USDA

Chemical Yields from Low-Temperature Pyrolysis of CCA-Treated Wood

Qirong Fu
Dimitris S. Argyropolous
Lucian A. Lucia
David C. Tilotta
Stan T. Lebow
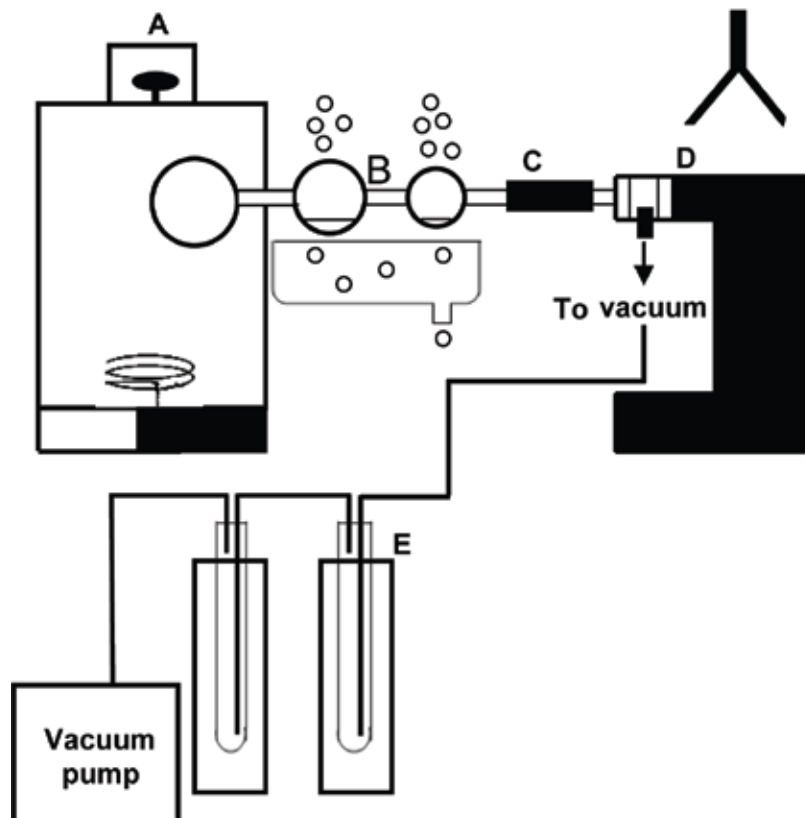
Abstract

Low-temperature pyrolysis offers a feasible option for wood-waste management and the recovery of a variety of useful chemicals. The effect of chromated copper arsenate (CCA) wood preservative on the yield and composition of various pyrolysis products was investigated in the present research. A novel quantitative ^{31}P nuclear magnetic resonance (NMR) spectroscopy methodology has been developed to quantify levoglucosan and levoglucosenone from the pyrolysate of CCA-treated and untreated wood. The CCA treatment of wood had a notable effect on the characteristics of the carbohydrate-derived degradation products of tar. In particular, yields of the important pharmaceutical precursors levoglucosan and levoglucosenone were elevated by 3 and 4.5 times, respectively, when compared with those from untreated wood. Phosphoric acid has proven to be an efficient catalyst to favor levoglucosenone formation. The pyrolysis of CCA-treated wood in the presence of phosphoric acid gave rise to high yields of levoglucosenone, demonstrating the potential for a new pathway in the rational use of CCA-treated wood waste. Pretreatment of wood with metal compounds has demonstrated that $K_2Cr_2O_7$ and $CuSO_4$ salts promote the formation of levoglucosan. The CrO_3 treatment was found to favor the formation of levoglucosenone. A kinetic study of the pyrolysis of CCA-treated wood by thermogravimetric analysis has shown that CCA components have a significant influence on the thermal decomposition behavior of CCA-treated wood and accelerate the weight loss of wood and the oxidation of the char.

Keywords: CCA, treated wood, disposal, low-temperature pyrolysis, tar, levoglucosenone

Acknowledgment

Contents

Chemical Yields from Low-Temperature Pyrolysis of CCA-Treated Wood

Qirong Fu, Graduate Student
Dimitris S. Argyropolous, Professor
Lucian A. Lucia, Associate Professor
David C. Tilotta, Associate Professor
Department of Wood and Paper Science, North Carolina State University, Raleigh, North Carolina

Stan T. Lebow, Research Forest Products Technologist
U.S. Forest Service, Forest Products Laboratory, Madison, Wisconsin

Introduction

Chromated copper arsenate (CCA) preservatives, introduced in the 1930s, have been the main chemical formulation used for pressure-treated wood. The most commonly used CCA formulation, CCA Type C, has an actives ratio of 47.5% CrO_3, 18.5% CuO, and 34.0% As_2O_5 (AWPA 2007). Each of the components of CCA preservative serves a specific purpose: copper is an effective fungicide and arsenic is an effective insecticide, whereas chromium serves to prevent corrosion and bind the chemical preservative to the wood (Lebow 2006). As recently as 2001, CCA was used in about 98% of the pressure-treated wood produced for residential uses.

Prior to 2004, CCA-treated wood was widely used for many outdoor applications, including utility poles, decks, fence posts, boat docks, and wooden playgrounds. However, an agreement between CCA manufacturers and the U.S. Environmental Protection Agency (EPA) has largely limited the current uses of CCA-treated wood to non-residential applications (Lebow 2004). The need for strategies for disposing of residual CCA-treated wood remains, however, because industry experts estimate that 75 billion board feet of CCA-treated boards are in current use nationwide (EPA 2003). Efficient recycling of decommissioned CCA-treated wood remains a challenging problem in the United States.

Environmentally friendly recovery or disposal technologies, or both, need to be developed for the large amounts of future CCA-treated lumber waste. Although CCA-treated wood can currently be placed in approved landfills in most regions of the United States, landfill disposal does not produce any benefit from either the wood fiber or preservative elements. Burning CCA-treated wood for energy production is one possible option, but this option faces challenges because it generates toxic gases (Marutzky 1990, Wilkins and Murray 1980, Dobbs and others 1978). Conventional pyrolysis systems (fixed bed, batch, or grate; fluidized bed; rotary kiln) operate at temperatures that can potentially volatilize the arsenic. However, the pyrolysis of CCA-treated wood at low temperatures may be a promising approach to the growing disposal problem, as low temperatures and no oxidizing agents are used (Helsen and others 1999), which may reduce

metals loss compared with combustion. The recombination and agglomeration of metals in the residue char allows the use of dry separation (pneumatic centrifugal separation) to recover the metals, which makes the metal recycling process more feasible.

