Structure and Formation of Cellulosic Chars

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Synopsis

The formation and structure of chars produced on heating of cellulose, lignin, and wood have been investigated by FTIR and CP/MAS ^{13}C-NMR, and the results have been discussed in conjunction with parallel permanganate oxidation studies reported before. These data show that when cellulose is heated for 5 min within the temperature range of 325–350°C, the IR bands associated with hydroxyl and glycosidic groups in cellulose disappear, and new bands signal the formation of unsaturation and carbonyl groups by dehydration and rearrangement. The NMR data also show the disappearance of the glycosyl carbons at 60–110 ppm and the appearance of methyl and other paraffinic carbons at 0–60 ppm, aromatic carbons at 110–170 ppm, carboxyl carbons at 170–190 ppm, and carbonyl carbons at 190–220 ppm. On heating at 400°C the IR and NMR signals for the glycosyl groups completely disappear, the signals for carbonyl and carboxyl groups diminish, and those for the aromatic and paraffinic groups expand. At this stage the char contains about 69% aromatic and 27% paraffinic carbons. At the temperature range of 400–500°C the paraffinic carbon content is reduced to 12%, and a highly aromatic (88%) char is produced. This is consistent with the permanganate oxidation studies which show the production of polycyclic aromatic structures resulting from extensive condensation and crosslinking at these temperatures. The chars produced from wood and lignin at 400°C had about the same aromatic carbon content as the corresponding cellulose char; however, the char yields were higher due to the presence of the methoxy phenyl groups that survive the heating process, as indicated by strong NMR signals at 55 and 148 ppm.

INTRODUCTION

Pyrolysis of cellulose and wood produces a mixture of gaseous and tarry materials and a carbonaceous residue known as char. The yield and composition of these products depend on the conditions of pyrolysis or more precisely the type of reactions which take place under these conditions.[1,2] The gas phase reactions and products have been extensively investigated, but very little is known about the chemical structure of the chars and the reactions involved in their development. In view of the significant roles of these chars in combustion and gasification of biomass, it has been desirable to investigate their properties and chemical composition. These studies have shown that nascent or freshly prepared char is highly reactive as measured by the rate of oxygen chemisorption.[3] The rapid rate of oxygen chemisorption at relatively low temperatures is in turn responsible for the pyrophoric properties of the fresh char.[4] Further studies on the kinetics of the char gasification and its catalysis[5] indicate that the structure and functionality of the cellulosic char should have a significant effect on its chemical reactivity.[6]

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Journal of Applied Polymer Science, Vol. 28, 3513–3525 (1983)
 CCC 0021-8995/83/113513-13$02.30

In a previous article in this series we described the development of aromaticity in char as studied by permanganate oxidation, which gives polycarboxyl benzene derivatives formed from the aromatic groups.[7] Analysis of these products showed the presence of aromatic structures and the extent of their crosslinking or condensation, which is directly related to the carboxylic substituents of the products. However, this method cannot provide quantitative data because of the extensive oxidation of the aromatic as well as the aliphatic groups.

Recently, solid state ^{13}C-NMR with cross polarization (CP) for enhancement of the signal/noise ratio and magic angle spinning (MAS) to remove chemical shift anisotropy has been applied to investigations of structure and functionality of fossil fuels.[8–12] This technique allows distinct resolution of NMR spectra of solid samples. It has been used for morphological investigation of cellulose samples[13–15] and is suitable for investigation of the structure and functionalities of char, particularly when corroborating chemical data are available from permanganate oxidation studies. An early attempt in using this method to resolve the structure of char was made by Earl,[16] who compared chars prepared at different temperatures from two kinds of wood.

In our study cellulose chars obtained from isothermal pyrolysis within the temperature range of 325–500°C were analyzed by CP/MAS ^{13}C-NMR in order to obtain more detailed chemical information and quantitative data on the structure of char and the related pyrolytic reactions in this range. The NMR analysis was further applied to chars prepared from wood and lignin pyrolyzed at 400°C to examine the effect of preexisting aromatic nuclei on char formation.

