

Products and Functional Group Distributions in Pyrolysis Oil of Chromated Copper Arsenate (CCA)-Treated Wood, as Elucidated by Gas Chromatography and a Novel ^{31}P NMR-Based Method

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Low-temperature pyrolysis offers a feasible option for wood waste management and the recovery of a variety of useful chemicals. In this study, the effect of chromated copper arsenate (CCA) wood preservatives on the yield and composition of various pyrolysis products was investigated over the temperature range of 275–350 °C. For this preliminary work, we examined the feasibility of using gas chromatography coupled with either flame ionization detection or mass spectroscopic detection and a novel ^{31}P nuclear magnetic resonance (NMR) spectroscopic method. Both methods worked well, with the gas chromatographic method being compound-specific and the ^{31}P NMR method being specific to the functional group (e.g., aliphatic alcohols, total phenols, and carboxylic acids). The present experiments showed that the CCA treatment on wood had a significant effect on the amount of main carbohydrate degradation products of tar. The yield of levoglucosan (LG) from CCA-treated wood increased, while the yields of hydroxyacetaldehyde and hydroxyacetone decreased.

1. Introduction

Preservatives are used in wood to prevent it from decaying from insects and fungi. One such preservative, chromated copper arsenate (CCA), has been the main chemical formulation used for pressure-treated wood. Based on different ratios of active salts in the preservatives (CrO_3 , CuO , As_2O_5), CCA can be divided into three categories: types A, B, and C.

CCA-treated wood is generally used for outdoor applications, such as telephone poles, decks, fence posts, boat docks, and wooden playgrounds. However, because arsenic-laced preservatives are considered a cancer risk, the United States Environmental Protection Agency (USEPA) announced in 2002 a phase-out of their use for consumer use, thus promoting the search for new alternative wood preservatives.¹ Yet, the current industrial landscape is grim, because industry experts estimate that 75 billion feet of CCA-treated boards are in use nationwide.² Thus, the disposal of hazardous CCA-treated wood waste has escalated into a challenging problem in the United States.

The pyrolysis of CCA-treated wood at low temperature is a promising approach to the disposal problem.³ Pyrolysis is the thermal decomposition of material in the absence of oxygen. For biomass, the product of pyrolysis is a mixture of solids char, liquids tar, and gas (methane, carbon monoxide, and carbon dioxide). With respect to the release of the metals from the CCA-treated wood,^{3–11} Helsen and co-workers determined that most copper and chromium remained in the pyrolysis residue, but the fate of arsenic showed a marked difference. Specifically, pentavalent arsenic can be reduced to trivalent arsenic, which causes the release of poisonous arsenic into the environment. However, reactor temperature and residence time can be controlled to reduce the amount of arsenic released during pyrolysis.⁴

One major advantage of low-temperature pyrolysis is the potential to extract valuable chemicals from the wood such as levoglucosan (LG), levoglucosenone (LGO), hydroxyacetone,

and hydroxyacetaldehyde. To our knowledge, there has been little research focused on the pyrolysis products from CCA-treated wood. Related research done by Wehlte et al. investigated the impact of CCB (chromium, copper, boron) wood preservatives on the flash pyrolysis of biomass and analyzed the liquid compounds in pyrolysis tar.¹² Thus, for this work, we performed pyrolysis experiments to investigate the effect of CCA preservatives on the yield and composition of tar products and analyzed the tar using gas chromatography (GC) coupled with mass spectroscopy (MS) and a novel ^{31}P nuclear magnetic resonance (^{31}P NMR) spectroscopy approach.

Gas chromatography, coupled with either mass spectroscopy (denoted as GC/MS) or flame ionization detection (denoted as GC-FID), has been applied to the analysis of lignocellulosics and other wood-derived compounds.^{13–15} It is a robust method and often provides analytical information on specific chemical species. However, GC methods generally require the use of standards or references to identify components in mixtures individually.

The application of ^{31}P NMR for the analysis of biopolymers found in woody tissue has also been well-developed.^{16–24} For example, solution ^{31}P NMR can be used to analyze soluble lignin and carbohydrate samples after phosphitylation with 1,3,2-dioxaphospholanyl chloride or its tetramethyl analogue.²² Also, ^{31}P NMR is a powerful method for determining the three principal forms of phenolic hydroxyls present in lignins (i.e., *p*-hydroxyphenyl, guaiacyl, and syringyl structures). Other functional groups present in lignins, such as primary hydroxyls, carboxylic acids, and the two diastereomeric forms of arylglycerol-*beta*-aryl ether units (β -O-4 structures), can also be quantified from a single ^{31}P NMR experiment. Thus, ^{31}P NMR has a unique advantage of being able to perform functional group analyses readily without the use of individual standards or references, as in the GC experiment.