The existing and emerging technologies for managing CCA-treated wood waste include recycling and recovery, chemical extraction, bioremediation, electrodialytic remediation, and thermal destruction (Helsen and others 2005). Many additional technological options to manage waste of CCA-treated wood are summarized below, all of which have their limitations and problems.

Management Options for Reuse

With the management option of reusing CCA-treated wood, the barriers are that wood waste is bulky and inefficient to transport and contaminated sawdust may be generated. This option could be good for industrial products but it is of limited potential for residential treated products.

Refining CCA-Treated Wood for Recycling

Wood-Based Composites

Presently the market is not in favor of using CCA-treated wood in conventional wood composite manufacturing. We also have questions about safety for workers and the environment.

- We need to address the issue of using metal-containing and contaminated wood and the loss of ownership of treated wood. (The product should be identified as one containing treated wood.)
- Landfill disposal is only deferred, not avoided.
- CCA tends to interfere with adhesives.

Biodegradation by Fungi

With our current technology, biodegradation by fungi as an option for refining CCA-treated wood for recycling is not economically feasible because of several barriers:

- Part of the contaminant is left in the wood.
- Fiber quality is lost.
- An end use for extracted wood and chemicals has not been developed.

- The system may be contaminated by other organisms.

Extracting CCA Components To Refine CCA-Treated Wood for Recycling

This management option has some potential for minor amounts of treated wood such as that produced as a by-product of milling. This method, however, has several barriers:

- This method is slow and not 100% effective.
- Recycling of CCA components is not proven.
- This method is not cost-effective at this time.
- Size reduction carries a high cost.

Treatment and Destruction

Wood Liquefaction

Wood liquefaction has only been done in initial lab-scale experiments where only 85% of the CCA was removed. Much more research is needed to improve, optimize, and evaluate the process.

Thermal Destruction

The management option of thermal destruction has potential if the metals collected in the ash are utilized and arsenic is trapped from the flue gas. This is the most common method used in Europe, but Canada has shown strong resistance to adopting it. A more favorable climate for this option is expected in the future.

- Energy recovery and significant reduction of waste volume are advantages.
- Ash is considered as hazardous waste.
- Arsenic compounds are volatile (modifications, controls, and monitoring are needed to meet air quality standards).
- Chipping or grinding is required, increasing the energy consumption and cost.

Energy and Raw Materials Recovery by Metallurgical Processes

We cannot yet transform all metal products to usable forms.

- The plant has to be well designed to scrub all volatile and particulate arsenic from the stacks.
- The relatively low CCA concentration in the lumber makes CCA recycling economically infeasible.

Landfill Disposal

Landfill disposal is not a preferred option because it does not recover any value from the used product.

- Disposal may not be acceptable at individual landfill sites.
- CCA chemical can leach from CCA-treated wood (both unburned and as ash) in quantities that exceed regulatory thresholds.
- Monofill results in the highest metal concentrations in the leachate compared with construction and demolition debris landfill and municipal solid waste landfills.

- The cost of landfilling at hazardous waste sites and lined landfills can be high.
- Landfill space is in short supply.

Low-Temperature Pyrolysis

The pyrolysis of CCA-treated wood at low temperatures, examined in this study, is a promising approach to the growing disposal problem (Helsen and others 1999). Pyrolysis is thermal decomposition of biomass at high temperatures (greater than 200 °C) in the absence of oxygen. The end product of pyrolysis is a mixture of solids (char), liquids (tar), and gases (methane, carbon monoxide, and carbon dioxide). Helsen discussed metal behavior during the low-temperature pyrolysis of CCA-treated wood (Helsen and Van den Bulck 1997, 1998, 2000b, 2003; Helsen and others 1997, 1998, 1999, 2003), noting that whereas most copper and chromium remained in the pyrolysis residue, the fate of arsenic was strongly affected by processing conditions. Reactor temperature and residence time could be controlled to reduce the amount of arsenic released during pyrolysis (Helsen and others 2003). Furthermore, it is feasible to extract valuable pharmaceutical precursors (e.g., levoglucosan (LG) and levoglucosenone (LGO), hydroxyacetone, and hydroxyacetaldehyde) from pyrolysis of CCA-treated wood at low temperatures with the purpose of minimizing metal release and maximizing production of pyrolysis oils. Although incineration of CCA-treated wood has been proposed as a mechanism of disposal (Solo-Gabriele and others 2000), to our knowledge, little research has focused on the utilization of the non-metallic pyrolysis products from CCA-treated wood. The most closely related research was done by Wehlte and others (1997), who investigated the effect of the wood preservative CCB (chromium, copper, boron) on the flash pyrolysis of biomass and analyzed the liquid compounds in pyrolysis tar. To fill the research gap, we performed pyrolysis experiments to investigate the effect of CCA preservatives on yield and composition of tar products.

Our research was designed to provide a preliminary overview of the low-temperature pyrolysis of CCA-treated wood, as to our knowledge, this work has not been done previously. In our study, pyrolysis tar was recovered and used as a source of the pharmaceutical precursors discussed in the previous paragraph. One objective of this study was to investigate LGO and LG formation from CCA-treated wood that has been pretreated with phosphoric acid, with the purpose of developing a new pathway in the rational use of CCA-treated wood waste.

Experimental

Materials

Untreated and CCA-treated (Type C) Southern Pine wood was used in this study. The active ingredients in this CCA preservative had the following compositions (based on 100% oxides): 47.5% CrO_3, 18.5% CuO, and 34.0% As_2O_5.
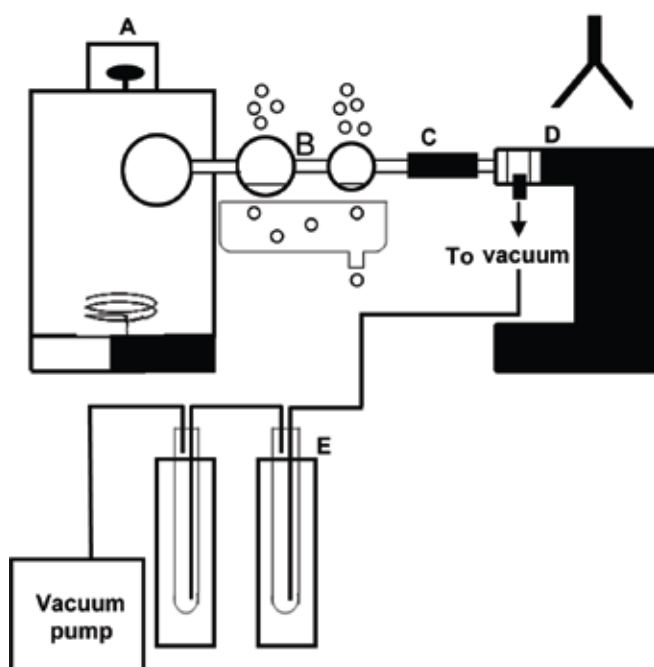
Figure 1—Kugelrohr short-path distillation apparatus (A, heated air-bath; B, receiving flasks; C, joint connection and a hose connector; D, motor drive; E, traps).