EXPERIMENTAL

Acid washed cellulose powder (Whatman CF-11), ground Douglas-fir heartwood and kraft lignin were used as substrates. Elemental compositions of these samples are shown in Table I. The pyrolysis was carried out in a preheated furnace for 5 min at several temperatures within the range of 325–500°C, under

TABLE I
Yields and Elemental Analysis of Substrates and Their Chars

Material	CPT (°C)	Char yield (wt %)	Composition (wt %) C	H	O[a]	Empirical formula (ref. to C_6)
Cellulose	No treatment	—	42.8	6.5	50.7	$C_6H_{11}O_{5.3}$
	325	63.3	47.9	6.0	46.1	$C_6H_9O_{4.3}$
	350	33.1	61.3	4.8	33.9	$C_6H_{5.6}O_{2.5}$
	400	16.7	73.5	4.6	21.9	$C_6H_{4.5}O_{1.3}$
	450	10.5	78.8	4.3	16.9	$C_6H_{3.9}O_{1.0}$
	500	8.7	80.4	3.6	16.1	$C_6H_{3.2}O_{0.9}$
Wood	No treatment	—	46.4	6.4	47.2	$C_6H_{9.9}O_{4.6}$
	400	24.9	73.2	4.6	22.2	$C_6H_{4.5}O_{1.4}$
Lignin	No treatment	—	64.4	5.6	24.8[b]	$C_6H_{6.5}O_{2.0}$
	400	73.3	72.7	5.0	22.3[c]	$C_6H_{5.0}O_{1.3}$

[a] By difference.
[b] Contains 1.2% sulfur.
[c] Contains 0.6% sulfur.

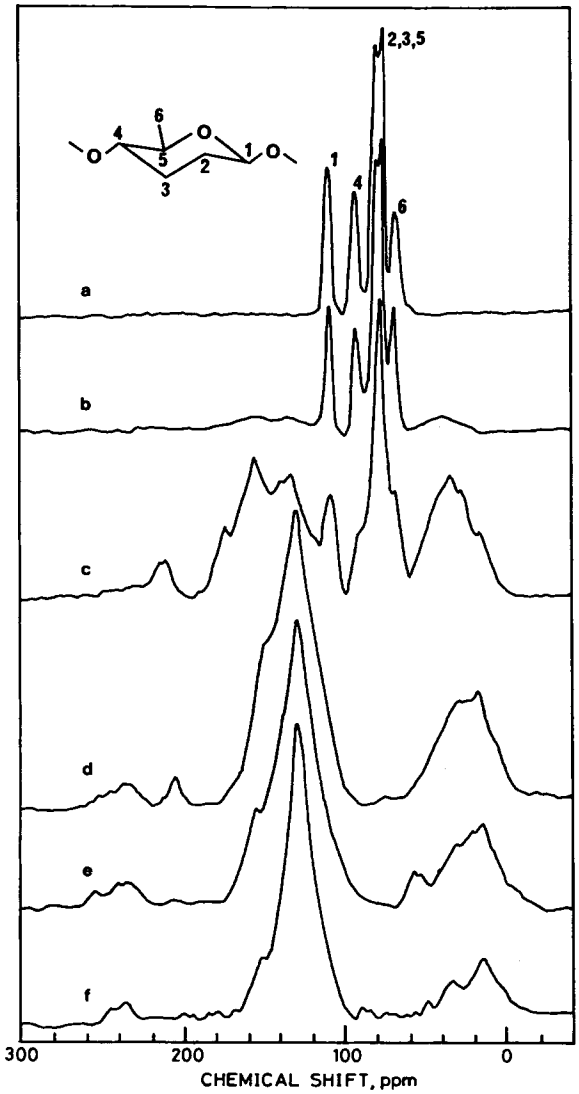

Fig. 1. CP/MAS ^{13}C-NMR spectra of cellulose chars prepared by heating for 5 min at different temperatures: (a) no treatment; (b) 325°C; (c) 350°C; (d) 400°C; (e) 450°C; (f) 500°C. (The small peaks located in the 240 ppm regions are spinning sideband.)

flowing nitrogen (60 mL/min), following the procedure described in the previous paper.[7]