The research presented here was designed as a preliminary study to examine the products found in the pyrolysis tars of CCA-treated wood using GC and ^{31}P NMR spectroscopy as analytical tools. As stated previously, the pyrolysis tar potentially can be recovered and used as a source of chemicals. However,

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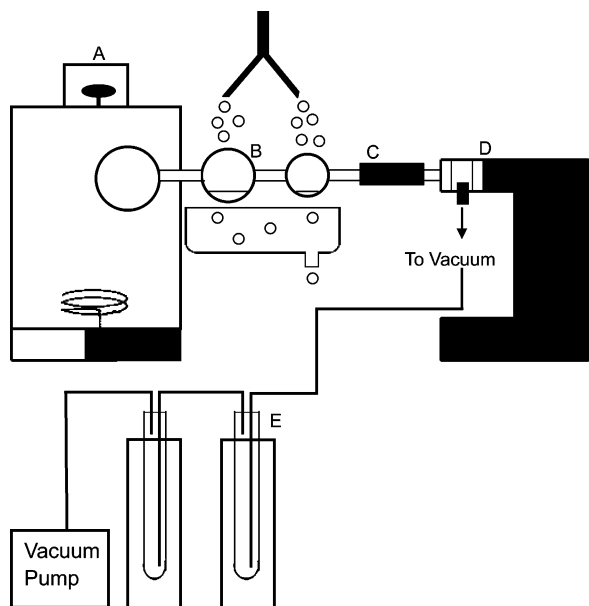


Figure 1. Kugelrohr short-path distillation apparatus. (Legend: A, heated air bath; B, receiving flasks; C, joint connection and a hose connector; D, motor drive; and E, traps.)

a necessary first step in this recovery procedure is the analysis of the tar product and the identification of the important chemicals and their quantities. For this work, we applied GC and NMR methods to the tars obtained from the pyrolysis of untreated southern yellow pine trees and CCA-treated southern yellow pine trees. Although none of the wood used in this study had been in service, the methods developed here should be applicable to weathered samples. Future work will examine this application.

2. Experimental Procedure

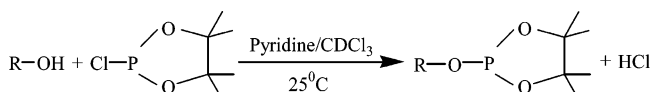
2.1. Chemicals and Reagents. 2.1.1. General. Chemicals and reagents used in this study, except where noted, were obtained from Sigma–Aldrich and had at least 97% purity. Pyridine and CDCl_3 were obtained from Cambridge Isotopes Laboratory (99.5%+ purity), nitric acid was obtained from Fluka Chemika (65% purity), and CH_2Cl_2 and ethanol were obtained from Arcos (HPLC grade).

2.1.2. Preparation of Levoglucosenone (LGO). Avicel microcrystalline cellulose (MCC, PH-105, average particle size of 20 μm) was pyrolyzed in the Kugelrohr short-path distillation apparatus (350 $^\circ\text{C}$, 30 min). The tar was collected in two sequentially connected receiving flasks. Pure LGO was obtained by separating the tar with CombiFlash chromatography (254 nm UV wavelength). A 12-g RediSep normal-phase silica gel column was used. The elution was programmed isocratically for 5 min with 100% CH_2Cl_2 , followed by a gradient from 0% to 30% ethanol in 9 min at a flow rate of 40 mL/min, and finally an isocratic period for 3 min. Pure LGO was confirmed by GC–MS, as well as via ^1H , ^{13}C , and ^{31}P NMR.

2.2. Materials. Untreated and CCA-treated (Type C) southern pine wood was used in this study. The active ingredients in the preserved wood had the following composition (based on a 100% oxide): 47.5% CrO_3 , 18.5% CuO , and 34.0% As_2O_5 . The wood was milled to a powder that had a particle size of 0.1–0.2 mm, and the moisture content was 8%.

2.3. Pyrolysis. The pyrolysis of wood samples was performed in a Kugelrohr short-path distillation apparatus (Figure 1). The sample weight was 3 g for each trial. The vacuum pressure was

Scheme 1. Phosphitylation Reaction with Tar^a



^a Here, R = residues of phenols, alcohols, aldehydes, sugars, and carboxylic acids.