The wood was milled to a powder with particle size between 0.1 and 0.2 mm and a moisture content of 8%. Chemically pure 85% phosphoric acid was used for impregnation in some tests.

Pyrolysis Apparatus

The pyrolysis of wood samples was carried out in a Kugelrohr short-path distillation apparatus (Sigma-Aldrich Corporation, St. Louis, Missouri; Fig. 1). The sample weight was 3 g for each trial. The vacuum pressure was controlled at 0.93 kPa. The thermal treatment was performed in the range of 275 to 350 °C. The duration of the pyrolysis process varied from 30 min (for 350 °C) to 1 h (for 275, 300, and 325 °C). The end product, char, was collected in the first flask, and the tar was collected in two consecutively connected receiving flasks (B) and condensed with ice water (0 °C) for further analyses. The distillate was condensed with dry ice–acetone at –70 °C in the first trap (E). Two replicates for pyrolysis of wood samples were run at each temperature.

Gas Chromatography Analysis

Qualitative tar analysis was performed using a Hewlett Packard G1800B GCD mass spectrometer system (Hewlett Packard, Wilmington, Delaware) with a DB-1701 (J&W) capillary column (Essex Scientific Laboratory Supplies, Ltd., Essex, England; 60 m × 0.25 mm i.d., 0.25 µm film thickness). Quantitative tar analysis was performed on a Hewlett Packard HP 6890 series gas chromatography (GC) flame ionization system using a DB-1701 (J&W) capillary column (60 m × 0.25 mm i.d., 0.25 µm film thickness). Fluoranthene was used as an internal standard. Two rep-

licates for each sample were injected for the quantitative analysis.

^{31}P NMR Analysis of Tar

^{31}P nuclear magnetic resonance (NMR) spectra were obtained on a Bruker 00MHz/67MM NMR spectrometer (Bruker Corporation, Billerica, Massachusetts). Preparation of solvents and derivatizing reagent followed the procedure described by Granata and Argyropoulos (1995). For the tar phosphitylation step, 30 mg of tar was weighed and then dissolved in the solvent mixture of 400-µl pyridine and 250-µl $CDCl_3$. For the quantitative analysis of LG with ^{31}P NMR, baseline corrections were made after running phase and calibration steps for the spectra.

Metal Analysis

The metal (Cr and Cu) contents of CCA-treated wood and pyrolysis char were determined on a PerkinElmer 2380 atomic absorption spectrometer (PerkinElmer Life and Analytical Sciences, Inc., Waltham, Massachusetts). The As content of CCA-treated wood and pyrolysis char was analyzed by inductively coupled plasma (ICP) spectrometry using a PerkinElmer Optima 2000DV. The samples for metal analysis were prepared according to the reflux method provided by Helsen and others (1997). The concentrations of Cr, Cu, and As in CCA-treated wood were 0.45%, 0.27%, and 0.44%, respectively.

Pyrolysis of Microcrystalline Cellulose

Avicel microcrystalline cellulose (MCC; PH-105; 20-µm average particle size; FMC BioPolymer Corporation, Princeton, New Jersey) was pyrolysed in the Kugelrohr short-path distillation apparatus (350 °C, 30 min). The tar was collected in two sequentially connected receiving flasks. Pure LGO was obtained by separating the tar with Combi-Flash chromatography (254 nm UV wavelength; Teledyne Isco, Inc., Lincoln, Nebraska). Pure levoglucosenone was confirmed by GC-MS, and ^{1}H, ^{13}C, and ^{31}P NMR.

Impregnation Studies with Phosphoric Acid

Solutions of phosphoric acid in methanol were prepared and mixed with untreated wood and CCA-treated wood (wood/ acid solution = 1:5) to obtain 2%, 4%, 5%, and 6% phosphoric acid based on weight of dry wood. The methanol was evaporated under vacuum, and the impregnated material was dried over a phosphorous pentoxide desiccator under vacuum. The thermal treatment was carried out at 350 °C for 30 min.

Materials for the Metal Salt Study

Southern Pine wood was milled repeatedly to particle sizes between 0.1 and 0.2 mm. The moisture content of the wood samples was 8%, as determined by oven-drying. Before pyrolysis, the milled wood was oven-dried in a vacuum oven at 40 °C until a constant weight was obtained.

Table 1—pH values of metal pre-treatment solutions for wood

Pre-treatment solutions	$K_2Cr_2O_7$	CrO_3	$CrO_3 + CuSO_4$	$CuSO_4$
pH value	3.9	1.8	1.8	3.7
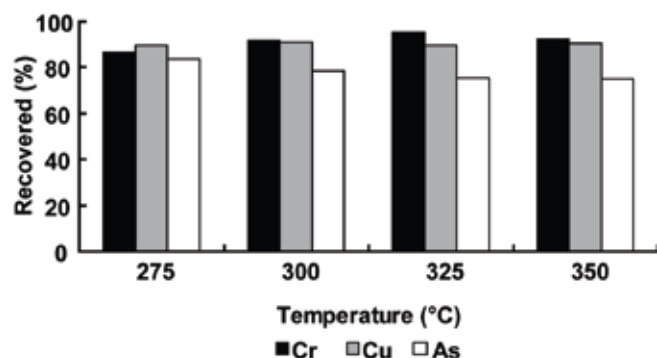
Figure 2—Recovery percentages of Cr, Cu, and As in pyrolysis char from CCA-treated wood.

Pretreatment of Wood with Metal Compounds

The wood powder (12 g) was immersed in aqueous solutions of 0.05 M metal salt ($CuSO_4 \cdot 5H_2O$, $K_2Cr_2O_7$), CrO_3 acid, or a 0.05 M CrO_3 + 0.024 M $CuSO_4 \cdot 5H_2O$ mixture. A vacuum was applied to remove air from the flasks and ensure saturation of the wood powder. The mixture was then filtered to recover the treated wood powder. The treated samples were then washed with deionized water to remove any of the metal compounds that were not bound to the wood powder. After being washed by deionized water, the products were air dried. $CuSO_4$- and CrO_3-treated MCC was also prepared with the same pretreatment method. The pH values of the pretreatment solutions are listed in Table 1.

Gravimetric Analysis

Thermogravimetric analysis (TGA) was carried out using a TGA Q500 Instrument (TA Instruments, New Castle, Delaware). Air-dried wood powder with a particle size between 0.1 and 0.2 mm was used in this study. The wood powder sample, weighing approximately 10–15 mg, was introduced into a platinum sample pan and heated following a preset temperature profile ramping procedure. For the ramping procedure, samples were heated at a constant rate from room temperature to the final temperature. Inert pyrolysis of wood powder was performed in nitrogen at heating rates of 5 and 50 °C/min. Combustion was carried out in air at heating rates of 5 and 50 °C/min. Compressed gas cylinders were used to supply air and nitrogen at 60 ml/min.