^{13}C-NMR measurements were made on a Nicolet NT-150 Spectrometer at 37.7 MHz with a home-built CP/MAS probe using 0.4 cc of the powdered sample. A pulse repetition time of 1.0 s and contact time of 1 ms were used, and usually 5000–15,000 scans were accumulated. The irradiation field for ^{1}H was 13 G and that for ^{13}C was 52 G. Magic angle spinning rates of 3.5–4.0 KHz were achieved with a spinner of the bullet type.[17] Chemical shifts were measured with respect to tetramethylsilane via hexamethylbenzene as a secondary substitution reference (aromatic peak at 132.3 ppm).[15] NMR peaks were assigned on the basis

of literature data,[12,18,19] and the quantification was performed by cutting and weighing the corresponding resonance area. The systematic errors introduced by overlapping of the aliphatic peaks with spinning sidebands from the aromatic region were found to be insignificant by running a typical sample on a JEOL FX-60Q MAS spectrometer at a ^{13}C frequency of 15 MHz and spinning rate of 2500 Hz. The sideband was resolved, but the relative integrated intensities did not change significantly.

IR spectra were recorded on Nicolet MX-1 FTIR instrument and all samples were measured in potassium bromide discs.

RESULTS AND DISCUSSION

The Charring Reactions of Cellulose

The ^{13}C-NMR spectra of cellulose samples, before heating, show several resonance peaks at 60–110 ppm associated with the carbon chain of glycosyl units (see Fig. 1). The carbons at positions 1, 4, and 6 show distinct peaks, and those at positions 2, 3, and 5 show a larger overlapping peak, with the ratios of 1:1:1:3, respectively. The corresponding FTIR spectra show the functionalities associated with these carbons, namely, a large hydroxyl absorption band at about 3500 cm^{-1} and a glycosidic band at about 900–1200 cm^{-1} (see Fig. 2).

On heating, within the temperature range of 300–500°C, cellulose is degraded by two alternative pathways involving depolymerization and charring.[1] In the latter process the remaining molecules are dehydrated and rearranged to form double bonds and carbonyl and carboxyl groups. Further heating and evolution of water, carbon monoxide, and carbon dioxide gives a highly carbonaceous char containing free radicals[3] and polycyclic aromatic groups as shown by permanganate oxidation studies.[7] These changes have been traced by the ^{13}C-NMR and FTIR spectroscopy of samples isothermally heated for 5 min at successively higher temperatures.

Heating at 325°C resulted in 37% weight loss and the remaining materials had the empirical formula of $C_6H_9O_{4.3}$, indicating the loss of H_2O (see Table I). The partial decomposition of the remaining materials produced small changes in ^{13}C-NMR and FTIR spectra. These changes include the appearance of two new bands at 1600 and 1700 cm^{-1} for C=C bonds and carbonyl groups in the IR spectrum and broad peaks on both sides of the glycosyl carbon peaks in the ^{13}C-NMR spectrum.

Heating at 350°C produced 67% weight loss and more drastic changes in the composition of the residue. The NMR spectrum showed new resonance peaks at 14 and 34 ppm for methyl and other paraffinic carbons, 132 ppm for C=C carbons adjacent to hydrogen or another carbon, 154 ppm for C=C carbons adjacent to oxygen, 173 ppm for —COOH and —COOR carbons, and 211 ppm for >C=O and —CHO carbons. It is difficult to distinguish between the olefinic and aromatic carbons. However, formation of aromatic groups are apparently initiated at this temperature because permanganate oxidation studies indicate 0% aromatic carbon content at 325°C and 2.8% at 350°C.[7]