Table 1. Concentration of Chromium, Copper, and Arsenic in Chromated Copper Arsenate (CCA)-Treated Wood

element	concentration (%)
chromium	0.45
copper	0.27
arsenic	0.44

controlled at 7 mm Hg. The thermal treatment was performed in the range of 275–350 $^\circ\text{C}$. The duration of the pyrolysis process varied from 30 min (for 350 $^\circ\text{C}$) to 1 h (for 275, 300, and 325 $^\circ\text{C}$). The end product (char) was collected in the first flask, whereas the tar was collected in two consequently connected receiving flasks (B in Figure 1) and condensed with ice water (0 $^\circ\text{C}$) for further analyses. The distillate was condensed with dry ice–acetone at -70 $^\circ\text{C}$ in the first trap (E in Figure 1). To avoid poisonous volatile arsenic, gas that was released from the pyrolysis experiment was directed into a hood through a vacuum pump. Two replicates for pyrolysis of the wood samples were run at each temperature.

2.4. Analytical Methods. 2.4.1. Gas Chromatography–Mass Spectroscopy (GC/MS) Analysis. Qualitative tar analysis was performed on a Hewlett–Packard G1800B GCD system with a DB-1701 (J&W) capillary column (60 m \times 0.25 mm inner diameter (id), 0.25 μm film thickness). Helium was used as a carrier gas, with a constant flow of 1.0 mL/min. The oven temperature was programmed from 45 $^\circ\text{C}$ (4 min isothermal) to 235 $^\circ\text{C}$ at a heating rate of 3 $^\circ\text{C}/\text{min}$ and then continuously increased to 260 $^\circ\text{C}$ at another heating rate of 10 $^\circ\text{C}/\text{min}$. The oven temperature was held at 260 $^\circ\text{C}$ for 6 min. The detector and injector were kept at a constant temperature of 280 and 250 $^\circ\text{C}$, respectively.

2.4.2. GC/FID Analysis. Quantitative tar analysis was performed on a Hewlett–Packard HP6890 series GC system, using a DB-1701 (J&W) capillary column (60 m \times 0.25 mm id, 0.25 μm film thickness) and an isothermal temperature profile at 45 $^\circ\text{C}$ for the first 4 min, followed by a 3 $^\circ\text{C}/\text{min}$ temperature gradient to 270 $^\circ\text{C}$ and finally an isothermal period at 270 $^\circ\text{C}$ for 7 min. Helium was used as a carrier gas, with a split ratio of 1:20 and a constant flow of 1.0 mL/min. The temperature of the detector and injector were maintained at 280 and 250 $^\circ\text{C}$, respectively.

For sample preparation, 70 mg of tar was weighed and dissolved in 5 mL of acetone. Fluoranthene was used as an internal standard. Two replicates for each sample were injected for the quantitative analysis.

2.4.3. ^{31}P Nuclear Magnetic Resonance (NMR) Analysis of Tar. ^{31}P NMR spectra were obtained on a Bruker 300 MHz/67MM NMR spectrometer. The preparation of the solvents and derivatizing reagent follows the procedure described in ref 22. For the tar phosphitylation step, 30 mg of tar was weighed and then dissolved in a solvent mixture of 400 μL of pyridine and 250 μL of CDCl_3 . The internal standard (*N*-hydroxynaphthalimide) was then added (100 μL), followed by 50 μL of relaxation reagent (chromium acetylacetonate) and the phosphitylation reagent (150 μL 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane). Finally, the solution was transferred to an NMR tube for analysis. The phosphitylation reaction with tar samples is depicted in Scheme 1.

Table 2. Yields of Pyrolysis Fractions of Untreated Wood and CCA-Treated Wood^a

fraction	Yield (wt %)							
	At 275 °C		At 300 °C		At 325 °C		At 350 °C	
	CCA	untreated	CCA	untreated	CCA	untreated	CCA	untreated
char	73.6	73.3	46.3	52.8	30.6	28.2	30.2	28.5
tar	14.6	14.5	34.9	29.2	46.4	46.0	57.7	59.6
distillate	7.9	7.7	11.0	10.7	12.4	12.1	4.6	3.0
total recovery	96.1	95.5	92.2	92.7	89.4	86.3	92.5	91.1

^a Expressed as a weight percentage, based on water-free wood.