Results and Discussion

1. Quantification of Tar Products from Pyrolysis of CCA-treated Wood and Untreated Wood

Yields of 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 tar, distillate, and char) from pyrolysis was around 90% at temperatures between 300 and 350 °C. The yields of the pyrolysis tar from CCA-treated wood were similar to those from untreated wood. Higher yields of tar were obtained at higher temperatures. Correspondingly, the yields of char were found to decrease as the temperature increased from 275 to 325 °C, indicating that more raw material was turned into tar products. The recovery percentages of Cr, Cu, and As in the pyrolysis char from CCA-treated wood are presented in Figure 2. Most Cr and Cu accumulated in the char at different pyrolysis temperatures and duration times. Temperature appeared to have the greatest effect on recovery of arsenic from the char. Approximately 16% of the arsenic was released when CCA-treated wood was pyrolysed at 275 °C for 1h. With the increase of pyrolysis temperature to 350 °C for 30 min, the arsenic release increased to approximately 25%. Similar observations have also been reported by Helsen and Van den Bulck (1997), who studied the release of metals during the pyrolysis of CCA-treated wood. The recoveries of Cr, Cu, and As in pyrolysis char from the CCA-treated wood pretreated with 4% H_3PO_4 were 82.7%, 87.5%, and 74.5%, respectively.

The quantified tar products are listed in Table 3. Although the tar compositions are qualitatively similar, quantitative differences appear to exist between yields from untreated and CCA-treated wood, with some compounds having greater yields for the CCA-treated wood.

A typical ^{31}P NMR spectrum for quantitative analysis of tar from the pyrolysis of CCA-treated wood is shown in Figure 3. In this spectrum, the integration ranges for the different

Table 2—Yields of pyrolysis fractions of untreated and CCA-treated wood (weight percentage based on water-free wood)

Fractions	275 °C		300 °C		325 °C		350 °C	
	CCA	Untreated	CCA	Untreated	CCA	Untreated	CCA	Untreated
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
Char	73.6	73.3	46.3	52.8	30.6	28.2	30.2	28.5
Total recovery	96.1	95.5	92.2	92.7	89.4	86.3	92.5	91.1

Table 3—Yields of tar compounds from pyrolysis of untreated and CCA-treated wood (weight percentage based on water-free tar)

Compound name	275 °C		300 °C		325 °C		350 °C	
	CCA	Untreated	CCA	Untreated	CCA	Untreated	CCA	Untreated
Hydroxyacetaldehyde	0.63	1.44	1.75	5.47	1.80	4.42	1.34	3.07
Acetic acid	0.80	1.05	1.72	1.86	1.67	1.67	1.92	1.87
Hydroxyacetone	0.52	0.83	0.74	1.57	0.72	1.37	0.75	1.36
2-Furaldehyde	0.21	0.26	0.58	0.40	0.68	0.31	0.70	0.34
Furfuryl alcohol	0.09	0.43	0.08	0.76	0.12	0.56	0.11	0.37
Furan- (5H)-2-one	0.22	0.51	0.41	1.39	0.44	1.20	0.40	1.10
Phenol	0.03	0.02	0.03	0.03	0.04	0.03	0.04	0.04
Guaiacol	0.12	0.13	0.47	0.40	0.54	0.39	0.60	0.41
o-Cresol	0.02	0.03	0.06	0.07	0.06	0.07	0.06	0.05
p-Cresol	0.05	0.06	0.05	0.06	0.06	0.07	0.07	0.07
Levoglucosenone	0.50	0.36	1.37	0.56	1.19	0.28	0.87	0.19
4-Methyl guaiacol	0.22	0.29	0.41	0.61	0.55	0.64	0.59	0.65
2, 4-dimethyl phenol	0.14	0.15	0.20	0.25	0.17	0.22	0.09	0.13
4-Ethyl-guaiacol	0.05	0.08	0.07	0.09	0.09	0.10	0.10	0.12
Eugenol	0.18	0.22	0.25	0.30	0.23	0.23	0.21	0.22
5-(hydroxy-methyl)-furaldehyde-(2)	1.66	1.83	2.21	1.41	2.03	1.12	2.01	0.99
Catechol	0.42	0.63	0.46	0.67	0.43	0.63	0.42	0.62
Isoeugenol	0.34	0.69	0.39	0.90	0.38	0.58	0.36	0.51
Vanillin	0.39	0.65	0.46	0.52	0.38	0.41	0.33	0.35
Acetoguaiacone	0.31	0.41	0.25	0.30	0.22	0.24	0.20	0.23
Guaiacyl acetone	0.49	0.81	0.38	0.55	0.34	0.42	0.36	0.45
Levoglucosan	8.14	0.98	12.88	1.57	13.90	3.77	14.66	4.86
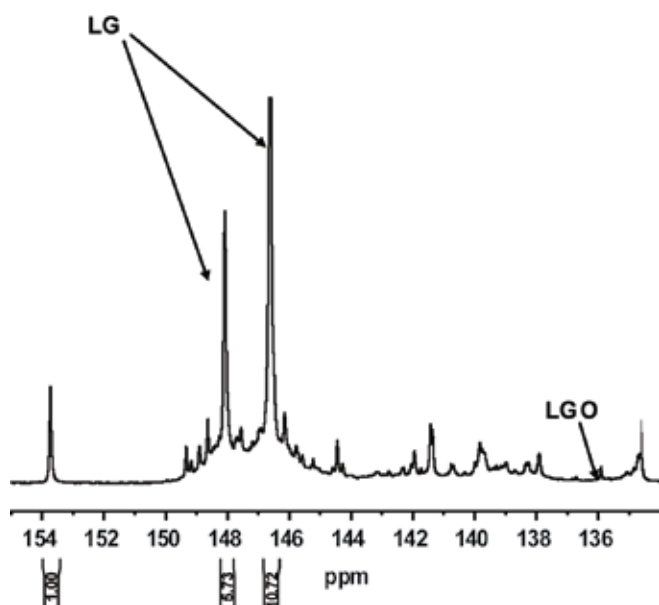
Figure 3—^{31}P nuclear magnetic resonance (NMR) spectrum of tar from pyrolysis of CCA-treated wood. LG is levoglucosan and LGO is levoglucosenone.