On heating at 400°C the weight loss amounted to 84% and the residual char

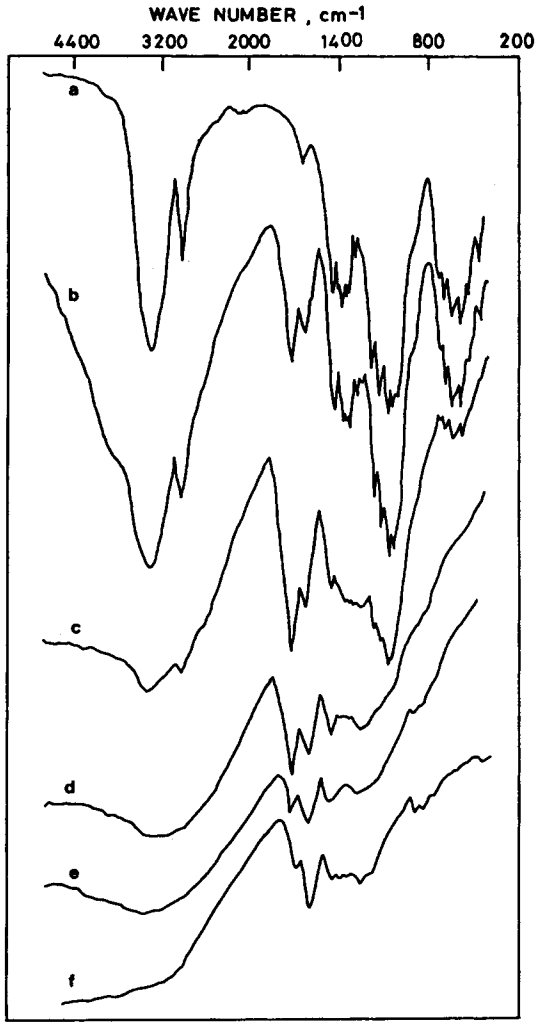

Fig. 2. FTIR spectra of cellulose chars prepared by heating for 5 min at different temperatures: (a) no treatment; (b) 325°C; (c) 350°C; (d) 400°C; (e) 450°C; (f) 500°C.

had a high carbon content of 73.5%. This char was relatively stable to thermal degradation and produced a relatively small weight loss on further heating (see Table I). Formation of the "stable" char corresponded with complete degradation of the glycosyl units as shown by the virtual disappearance of the glycosidic band at 900–1200 and the hydroxyl band at 3500 cm^{-1} in the IR spectrum as well as the glycosyl carbon peaks at 60–110 ppm in the NMR spectrum. The increased carbon content or reduction in the oxygen content and the related functionalities was also reflected in the NMR signals that were gathered mainly in the paraffinic and aromatic carbon regions.

After complete decomposition of the glycosyl units and formation of the carbonaceous char, further heating at 450°C and 500°C produced only minor changes, reflecting further condensation and crosslinking of the carbon chain,

and increased formation of polycyclic aromatic structures as shown by the permanganate oxidation. The increased aromaticity of the chars produced at these temperatures can be seen by enhancement of the C=C band at 1600 cm^{-1} in the IR spectra and the higher intensity of the aromatic signals at 110–150 ppm in the NMR spectra.

Quantitative Analysis of Cellulose Chars by CP/MAS ^{13}C-NMR

Following the correlation of NMR data with development of various functionalities in the carbon skeleton of char discussed above, quantitative analysis of these data were used to determine the carbon concentration of each functionality at different stages of the charring process. It should be noted here that in the CP process different types of carbon show different sensitivities to ^{13}C magnetization; consequently, the intensity of the NMR signals depends on the contact time, and the results could be questionable.[20–23] However, in the investigation of fossil fuels,[23,24] it has been shown that 1-ms contact time provides reliable quantitative data. This contact time also provided the best signal to noise ratio in this study and therefore was used for the quantitative measurements described here.

The NMR spectra shown in Figure 1 were divided into four major regions: paraffinic carbons (0–60 ppm); glycosyl carbons (60–110 ppm); aromatic carbons (110–160 ppm); C=O and COO— carbons (160–220 ppm). Some of these regions were further subdivided as listed in Table II. The assignment of these regions is based on analogy with the NMR data for pure compounds.[12,18,19] However, it should be recognized that unequivocal assignment is impossible due to the heterogeneity of the substrate. The concentrations of carbon species in each of these categories, found for different chars, are given in Table II.

