleaching, respectively.

Fewer structural modifications occurred to holocellulose and cellulose, relative to lignin during extraction (Figure 1c,d and Figure 2c,d), and ^{13}C CP MAS NMR spectra were similar to those previously published (Atalla *et al.*, 1980; Kolodziejski *et al.*, 1982). Extraction of holocellulose from PMS with sodium chlorite (yield 72.65%) resulted in minor changes in the ^{13}C CP MAS NMR spectrum, including the removal of the methoxyl signal at 56 ppm, attributable to lignin, and a slight increase in signal intensity at 65 ppm, attributable to cellulose carbon C-6 (Figure 1c). The FTIR spectrum of holocellulose revealed a substantial loss of carbonyl signal intensity (1630−1660, 1720 cm^{-1}) relative to unextracted PMS. Evidence suggested that some degree of cellulose (1630−1660 cm^{-1}) and possibly uronic acid (1720 cm^{-1}) removal occurred during extraction of holocellulose from PMS with sodium chlorite, since carbonyl peaks were present in the difference spectrum (Figure 2e) obtained between PMS (Figure 2a) and extracted holocellulose (Figure 2c).

Loss of some C-2, C-3, and C-5 atoms of cellulose (72 and 75 ppm; Figure 1d), methoxyl carbons of uronic acids (61 ppm, Figure 1d; 1720 cm^{-1}, Figure 2d), and carbonyl groups (1630−1720 cm^{-1}; Figure 2d) occurred during extraction of cellulose (yield 57.08%) from holocellulose (Table 1). Loss of the previous signals therefore suggested that the uronic acid groups of hemicellulose, together with some cellulose constituents, were removed following extraction of cellulose from holocellulose. The lack of lignin in PMS was further confirmed by the absence of a lignin-like spectrum (FTIR and ^{13}C CP MAS NMR) when the difference spectrum (Figures 1e and 2e) between PMS (Figure 1a or 2a) and holocellulose (Figure 1c or 2c) was obtained.

The spectra of hemicellulose (Figures 1f and 2f) in PMS were obtained indirectly by subtracting the cellulose spectrum (Figure 1d or 2d) from the holocellulose spectrum (Figure 1c or 2c), and the ^{13}C CP MAS NMR spectrum exhibited no similarities with previously published spectra of hemicelluloses (Kolodziejski *et al.*, 1982). All of the signals present in the ^{13}C CP MAS NMR spectrum of hemicellulose could be assigned to cellulose, whereas few peaks existed in the FTIR spectrum (Figure 2f), indicating little hemicellulosic material was present in PMS. The spectroscopic evidence obtained however was contradictory to the hemicellulose content as determined by chemical extraction (11.23%; Table 1). The shoulder on the high-shielding side of the signal at 65 ppm, which was previously assigned to uronic acid groups of hemicellulose, however was not present in the ^{13}C CP MAS NMR spectrum of hemicellulose. This result supported the previous finding that the uronic acid content in PMS was indeed very small. The overestimation of hemicellulose content in the PMS was due to the occurrence of cellulose degradation products in the filtrate as a result of holocellulose treatment with 24% potassium hydroxide. The hemicellulose chemical extraction procedure therefore cannot be used to accurately quantitate the hemicellulose content in PMS, due to excessive cellulose degradation caused by a lack of selectivity of potassium hydroxide for hemicelluloses. Such alkali extractions have further disadvantages, including almost complete deacetylation of hemicelluloses and the tendency to extract xylans more efficiently than glucomannans (Sjöström, 1993).

The difference spectra in Figure 1g and Figure 2g were obtained by subtraction of the PMS spectrum (Figure 1a or 2a) from that of cellulose (Figure 1d or 2d). These spectra should represent the noncellulose fraction in PMS. Since the signals that exist in the ^{13}C CP MAS NMR spectrum can be assigned primarily to cellulose degradation products (72, 83, 89, and 105 ppm), except a small contribution from lignin (56 ppm) and uronic acids (61 ppm), evidence suggested that the PMS consisted almost entirely of cellulose type I.

In summary, the lack of lignin removal and low level of lignin selectivity exhibited by the pulping and bleaching processes, together with the mechanical degradation of wood polysaccharides during TMP pulping and paper processing, were responsible for the production of a PMS with a high cellulose and low lignin content. The standard chemical extraction methods used could not quantitatively isolate lignin in its intact form in the PMS. Extraction of holocellulose, cellulose, and hemicellulose resulted in sample degradation and incorrect yield determinations. Considerable modification to functionality and structural organization occurred during the chemical extractions, and therefore these methods cannot be used to accurately quantitate the rate of lignin, holocellulose, cellulose, or hemicellulose decomposition during PMS composting. Spectroscopic examination of the PMS with ^{13}C CP MAS NMR and FTIR was found to provide a more reliable, semiquantitative assessment of actual organic composition.

ABBREVIATIONS USED

PMS, pulp and paper mill sludge; FTIR, Fourier transformed infrared spectrsocopy; ^{13}C CP MAS NMR, carbon-13 cross polarization magic angle spinning nuclear magnetic resonance spectroscopy; ANM, Australian Newsprint Mills; TMP, thermomechanical pulping mill; CMP, chemimechanical pulping mill.