groups are as follows: total aliphatic –OH groups, 149.6–145.0 ppm; total phenolic –OH group (except one peak at 141.3 ppm), 143.8–137.4 ppm; total –COOH group, 135.5–134.3 ppm. The internal standard N-hydroxynaphthalimide gives a sharp signal at 153.8 ppm. Two sharp signals around 148.1 and 146.6 ppm are assigned to the phosphitylated hydroxyls from levoglucosan (LG). After integration with the internal standard, the relative intensities of these two signals are around 1:2. There are three hydroxyl groups in one LG unit. Thus, one signal at 148.1 ppm in the spectrum comes from the –OH group on C-2. Another signal at 146.6 ppm comes from the –OH groups on C-3 and C-4. Levoglucosenone (LGO) gives rise to a small signal at 135.8 ppm. ^{31}P NMR of pure levoglucosan and levoglucosenone 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 4. 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 qualitative ^{31}P NMR spectrum of tar from pyrolysis of microcrystalline cellulose is shown in Figure 5. In comparison to the wood samples, few signals are present in the MCC
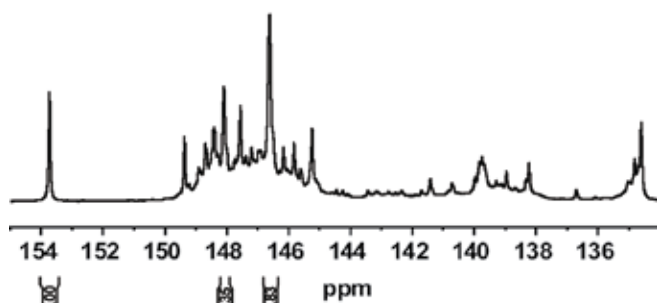
5

Figure 4—[31]P nuclear magnetic resonance (NMR) spectrum of tar from pyrolysis of untreated wood.
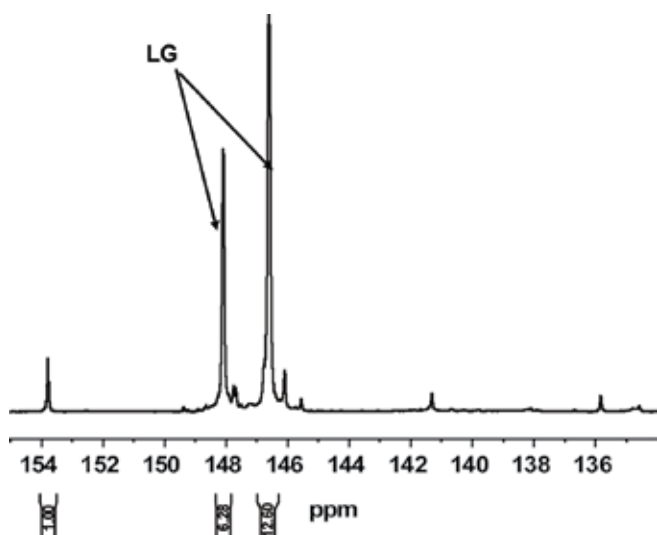

Figure 5—[31]P nuclear magnetic resonance (NMR) spectrum of tar from pyrolysis of microcrystalline cellulose. LG is levoglucosan.
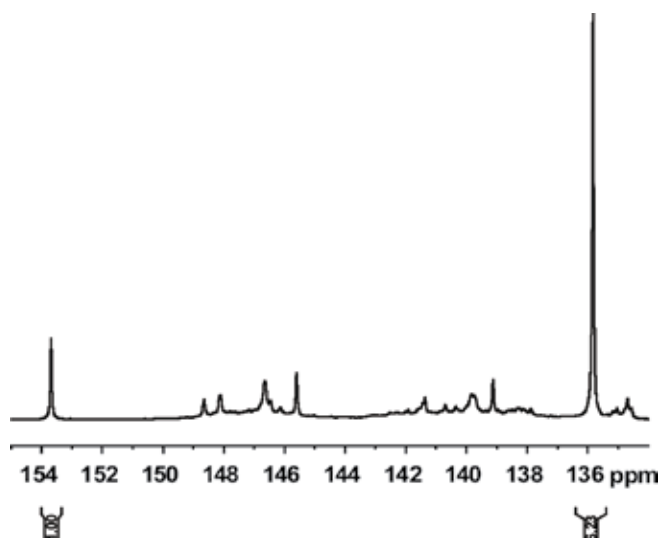

Figure 6—[31]P nuclear magnetic resonance (NMR) spectrum of tar from pyrolysis of untreated wood (pretreated with 4% H_3PO_4).

Table 4—Yield of levoglucosenone from ^{31}P NMR and gas chromatography with flame ionization detection (GC-FID) analysis. Weight percentage is based on water-free tar.

Sample (350 °C)	^{31}P NMR (%)	GC-FID (%)
CCA (no acid-treated)	0.5	0.9
CCA (2% H_3PO_4)	6.2	7.2
CCA (4% H_3PO_4)	22.3	20.8
Untreated (no acid treated)	0.1	0.2
Untreated (2% H_3PO_4)	18.5	18.4
Untreated (4% H_3PO_4)	24.8	24.7

Table 5—Quantitative analysis of levoglucosan with ^{31}P NMR and gas chromatography with flame ionization detection (GC-FID) analysis (weight percentage based on water-free tar)

Sample	^{31}P NMR (%)	GC-FID (%)
CCA (350 °C)	14.0	14.6
CCA (325 °C)	13.3	13.9
CCA (300 °C)	12.2	12.9
Untreated (350 °C)	4.1	4.8
Untreated (325 °C)	3.9	3.8

spectrum. A large amount of total aliphatic alcohols are generated, including LG, hydroxyacetaldehyde, hydroxyacetone, furfural, and furfuryl alcohol. The source of the small signal at 141.3 ppm in all three spectra has not been confirmed yet, but its presence in the MCC spectrum may indicate this peak comes from carbohydrate-derived degradation products.

A typical ^{31}P NMR spectrum of tar from pyrolysis of untreated wood pretreated with 4% H_3PO_4 is shown in Figure 6. The strong signal at 135.8 ppm shows that the yield of levoglucosenone increased drastically as a result of the H_3PO_4 treatment, whereas the reduction in signals at 148.1 and 146.6 ppm shows that the yield of levoglucosan decreased. Phosphoric acids as catalysts change the depolymerization and dehydration mechanisms during pyrolysis, which promotes the formation of LGO converted from LG.

For quantitative analysis, the amount of LGO and LG can be directly obtained by the integration with the internal standard. The results are shown in Tables 4 and 5. Quantities of LG and LGO determined by ^{31}P NMR were very similar to those determined by gas chromatography with flame ionization detection (GC-FID) analysis.