This table also shows the yield of different carbon species based on the carbon content of the original molecule (see the figures in parentheses). The percentage of the different carbon species in the chars are quite different from their yields, because of the weight loss on charring. The difference between these two sets of data can be seen by comparing Figure 3, which shows the concentration of the different carbon species in the remaining chars, with Figure 4, which shows the yield of each carbon species in the same chars. These two figures show the formation and decomposition of different groups according to their thermal stability. Within the temperature range of 300–400°C the glycosyl units of the polysaccharides are partly depolymerized through intramolecular transglycosylation, to levoglucosan which evaporates and partly decomposes with evolution of water, carbon monoxide, and carbon dioxide.[1,2] Consequently, as shown in Figures 3 and 4, the glycosyl carbons rapidly decrease and completely disappear at 400°C. This leaves a more stable carbonaceous residue (stable char) containing 29% of the original carbon atoms as aromatic and paraffinic species. The intermediate chars produced at 325–350°C contain 8–10% carbonyl and carboxyl groups, which are drastically reduced on further heating, presumably through homolytic cleavage of CO and CO_2 creating free radicals involved in the cyclization and condensation of the remaining carbon skeleton to polycyclic aromatic structures. The methyl and other paraffinic carbons are formed largely at 350°C and reach the maximum concentration of 27% at 400°C. They are then gradually reduced to 12% at 500°C. The formation of aromatic rings starts with decom-

TABLE II
Distribution of Carbon Species in Chars Prepared at 325–500°C

	Chemical shift region (ppm)	Char preparation temperature (°C)				
		325	350	400	450	500
1. Paraffinic						
CH_3—	0–30	4[a](3)[b]	9(4)	14(4)	10(2)	6(1)
Others	30–60		15(7)	13(4)	11(2)	6(1)
Subtotal		4(3)	24(11)	27(8)	21(4)	12(2)
2. Glycosylic	60–110	85(59)	30(15)	<1(0)	≃0	—
3. Aromatic						
ϕ-H, ϕ-C	110–150	3(2)	23(11)	56(16)	66(12)	79(12)
ϕ-O	150–170	3(2)	13(6)	13(4)	11(2)	9(1)
Subtotal			36(17)	69(20)	77(14)	88(13)
4. Oxygen functional group						
—COOH, —COOR	170–190	8(15)	5(2)	1(0)	1(0)	—
—C=O, —CHO	190–220		5(1)	2(0)	1(0)	<1(0)
Subtotal			10(3)	3(1)	2(0)	1(0)
Total		100(79)	100(46)	100(29)	100(18)	101(15)

[a] Based on the carbon atoms in char.
[b] Distribution (%, shown in parentheses) based on the carbon atoms in original cellulose.

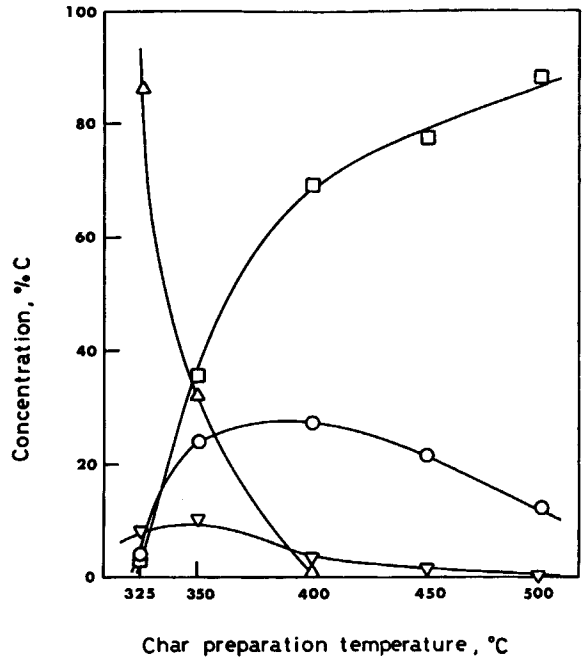

Fig. 3. Concentration of different carbon species in char prepared at 325–500°C: (△) glycosylic; (□) aromatic; (○) paraffinic; (▽) carbonyl and carboxyl.

position of the glycosyl units, presumably involving dehydration and cyclization of the carbon chain, and proceeds rapidly as evidenced by the rapid increase in the concentration of aromatic carbons from 3% at 325°C to 36% at 350°C and