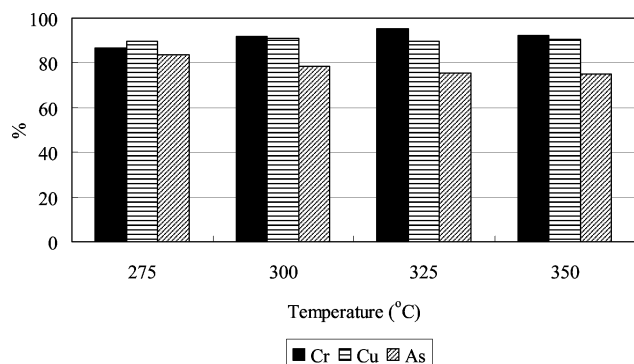


Figure 2. Recovery percentages of chromium, copper, and arsenic in the pyrolysis char from chromated copper arsenate (CCA)-treated wood.

For the quantitative analysis of LG with ³¹P NMR spectroscopy, a spectral baseline correction was necessary to remove the contributions of other compounds. The correction step was performed after the phase and calibration steps and started by selecting baseline points in the valley between the peaks (using “def-pts”). These points were then used to interpolate a new spectrum that was subtracted from the original.

2.4.4. Metal Analysis. The chromium and copper content of CCA-treated wood and pyrolysis char was determined by atomic absorption spectroscopy on a Perkin–Elmer model 2380 instrument. Analytical wavelengths for these analyses were 357.9 nm for chromium and 324.8 nm for copper. The arsenic content of the CCA-treated wood and pyrolysis char was determined by inductively coupled plasma (ICP) spectrometry, using a Perkin–Elmer Optima 2000DV.

The samples for all metal analyses were prepared according to the reflux method provided by Helsen et al.⁵ This method ensures complete solubilization of the matrix via a nitric acid solution without any loss of the metal elements. To accomplish dissolution, 0.1 g of dried wood powder (or pyrolysis char) was placed into a conical flask equipped with a water cooler, and then 10 mL of 65% HNO₃ was added. The flask was then heated on a plate until the sample dissolved completely (~2 h). The resulting concentrations of chromium, copper, and arsenic in the CCA-treated wood are shown in Table 1.

3. Results and Discussion

3.1. Yields of Pyrolysis Fractions from Untreated and CCA-Treated Wood. The yields of the pyrolysis fractions of untreated wood and CCA-treated wood, as a function of temperature, are shown in Table 2. The total recovery (the sum of the yield of char, tar, and distillate) from pyrolysis was ~90% at temperatures in the range of 300–350 °C. The yields of the pyrolysis tar from CCA-treated wood were similar to those from untreated wood. Higher yields of tar can be obtained at higher temperatures. Correspondingly, the yield of char decreased as the temperature increased, which indicated more raw materials were converted to tar products. The recovery percentages of chromium, copper, and arsenic in the pyrolysis char from CCA-treated wood are presented in Figure 2. Most chromium and copper remained in the char at different pyrolysis temperatures and duration times. The fate of arsenic makes a big difference. An arsenic quantity of 16.4% was already released when CCA-treated wood was pyrolyzed at 275 °C for 1 h. With the increase of temperature, pyrolysis at 350 °C for 30 min would result in an arsenic release of 24.8%. Similar observations have also been reported by Helsen and Van den Bulck,⁶ who studied the release of metals during the pyrolysis of CCA-treated wood.

3.2. Quantification of Tar Products Using Gas Chromatography. The gas chromatogram of pyrolysis tar from CCA-treated wood (350 °C) is shown in Figure 3, and the quantified tar products are listed in Table 3. As shown in this table, the tar compositions are qualitatively identical, but their quantitative analyses are significantly different between untreated and CCA-treated wood. A large proportion of tar compounds come from carbohydrate thermal degradation. The main degradation of carbohydrate began at 300 °C. Thus, the yield of most of tar products was lower at 275 °C, which can also be reflected from the lowest yield of tar and the highest yield of char at this temperature (see Table 2).