The functional group content of pyrolysis tar is shown in Table 6. Pyrolysis tar from CCA-treated wood contains a greater amount of total aliphatic alcohols than does 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 attribut-

Table 6—Functional group content of pyrolysis tar from untreated and CCA-treated wood by quantitative ^{31}P NMR (mmol/g based on water-free tar)

Functional group	Integrated chemical shift range (ppm)	300 °C		325 °C		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	0.77	0.86	0.75	0.98	0.90	0.94
Non-condensed 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

Table 7—Yields of pyrolysis fractions of untreated wood pretreated with H_3PO_4 and CCA-treated wood at 350 °C (weight percentage based on dry wood)

Fractions	No pretreatment		2% H_3PO_4		4% H_3PO_4		5% H_3PO_4		6% H_3PO_4	
	CCA	Untreated	CCA	Untreated	CCA	Untreated	CCA	Untreated	CCA	Untreated
Tar	57.7	59.6	40.7	36.4	36.3	19.1	26.3	13.8	20.3	12.1
Distillate	4.6	3.0	14.7	18.0	13.2	26.6	20.1	24.6	25.6	29.8
Char	30.2	28.5	34.7	40.9	41.3	49.8	43.7	49.3	46.2	52.0
Total recovery	92.5	91.1	90.1	95.3	90.8	95.5	90.1	87.7	92.1	93.9

able to a large amount of levoglucosan produced from CCA-treated wood. A comparison of quantities of condensed, non-condensed, and total phenols shows that thermal degradation of untreated wood produced a high amount of phenols. For example, a comparison of the non-condensed 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 non-condensed phenolic groups. The GC-FID analysis supports the increase in phenols. The non-condensed 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 non-condensed phenolic units of tar is higher than that of the condensed phenolic units, which indicates that most lignin-derived products are monomeric phenols. This can be rationalized on the basis that pyrolysis of lignin is known to cause cleavage of aryl glycerol ß-O-4 structures (Evans and others 1986). Their cleavage will result in the concomitant increase of the free phenolic hydroxyl content of the lignin. There is no obvious difference in the amount of total –COOH groups between untreated wood and its corresponding CCA-treated wood.

2. Pyrolysis of CCA-Treated Wood in the Presence of Phosphoric Acid

Various additives have been investigated to change the pyrolysis product distribution and convert cellulosic materials to value-added products. Acid catalysts are known to promote dehydration reactions and favor the formation of LGO. Phosphoric acid, in particular, has proved to be an efficient catalyst to enhance the yield of LGO from the pyrolysis of

cellulosic materials (Dobele and others 1999, 2001, 2003). Because LGO was detected through the thermal degradation of cellulose in the presence of acidic additives such as phosphoric acid (Halpern and others 1973), this research area has attracted much interest. Phosphoric acid is less damaging to cellulose than are other mineral acids (Dobele and others 1999) and it has lower volatility than sulfuric acid or hydrochloric acid (Shafizadeh and others 1979b). It is also well known for its swelling properties, resulting in easier penetration into interfibrillar reaction centers (Akim 1984). During pyrolysis, phosphoric acid can change the depolymerization and dehydration mechanisms of cellulose. Many researchers (Kaur and others 1987a,b; Jain and others 1987; Kishore and Mohandas 1982; Kennedy and others 1996) have observed that the presence of phosphoric acid in cellulosic materials lowered decomposition temperatures, suppressed volatiles production, and increased char yields.

Yields of 350 °C pyrolysis fractions for untreated wood and CCA-treated wood pretreated with phosphoric are shown in Table 7. The total recovery (the sum of the yields of tar, distillate, and char) from pyrolysis was around 90%. The introduction of phosphoric acid to wood results in a considerable change in the thermal decomposition mechanism, as demonstrated by a decrease in the amount of volatile products (Fig. 7). The amount of tar obtained from pyrolysis of CCA-treated wood was higher than that obtained from untreated wood, from which it may be concluded that the CCA treatment accelerated formation of tar. Correspondingly, the amount of char increased with the increase in the concentration of phosphoric acid (Fig. 8). This demonstrates that the impregnation of wood powder with phosphoric acid
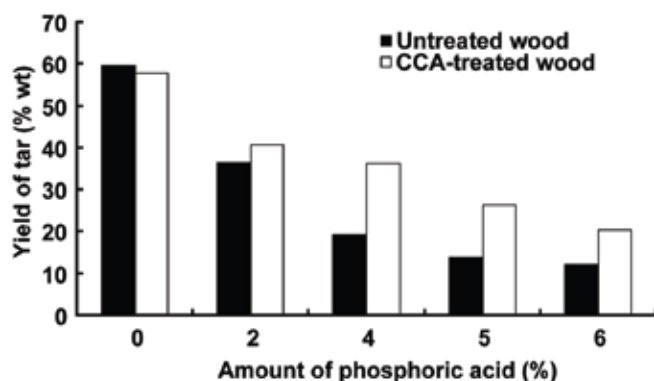
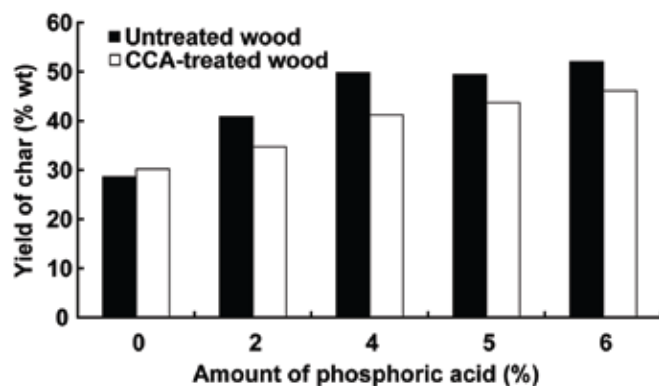**Figure 7—Yield of tar from untreated wood and CCA-treated wood pretreated with H_3PO_4.**

Figure 8—Yield of char from untreated wood and CCA-treated wood pretreated with H_3PO_4.

promotes dehydration reactions resulting in the formation of condensed structures, which cannot, therefore, degrade further to monomeric volatile products (Dobele and others 1999). Taylor and others (2001) reported that metal ions in CCA-treated wood could be extracted by phosphoric acid. This is also one of the options for recycling the CCA components when managing CCA-treated wood waste (Helsen and Van den Bulck 2005). In our study, the same amount of phosphoric acid was used to pretreat untreated and CCA-treated wood. It is likely that a portion of metal ions were removed by phosphoric acid, which would consume some phosphoric acid. Thus, less acid may have been available to further react with CCA-treated wood material compared with untreated wood. Dehydration reactions would then be reduced compared with those for untreated wood. This may explain why the formation of condensed structures in CCA-treated wood was less than that in untreated wood, and why the char observed from CCA-treated wood was less than that from untreated wood.