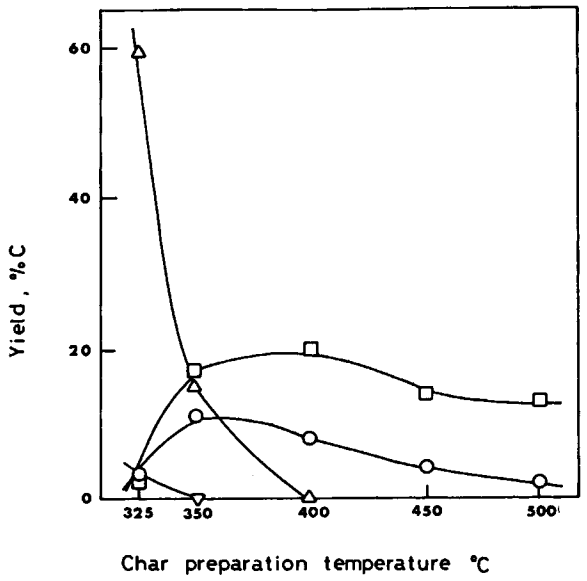

Fig. 4. Yield of different carbon species based on the original carbon content of cellulose: (△) glycosylic; (□) aromatic; (○) paraffinic; (▽) carbonyl and carboxyl.

69% at 400°C. The aromatic groups formed in this range, however, are partly phenolic and carry a relatively large number of carbons attached to oxygen atoms. On further heating from 400°C to 500°C the concentration of aromatic carbons increases from 69% to 88%, while the concentration of the oxygen substituted aromatic carbons is reduced from 13% to 9%.

Consideration of the carbon yields shown in Figure 4 indicates that at 350°C the intermediate char retains 46% of the original carbons of cellulose molecules distributed between 17% aromatic, 15% glycosyl, 11% paraffinic, and 3% carbonyl and carboxyl carbons. At 400°C the stable char retains 29% of the original carbons, distributed between 20% aromatic, 8% paraffinic, and 1% carbonyl and carboxyl groups. At 500°C about 16% of the original carbons survive as 13% aromatic, 2% paraffinic, and 1% carbonyl carbons. This represents a net loss of both aromatic and paraffinic carbons. The increased aromaticity of the char between 400°C and 500°C (see Fig. 3) is due to the preferential loss of the less stable paraffinic groups. Homolytic cleavage of these groups and other substituents of the aromatic rings creates free radicals, promoting further cyclization and crosslinking. The crosslinking of individual aromatic clusters into highly condensed polycyclic structures has been detected by permanganate oxidation[7] and is supported by the observation that between 450°C and 500°C the aromatic carbon content remains constant, while the hydrogen content is reduced (see Tables I and II).

Char Formation in the Presence of Aromatic Nuclei

According to the above description, the formation of phenolic rings and their condensation to polycyclic aromatic groups are significant steps in the charring process. Therefore, it is interesting to know whether or not phenolic groups existing prior to pyrolysis could increase the aromaticity of the char. This was studied by charring wood and lignin. The wood sample in this study contained about 70% holocellulose (44% cellulose and 26% hemicellulose) and 30% guaiacyl lignin, consisting of methoxy-substituted phenyl propane structural units.

Table I shows char yields and the elemental composition of chars and the starting materials. It has been shown before that lignin forms more char than wood, and wood forms more char than cellulose.[25,26] As expected, the same relation was observed, and lignin yielded 73.3% char. However, the elemental composition of the chars from lignin, wood, and cellulose were similar.

As shown in Figure 5, the NMR spectra of lignin and wood chars produced at 400°C were different from the corresponding spectrum of cellulose char, and showed two new peaks at the paraffinic (0–60 ppm) and aromatic (100–170 ppm) regions. The new paraffinic peak at 55 ppm was larger for the lignin char. This peak is assigned to —O—CH_3 and is readily recognized in unpyrolyzed wood and lignin. The peak at 148 ppm is assigned to aromatic carbons attached to oxygen —O—C⟨◯⟩. These resonances are believed to represent the carbons bridged by the same oxygen atoms such as CH_3—O-ϕ, which have survived due to their high thermal stability.[16] The relative intensity of the lignin peak at 55 ppm was used to calculate the proportion of char formed from the lignin component of wood. This calculation showed that approximately 72% of wood char was formed