LG is the major carbohydrate thermal decomposition product.²⁵ Its yield increased with temperature. The amount of LG derived from CCA-treated wood was higher than that from untreated wood over the entire temperature range. Especially at 350 °C, the LG yield from CCA-treated wood was ~3 times higher than that of untreated wood. This is also in agreement

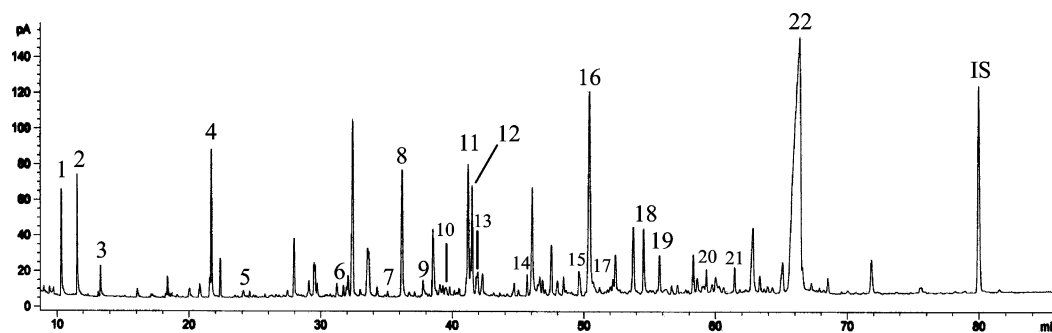


Figure 3. Gas chromatogram of the pyrolysis tar from CCA-treated wood (350 °C).

Table 3. Yields of Tar Compounds from the Pyrolysis of Untreated and CCA-Treated Wood^a

number	compound name	Yield (wt %)							
		At 275°C		At 300°C		At 325°C		At 350°C	
		CCA	untreated	CCA	untreated	CCA	untreated	CCA	untreated
1	hydroxyacetaldehyde	0.63	1.44	1.75	5.47	1.80	4.42	1.34	3.07
2	acetic acid	0.80	1.05	1.72	1.86	1.67	1.67	1.92	1.87
3	hydroxyacetone	0.52	0.83	0.74	1.57	0.72	1.37	0.75	1.36
4	2-furaldehyde	0.21	0.26	0.58	0.40	0.68	0.31	0.70	0.34
5	furfuryl alcohol	0.09	0.43	0.08	0.76	0.12	0.56	0.11	0.37
6	furan-(5H)-2-one	0.22	0.51	0.41	1.39	0.44	1.20	0.40	1.10
7	phenol	0.03	0.02	0.03	0.03	0.04	0.03	0.04	0.04
8	guaiacol	0.12	0.13	0.47	0.40	0.54	0.39	0.60	0.41
9	<i>o</i> -cresol	0.02	0.03	0.06	0.07	0.06	0.07	0.06	0.05
10	<i>p</i> -cresol	0.05	0.06	0.05	0.06	0.06	0.07	0.07	0.07
11	levoglucosenone	0.50	0.36	1.37	0.56	1.19	0.28	0.87	0.19
12	4-methyl guaiacol	0.22	0.29	0.41	0.61	0.55	0.64	0.59	0.65
13	2,4-dimethyl phenol	0.14	0.15	0.20	0.25	0.17	0.22	0.09	0.13
14	4-ethyl-guaiacol	0.05	0.08	0.07	0.09	0.09	0.10	0.10	0.12
15	eugenol	0.18	0.22	0.25	0.30	0.23	0.23	0.21	0.22
16	5-(hydroxy-methyl)-furaldehyde-(2)	1.66	1.83	2.21	1.41	2.03	1.12	2.01	0.99
17	catechol	0.42	0.63	0.46	0.67	0.43	0.63	0.42	0.62
18	isoeugenol	0.34	0.69	0.39	0.90	0.38	0.58	0.36	0.51
19	vanillin	0.39	0.65	0.46	0.52	0.38	0.41	0.33	0.35
20	acetoguaiacone	0.31	0.41	0.25	0.30	0.22	0.24	0.20	0.23
21	guaiacyl acetone	0.49	0.81	0.38	0.55	0.34	0.42	0.36	0.45
22	levoglucosan	8.14	0.98	12.88	1.57	13.90	3.77	14.66	4.86

^a Expressed as a weight percentage, based on water-free tar.