The quantified pyrolysis tar products from untreated wood and CCA-treated wood pretreated with phosphoric acid are listed in Table 8. The LG yield reached a maximum for both wood materials at the addition of 2% H_3PO_4. For CCA-treated wood, the amount of LG increased to 17.5%

and then decreased to 0.6% (based on water-free tar) as the phosphoric acid content rose from 0% to 6%. The untreated wood showed a similar trend in the yield of LG. Other researchers previously report that LGO is the main product of catalytic depolymerization resulting from the dehydrated glucopyranose cycles (Dobele and others 1999). In the present study, yields of LGO rose and reached a maximum of 26.4% (based on water-free tar) for untreated wood pretreated with 4% phosphoric acid. For CCA-treated wood, the amount of LGO increased from 0.9% to 22.3% (based on water-free tar) as the phosphoric acid content rose to 6%.

Acid extraction of CCA components from treated wood has been explored in previous studies, demonstrating that both organic and mineral acids can solubilize various fractions of CCA components. Several studies investigated the extraction of CCA components with organic acids such as citric acid, acetic acid, formic acid, oxalic acid, and malic acid (Cooper 1991, Pasek and McIntyre 1993, Knzi and Cooper 1998, Stephan and others 1993) and mineral acids such as sulfuric, hydrochloric, nitric, and phosphoric acids (Pasek and McIntyre 1993, Honda and others 1991, Stephan and others 1993, Taylor and others 2001, Kakitani and others 2004). Treatment with phosphoric acid can result in relatively high copper leaching and slight extraction of chromium and arsenic (Taylor and others 2001). Kakitani and others (2004) also showed that 0.5 N phosphoric acid can extract 24% Cr, 65% Cu, and 44% As from CCA-treated wood exposed at 25 °C for 1 h. In addition, higher concentrations of phosphoric acid removed the elements more efficiently than did lower concentrations. Thus, in our study, it is likely that the initial addition of phosphoric acid removed some Cu, Cr, and As from CCA-treated wood, although the metal analysis indicates that most of the removed metals remained in the char. The yield of LGO for CCA-treated wood may have been lower at the initial addition of phosphoric acid because of the extraction of the metals. Subsequently, the coordination of metal ions by the phosphoric acid increased the yield of LGO up to 22.3%. Because the yield of tar decreased with the addition of phosphoric acid (Fig. 7), the yield of LGO (based on dry wood) for untreated wood decreased. But for CCA-treated wood, the yield of LGO (based on dry wood) increased until it leveled off at 3.4%.

3. Understanding Pyrolysis of Wood Pretreated with Metal Compounds

The effects of metal salts on pyrolysis of wood and cellulose have been studied extensively (Halpern and Patai 1969, Madorsky and others 1956, Fug and others 1972, Richards and others 1983, Müller-Hagedorn and others 2003). The presence of different sodium salts during thermal decomposition has been shown to substantially lower the activation energy of the overall thermal decomposition process; the amount of char is increased and the LG-forming reactions are suppressed. Researchers have proposed that the salts catalyzed the dehydration of cellulose by scission of the C-O bonds

Table 8—Yields of tar compounds from pyrolysis of untreated wood pretreated with H_3PO_4 and CCA-treated wood (weight percentage based on water-free tar)

Compound name	No pretreatment		2% H_3PO_4		4% H_3PO_4		5% H_3PO_4		6% H_3PO_4	
	CCA	Untreated	CCA	Untreated	CCA	Untreated	CCA	Untreated	CCA	Untreated
Hydroxyacetaldehyde	1.34	3.07	0.35	0.31	0.27	0.19	0.19	0.17	0.16	0.15
Acetic acid	1.92	1.87	0.49	0.83	0.36	0.29	0.91	0.31	0.99	0.22
2-Furaldehyde	0.70	0.34	0.27	0.49	0.24	0.14	0.43	0.08	0.35	0.06
Furan- (5H)-2-one	0.40	1.10	0.14	0.14	0.13	0.12	0.14	0.15	0.17	0.13
Phenol	0.04	0.04	0.05	0.05	0.05	0.05	0.05	0.06	0.07	0.05
Guaiacol	0.60	0.41	0.23	0.24	0.25	0.22	0.24	0.20	0.30	0.18
Levoglucosenone	0.87	0.19	8.17	17.73	14.14	26.40	18.29	22.74	22.25	22.94
Levoglucosenone[a]	0.40	0.07	2.93	4.67	3.49	3.28	3.46	1.72	3.33	1.71
2, 4-dimethyl phenol	0.09	0.13	0.10	0.08	0.08	0.08	0.07	0.11	0.07	0.12
4-Ethyl-guaiacol	0.10	0.12	0.07	0.06	0.07	0.06	0.08	0.08	0.08	0.08
Eugenol	0.21	0.22	0.09	0.10	0.10	0.13	0.11	0.16	0.12	0.18
5-(hydroxymethyl)-furaldehyde-(2)	2.01	0.99	1.13	1.08	0.83	1.19	0.76	1.30	0.71	1.12
Isoeugenol	0.36	0.51	0.11	0.11	0.05	0.03	0.03	0.05	0.03	0.05
Vanillin	0.33	0.35	0.27	0.18	0.38	0.25	0.24	0.34	0.24	0.35
Acetoguaiacone	0.20	0.23	0.16	0.06	0.11	0.08	0.10	0.11	0.07	0.13
Guaiacyl acetone	0.36	0.45	0.26	0.23	0.24	0.36	0.23	0.44	0.23	0.48
Levoglucosan	14.66	4.86	17.46	9.41	7.23	2.80	2.77	0.37	0.62	0.61
Levoglucosan[a]	6.77	1.88	6.26	2.48	1.79	0.35	0.52	0.03	0.09	0.05

[a] Percentage based on dry wood.

of cellulose, resulting in the destruction of the hexose units and the increase of water and char yields at the expense of LG (Halpern and Patai 1969, Madorsky and others 1956, Fug and others 1972, Richards and others 1983, Müller-Hagedorn and others 2003).

Pyrolysis of lignin in the presence of metal salts can cause significant differences in the distribution of phenolic compounds. The yield of pyrolysis products varies with different inorganic substances by pyrolyzing various wood materials and lignins (Ripley and Fung 1971, Kuroda and others 1990). Several literature accounts provide various approaches for the production of phenolic compounds in the presence of transition metals as catalysts (DiCosimo and Szabo 1988; Evans and others 1986; Watson and others 1993a,b,c; Wu and others 1994;). Wu and others (1994) found that Cu(II) and Fe(III) salts showed better selectivity for production of some guaiacyl and syringyl compounds comprising aldehyde functionalities. Mn(III) cations presented better selectivity than Co(III) cations for the oxidative degradation of lignin model compounds to benzoic acids and aromatic aldehydes (DiCosimo and Szabo 1988). Watson and others (1993a,b,c) showed that cobalt, iron, and rhodium transition metal salt complexes can effectively catalyze the production of monomeric phenols by the thermal degradation of lignin dimeric model compounds.