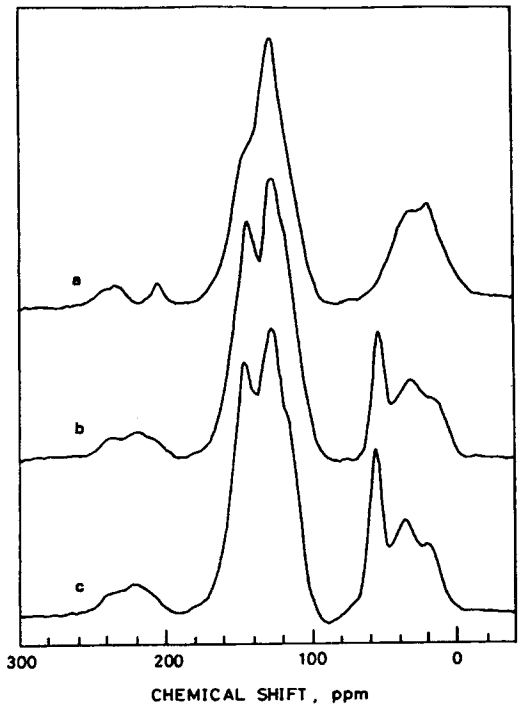

Fig. 5. CP/MAS ^{13}C-NMR spectra of chars from: (a) cellulose; (b) wood; (c) lignin prepared by heating for 5 min at 400°C. (The small peaks located in the 240 ppm region are spinning sideband.)

from lignin. Considering that wood gives about 25% char at 400°C, this means that 100 g of wood should give 7 g of char from cellulose and 18 g from lignin (Table I). The char yield from each component can be estimated by another procedure: assuming that on charring there is no interaction between lignin and cellulose, kraft lignin reacts exactly the same as lignin in wood, and holocellulose reacts as cellulose. As shown in Table I, the char yield from cellulose and lignin was 16.7% and 73.3%, respectively. Since the wood sample was composed of 70% of holocellulose and 30% of lignin, theoretically 100 g of wood should give 11.7 g of cellulose char and 22.0 g of lignin char. This is in line with the yields obtained by the NMR analysis, namely, 7 g from cellulose and 18 g from lignin, particularly in view of the assumptions which have been made.

In order to determine the extent of condensation or crosslinking, the chars were subjected to permanganate oxidation, and the benzene polycarboxylic acids formed from oxidation of substituted aromatic rings were analyzed, as discussed in a previous paper.[7] The results obtained from the lignin, wood, and cellulose chars prepared at 400°C were quite similar and showed the highest yield for benzene tetracarboxylic acid (B4C) followed by penta- (B5C), hexa- (B6C), and tri- (B3C) carboxylic acids. There was also a small yield of phthalic acid (B2C). These data listed in Table III indicate that the aromatic groups in these chars are considerably substituted or crosslinked. Furthermore, total yields of benzene carboxylic acids in each char were similar, implying similar content of aromatic carbons. This similarity was confirmed by NMR studies that showed 69%, 70%,

TABLE III
Benzene Polycarboxylic Acids Formed on Permanganate Oxidation of Chars

	Product yields (%)[a]					
	B2C[b]	B3C[b]	B4C[b]	B5C[b]	B6C[b]	Total
Cellulose char	0.2	1.1	3.0	2.2	1.1	7.6
Wood char	0.2	0.7	2.1	2.0	1.1	6.1
Lignin char	0.2	1.0	2.0	1.8	1.1	6.1

[a] Based on carbon content of the char.
[b] B2C = benzene dicarboxylic acid; B3C = benzene tricarboxylic acid; etc.

and 66% aromatic carbons in char from cellulose, wood, and lignin, respectively. The close similarity of the aromatic content in these chars indicates that the preexisting aromatic group in lignin does not increase the aromatic content of the char, although it provides more char. Moreover, apparently it has no effect on charring of cellulose in wood.