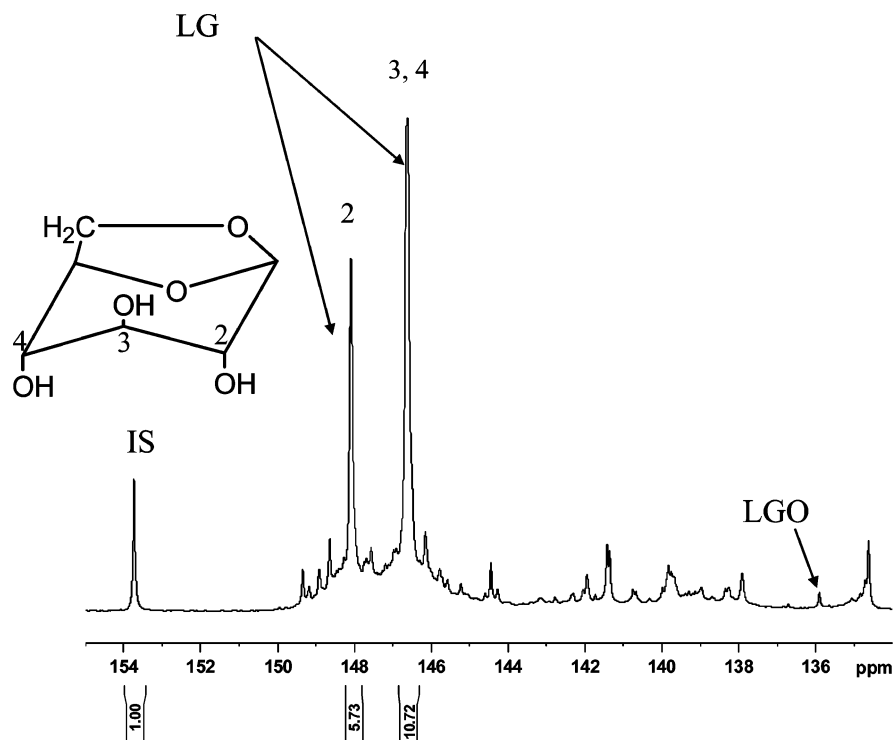


Figure 4. ³¹P NMR spectrum of tar from the pyrolysis of CCA-treated wood.

with the similar findings of Wehlte et al.,¹² who studied the impact of CCB wood preservatives on the flash pyrolysis of biomass. Their work showed that the LG yield in the pyrolysis liquid from the CCB-treated softwood increased by a factor of ~6, compared to the untreated wood. As shown in Table 3, the amount of LGO from CCA-treated wood was also higher than that of untreated wood over the entire temperature range of 275–350 °C.

In contrast, the CCA treatment did not promote the formation of hydroxyacetaldehyde and hydroxyacetone. As shown in Table 3, the yield of hydroxyacetaldehyde from untreated wood decreased from 5.5% at 300 °C to 3.1% at 350 °C, whereas the

yield from CCA-treated wood remained at ~1.5% in the same temperature range. The yield of hydroxyacetone showed the same trend with that of hydroxyacetaldehyde over the entire temperature range.

There is not much difference in the amount of acetic acid between the untreated and CCA-treated wood. There is a lumped trend for the yields of LGO, hydroxyacetaldehyde, and hydroxyacetone in these data. These yields reach a maximum at 300 °C, which is due to an increase in the volatiles release rate via the primary degradation reactions. As the temperature increases, secondary vapor-phase degradation reactions then occur, which cause a decrease in the amount of these products.²⁶

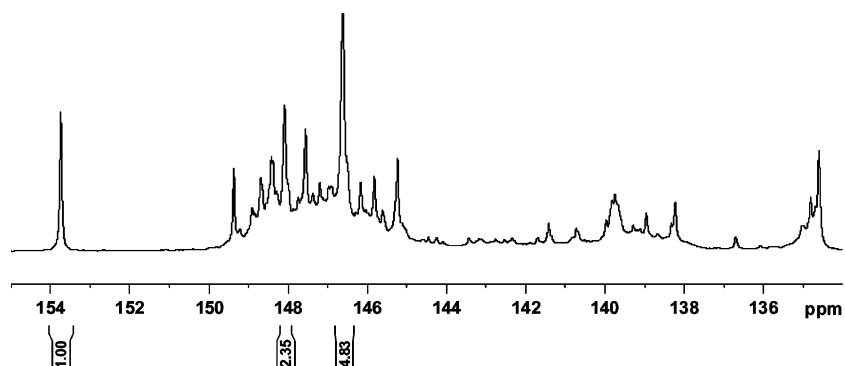


Figure 5. ^{31}P NMR spectrum of tar from the pyrolysis of untreated wood.