ACKNOWLEDGMENT

We thank Graham Rowbottom, Central Science Laboratory, University of Tasmania, and Tim Bastow, CSIRO

Division of Materials Science and Technology, Victoria, for FTIR and ^{13}C CP MAS NMR analyses.

LITERATURE CITED

Atalla, R. H.; Gast, J. C.; Sindorf, D. W.; Bartuska, V. J.; Maciel, G. E. High resolution, magic angle sample spinning ^{13}C NMR of solid cellulose I. *J. Am. Chem. Soc.* **1980**, *102*, 3251−3252.

Bartuska, V. J.; Maciel, G. E.; Bolker, H. I.; Fleming, B. I. Structural studies of lignin isolation procedures by ^{13}C NMR. *Holzforschung* **1980**, *34*, 214−217.

Browning, B. L. *Methods of Wood Chemistry*; Wiley Interscience: New York, 1967.

Browning, B. L. *The Chemistry of Wood*; Krieger Publishing: New York, 1975.

Dudley, R. L.; Fyfe, C. A.; Stephenson, P. J.; Deslandes, Y.; Hamer, G. K.; Marchessault, R. H. High-resolution ^{13}C CP/MAS NMR spectra of solid cellulose oligomers and the structure of cellulose II. *J. Am. Chem. Soc.* **1983**, *105*, 2469−2472.

Gerasimowicz, W. V.; Byler, D. M. Carbon-13 CPMAS NMR and FTIR spectroscopic studies of humic acids. *Soil Sci.* **1985**, *139*, 270−278.

Hatcher, P. G.; Schnitzer, M.; Dennis, L. W.; Maciel, G. E. Aromaticity of humic substances in soils. *Soil Sci. Soc. Am. J.* **1981**, *45*, 1089−1094.

Haw, J. F.; Maciel, G. E.; Schroeder, H. A. Carbon-13 nuclear magnetic resonance spectrometric study of wood and wood pulping with cross polarization and magic-angle spinning. *Anal. Chem.* **1984**, *56*, 1323−1329.

Jackson, M. J.; Line, M. A. Composting pulp and paper mill sludge—effect of temperature and nutrient addition method. *Compost Sci.* **1997**, *5*, 74−81.

Johnston, H. H. The relationship of brown humus to lignin. *Plant Soil* **1964**, *21*, 191−200.

Kolodziejski, W.; Frye, J. S; Maciel, G. E. Carbon-13 nuclear magnetic resonance spectrometry with cross polarization and magic-angle spinning for analysis of lodgepole pine wood. *Anal. Chem.* **1982**, *54*, 1419−1424.

Lai, Y. Z.; Sarkanen, K. V. Isolation and structural studies. In *Lignins, Occurrence, Formation, Structure and Reactions;* Sarkanen, K. V., Ludwig, C. H., Eds.; Wiley Interscience: New York, 1971; pp 165−240.

McBride, B. W. ^{13}C CP-MAS NMR spectroscopy of cellulose and forages. *N. Z. J. Agric. Res.* **1991**, 34, 257−262.

McGovern, J. N.; Berbee, J. G.; Bockheim, J. G.; Baker, A. G. Characteristics of combined effluent treatment sludges from several types of pulp and paper mills. In *Proceedings of the TAPPI Environmental Conference*; TAPPI Press: Atlanta, GA, 1982; pp 101−105.

Maciel, G. E.; O'Donnell, D. J.; Ackerman, J. J. H.; Hawkins, B. H; Bartuska, V. J. A ^{13}C NMR study of four lignins in the solid and solution states. *Makromol. Chem.* **1981**, *182*, 2297−2304.

Marchessault, R. H. Application of infra-red spectroscopy to cellulose and wood polysaccharides. In *Proceedings of the Wood Chemistry Symposium*; Butterworth: Montreal, Canada, 1961; pp 107−129.

Piotrowski, E. G.; Valentine, K. M.; Pfeffer, P. E. Solid state, ^{13}C, cross-polarization, "magic-angle" spinning, NMR spectroscopy studies of sewage sludge. *Soil Sci.* **1984**, *137*, 194−203.

Scott, G. M.; Smith, A. Sludge characteristics and disposal alternatives for recycled fibre plants. In *Proceedings of the TAPPI Recycling Symposium*; TAPPI Press: Atlanta, GA, 1995; pp 239−249.

Sjöström, E. *Wood Chemistry: Fundamentals and Applications*; Academic Press: San Diego, 1993; Chapter 7.

Stevenson, F. J. *Humus Chemistry: Genesis, Composition, Reactions*; Wiley: New York, 1982.

TAPPI Standard Method. Kappa Number of Pulp. 1993, No. T236.

Worobey, B. L; Barrie Webster, G. R. Indigenous ^{13}C-NMR structural features of soil humic substances. *Nature* **1981**, *292*, 526−529.

Received for review December 3, 1996. Revised manuscript received March 19, 1997. Accepted March 20, 1997.⊗ We thank ANM for the provision of financial assistance.

JF960946L

⊗ Abstract published in *Advance ACS Abstracts,* May 15, 1997.