Confirmation of the Quantitative CP/MAS ^{13}C-NMR Data

It has been shown that the quantitative NMR data are affected by the analytical conditions. The aromatic carbon content determined by the NMR method was therefore compared with the data obtained by fixed carbon analysis,[27] involving heating at 950°C for 7 min, which is expected to leave the aromatic carbons. Recently Grant and co-workers[9] found a strong correlation between these two methods for coal, having carbon contents of 77–87%. In this study we used chars with the carbon content of 48–80%. As shown in Figure 6, plotting of the aromatic carbon content calculated from the NMR data against the fixed carbon gave a linear relationship between the two methods. This correlation suggests that the quantitative NMR values fairly represent the actual trend of

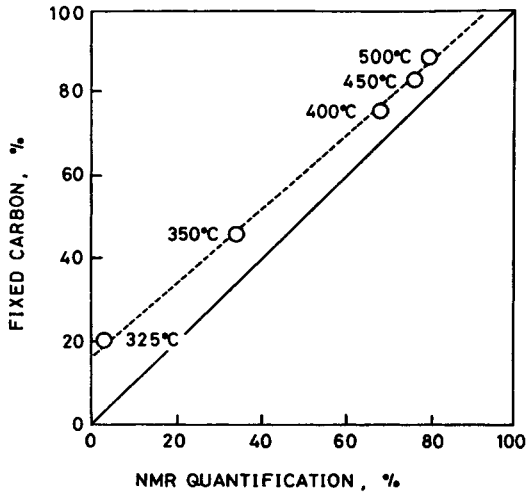

Fig. 6. Comparison of the aromatic carbon content determined by CP/MAS ^{13}C-NMR with the fixed carbon content.

TABLE IV
O/C Atomic Ratio of Cellulosic Chars Determined by Elemental Analysis and NMR

	Char preparation temperature (°C)			
	350	400	450	500
By NMR	0.52	0.18	0.15	0.10
By elemental analysis	0.42	0.22	0.16	0.15

the aromatic carbon content. For the chars, however, the quantitative NMR values were always slightly lower than those determined by the fixed carbon, whereas, for coal samples studied by Grant and co-workers, the situation was reversed. This appears to be mainly due to the differences in sample composition because coal samples contain a large amount of volatile matter and are partially extractable by organic solvent, whereas the cellulosic chars contain little extractable material.

The atomic ratio of oxygen to carbon (O/C) can be calculated from the elemental analysis of the chars as well as the oxygenated carbon atoms analyzed by the NMR, taking into account different oxygen functionalities. The O/C ratios obtained in this manner are compared in Table IV. The NMR data in this table are in good agreement with the values from the elemental analysis, except for the char prepared at 350°C. The discrepancy shown by this char is probably due to the transition at 350°C involving simultaneous decomposition of glycosyl units and formation of aromatic skeletons. As a result, the NMR spectrum contains unresolved and overlapping peaks, which hinder exact measurements. The results obtained with other chars, however, support the reliability of quantitative CP/MAS ^{13}C-NMR data.

CONCLUSION AND SUMMARY

Pyrolysis of cellulose between 300°C and 400°C involves depolymerization of some of the glycosyl units to levoglucosan and decomposition of the rest to water, carbon monoxide, carbon dioxide, and char.

The intermediate char formed on heating at 350°C for 5 min contains 46% of the original carbon atoms in cellulose, including 15% of the glycosyl units, and 31% of the newly formed carbon species consisting of about 17% aromatic carbons, 11% methyl and other paraffinic carbons, and 3% carboxyl and carbonyl carbons. At 400°C the glycosyl groups completely disappear and a "stable" char is formed containing mainly aromatic groups with intermittent paraffinic groups.

Between 400°C and 500°C the aromaticity of the char is further increased by preferential decomposition of the aliphatic groups, homolytic cleavage of various substituents, and condensation of the free radicals. This provides a highly condensed char containing 88% polycyclic, aromatic structures.

This investigation was extended to wood and lignin chars prepared at 400°C to determine the effect of preexisting aromatic nuclei of lignin in the charring reactions. The permanganate oxidation and NMR studies indicated that these chars are similar to the corresponding cellulose char and have considerably condensed or crosslinked aromatic structures, even at 400°C. The preexisting aromatic nuclei in lignin thus did not increase the aromatic carbon content, although the char yield was increased.

The authors are grateful to the NBS Center for Fire Research for supporting this study under Grant no. NB81NADA2066 and Dr. Thomas J. Ohlemiller for his personal interest. They are also pleased to acknowledge the contributions of the Colorado State University Regional NMR Center, funded by NSF Grant no. CHE-82-08821.

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Received February 10, 1983
Accepted May 24, 1983