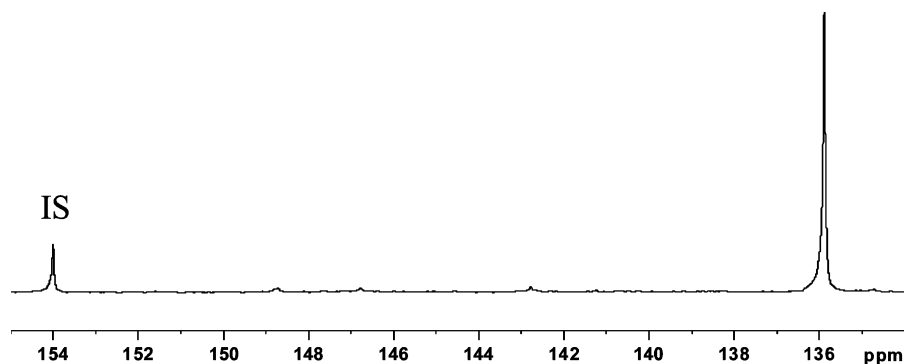


Figure 6. ^{31}P NMR spectrum of levoglucosenone (LGO).

The continuous increase of the LG yield correlating with the increase in temperature shows that LG originates from the primary decomposition of depolymerized cellulose.²⁶

3.3. Quantitative Analysis of Tar Products with ^{31}P NMR.

A typical ^{31}P NMR spectrum of tar from the pyrolysis of CCA-treated wood is shown in Figure 4. In this spectrum, the integration ranges for different groups are as follows: total aliphatic $-\text{OH}$ groups, 149.6–145.0 ppm; total phenolic $-\text{OH}$ group (except one peak at 141.3 ppm), 143.8–137.4 ppm; and total $-\text{COOH}$ group, 135.5–134.3 ppm. The internal standard *N*-hydroxynaphthalimide gives a sharp signal at 153.8 ppm. Two sharp signals near 148.1 and 146.6 ppm are assigned to the phosphitylated hydroxyls from LG. After integration with the internal standard, the relative intensities of these two signals are $\sim 1:2$. There are three hydroxyl groups in one LG unit. Thus, one signal at 148.1 ppm in the spectrum comes from the $-\text{OH}$ group on C-2. Another signal at 146.6 ppm comes from the $-\text{OH}$ groups on C-3 and C-4. LGO gives rise to a small signal at 135.8 ppm. ^{31}P NMR of pure LG and LGO samples were also run to confirm their chemical shifts on the spectrum. ^{31}P NMR of pure LGO (Figure 6) and LG samples were also run to confirm their chemical shifts on the spectrum. The corresponding ^{31}P NMR spectrum of tar from pyrolysis of untreated wood is shown in Figure 5. Considerably reduced signal intensities at 148.1 and 146.6 ppm were obtained, which shows that the LG content of tar from CCA-treated wood was higher than that of untreated wood. The small signal at 141.3 ppm in the spectrum from untreated wood, and its corresponding CCA-treated wood has not been confirmed yet; however, it is possible that this peak comes from carbohydrate degradation products.

For quantitative analysis, the amount of LGO can be directly obtained by the integration with the internal standard in the spectrum. The results are shown in Table 4. Compared to GC-FID analysis (see Table 3), quantitative determination from ^{31}P NMR can obtain the same results, in regard to the yield of LGO.

Table 4. Yield of Levoglucosenone (LGO) from ^{31}P NMR and GC-FID Analysis^a

sample (at 350 °C)	Yield (wt %)	
	^{31}P NMR	GC-FID
CCA-treated wood	0.5	0.9
untreated wood	0.1	0.2

^a Expressed as a weight percentage, based on water-free tar.

Table 5. Quantitative Analysis of Levoglucosan with ^{31}P NMR and GC-FID^a

sample	Yield (wt %)		
	^{31}P NMR, without baseline correction	^{31}P NMR, with baseline correction	GC-FID
CCA			
350 °C	22.7	14.0	14.6
325 °C	20.3	13.3	13.9
300 °C	20.0	12.2	12.9
untreated			
350 °C	9.7	4.1	4.8
325 °C	8.8	3.9	3.8

^a Expressed as a weight percentage, based on water-free tar.

The process of determining the amount of LG with ^{31}P NMR is not as straightforward as the LGO determination, because any compound that contains aliphatic $-\text{OH}$ groups will exhibit spectral overlap in the range of 149.6–145.0 ppm. Thus, to remove the contributions of any other compounds in this range, we first performed a baseline correction on the spectrum (as discussed in the Experimental Section). Without baseline correction, the experimental results show a factor of ~ 2 error in the concentration of LG. However, after correction, quantification from the ^{31}P NMR experiment is similar to that of the GC method (see Table 5).

The functional group content of pyrolysis tar is shown in Table 6. As the pyrolysis temperature increased, the amount of total aliphatic alcohols, total phenols, and total carboxylic acids of tar from untreated and CCA-treated wood increased. Pyrolysis

Table 6. Functional Group Content of Pyrolysis Tar from Untreated and CCA-Treated Wood,^a Using Quantitative ³¹P NMR

functional group	integrated chemical shift range (ppm)	Content (mmol/g)					
		At 300°C		At 325°C		At 350°C	
		CCA	untreated	CCA	untreated	CCA	untreated
aliphatic alcohols	149.6–145.0	7.97	6.36	8.53	6.75	8.53	7.08
condensed phenols	143.8–140.2 (except peak at 141.3 ppm)	0.77	0.86	0.75	0.98	0.90	0.94
noncondensed phenols	140.2–137.4	1.28	1.67	1.35	1.63	1.32	1.67
total phenols	143.8–137.4	2.05	2.53	2.10	2.61	2.22	2.61
carboxylic acids	135.5–134.3	0.45	0.45	0.49	0.46	0.54	0.64

^a Expressed in terms of mmol/g, based on water-free tar.

tar from CCA-treated wood contained a greater amount of total aliphatic alcohols, compared to the untreated wood. For example, the aliphatic hydroxyl group content of tar from CCA-treated wood was 17% greater than that of tar from untreated wood at 350 °C, which is attributable to a large amount of LG produced from CCA-treated wood. The amount of condensed phenols, noncondensed phenols, and total phenols show that the thermal degradation of untreated wood produced a higher amount of phenols. For example, a comparison of the noncondensed phenolic hydroxyl group content of tar from CCA-treated wood with that from untreated wood at 350 °C indicates that the latter contained 21% more noncondensed phenolic groups. GC–FID analysis can also confirm the same results. The noncondensed phenolic structure comes from single-ring phenolic compounds such as guaiacol, phenol, eugenol, and vanillin. The condensed phenolic units may be due to the formation of those structures, such as 5–5' biphenolic units. The amount of noncondensed phenolic units of tar is greater than that of the condensed phenolic units, which indicates that most lignin degradation products are monomeric phenols. This can be rationalized on the basis that the pyrolysis of lignin is known to cause the cleavage of β -aryl ether linkages in β -O-4 structures.²⁷ Their cleavage is concomitant with an increase of the free phenolic hydroxyl content of the lignin. There is no big difference in the amount of total –COOH groups between untreated wood and its corresponding CCA-treated wood.

The present quantitative ³¹P NMR approach offers a convenient way to determine the amount and the functional group distributions present in pyrolysis tars. With the GC technique, the amount of total phenols can be calculated from the sum of the amount of all individual phenolic products. However, the present approach is more accurate, because it also allows one to arrive at otherwise nonvolatile condensed phenols. By summing up the total amounts of condensed and noncondensed phenolic environments, it becomes possible to determine the total phenols in pyrolysis tars. Thus, the ³¹P NMR technique provides a novel route to elucidate the structure of pyrolysis tar.

4. Conclusions

The chromated copper arsenate (CCA) treatment has a significant effect on the amount of the main carbohydrate degradation products of tar. The yield of levoglucosan (LG) from CCA-treated wood increased while the yields of hydroxyacetaldehyde and hydroxyacetone decreased. Most metals remained in the char, but ~25% arsenic was released at the pyrolysis temperature of 350 °C for a pyrolysis time of 30 min. The yield of some products, such as isoeugenol, 4-methyl guaiacol, eugenol, and catechol, decreased slightly.

Gas chromatography using either flame ionization detection or mass spectroscopic detection was determined to be able to identify and/or quantify at least 22 individual compounds from the pyrolysis tar of wood. Further identification of unknown

compounds may be possible if the appropriate standards and/or reference spectra can be determined.

The ³¹P NMR technique, while not being able to speciate individual components, provides a novel and rapid route to elucidate key functional groups in pyrolysis tar. Further use of this technique can give a good quantitative analysis of the yield of LG and LGO in tar. The aliphatic alcohol and total phenol, as well as carboxylic acid groups, may also be quantified using the ³¹P NMR approach.

Acknowledgment

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