Transition metals can also promote pyrolysis reactions. For example, it has been reported that cupric and ferrous ions

favored tar formation and that the highest yield of LG can be obtained from ferrous-treated wood samples (Richards and Zheng 1991). Shafizadeh and others (1978) studied the effect of inorganic substances on cellulose pyrolysis using differential thermal analysis (DTA), thermogravimetric (TG), and thermal evolution analysis (TEA). They reported that pure cellulose rapidly degraded within the 325 to 375 °C temperature range. But the addition of $ZnCl_2$ to cellulose would lower the onset temperature of pyrolysis at about 200 °C, with a broad decomposition endotherm in the 200 to 358 °C range.

Finally, the amounts of inorganic substances (K, Ca, and Mg) in natural wood are between 0.2% and 0.5% (Fengel and Wegener 1984). When wood samples are washed by acid to remove the inorganics before pyrolysis, the yield of LG can be enhanced dramatically (Shafizadek and others 1979a, Piskorz and others 1989), and the char yield can also be reduced (DeGroot and Shafizadek 1984).

We have demonstrated that the CCA treatment of wood has a significant effect on the amount of main carbohydrate-derived degradation products. Thus, it is necessary to understand how CCA preservatives influence the distribution and yields of the pyrolysis products. Do the metal ions (chromium and copper) contribute to the influence individually, or is the coordination of these two metal compounds key to the pyrolysis process? In this study, we examine the influence of some metal compounds ($CuSO_4$, $K_2Cr_2O_7$, and

Table 9—Concentration of Cr and Cu in pretreated raw materials

Pretreated samples	Chromium (%)	Copper (%)
$K_2Cr_2O_7$	0.23	—
CrO_3	2.49	—
$CrO_3 + CuSO_4$	1.71	0.002
$CuSO_4$	—	0.21
Cu-MCC	—	0.03
Cr-MCC	0.08	—
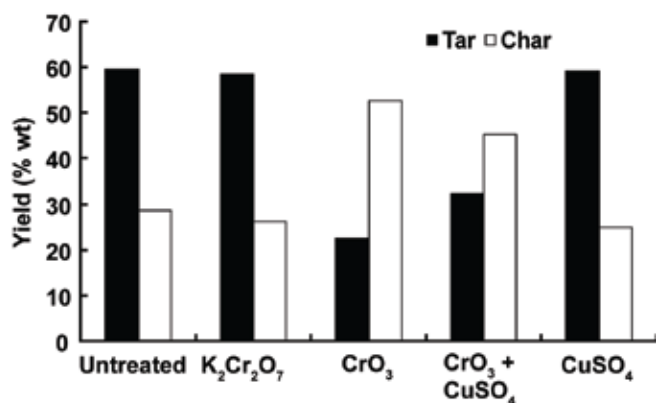
Figure 9—Yields of tar and char from pyrolysis of wood pretreated with metal compounds.

CrO_3) on the pyrolysis of pretreated Southern Pine wood, as to our knowledge this work has not been done previously. These metal compounds are selected from the prescribed formula for waterborne CCA preservatives (AWPA 1999). In addition, ^{31}P NMR was applied to elucidate the structure of pyrolysis tar for untreated and pretreated wood.

The percentages of Cr and Cu content in the pretreated wood test samples are listed in Table 9. Wood powder pretreated with 0.05 M $CuSO_4$ solution contained 0.21% Cu ions, which was similar to the Cu concentration (0.27%) in the commercially prepared treated wood. Thus, in our study, 0.05 M metal compound solutions were selected to pretreat Southern Pine wood powder, and the pyrolysis results were compared with those from commercially prepared CCA-treated wood. As can be seen from Table 10, the Cr concentration was 2.49% in the CrO_3-treated wood and 1.71% in the $CrO_3 + CuSO_4$-treated wood, which was higher than the Cu concentration in the pretreated wood. This result

indicates that the Cr ion is more easily absorbed by the wood.

Yields of pyrolysis fractions (at 350 °C) of pretreated wood and MCC are shown in Table 10. Figure 9 shows the yields of tar and char from pyrolysis of pretreated wood. The total recovery (the sum of the yields of tar, distillate, and char) from pyrolysis of pretreated wood was around 90%. The yields of pyrolysis tar from $K_2Cr_2O_7$-treated wood and $CuSO_4$-treated wood were similar to that from untreated wood. Correspondingly, the yields of char from pretreated wood were found to be close to that from untreated wood. For CrO_3- and $CrO_3 + CuSO_4$-treated wood, however, the char yields were quite different. The yields of tar decreased drastically, while the yields of char increased to around 50% (Fig. 9). Chromic acid treatment has been used to improve wood surface properties, and it has been reported that chromic acid-modified wood exhibits greatly improved water repellency, better mildew resistance, and reduced extractives staining (Rak 1975, Williams and Feist 1985, Feist 1983). Chromic acid causes chemical changes in the surface of wood (Williams and Feist 1984). The fixation of chromium(VI) trioxide results from the formation of insoluble complex salts that coordinate with free hydroxyls in the carbohydrates and lignin (Duncalf and Dunn 1964, Van Nice and Farlee 1976, Bravar and others 1973). Because these hydroxyls are unavailable for hydrogen bonding with water, the wood has greater water repellency and dimensional stability (Williams and Feist 1985). Furthermore, this altered chemistry would result in the formation of condensed structures during the pyrolysis process. Cellulose and lignin cannot degrade further to small molecule volatile products. Thus, in our trial, the yields of tar decreased, whereas the yields of char increased.

Cr-treated MCC also showed similar results, with low yield of tar and high yield of char. The quantified pyrolysis tar products from untreated wood and its metal compound pretreated wood counterpart are listed in Table 11. As can be seen from this table, the quantitative analysis of tar compounds indicates a substantial difference between untreated and pretreated wood. A large amount of tar fraction comes from carbohydrate thermal degradation. The yield of carbohydrate-derived products varied considerably with treatment of different metal compounds. The amount of LG increased drastically when wood samples were treated by $CuSO_4$ and $K_2Cr_2O_7$ solution, which was around three and five times

Table 10—Yields of pyrolysis fractions of pre-treated wood and microcrystalline cellulose (MCC) at 350 °C (weight percentage based on water-free raw material)

Fractions	Untreated	$K_2Cr_2O_7$	CrO_3	$CrO_3 + CuSO_4$	$CuSO_4$	MCC	Cu-MCC	Cr-MCC
Tar	59.6	58.5	22.6	32.2	59.1	83.1	74.4	64.6
Distillate	3.0	10.5	14.0	16.0	4.4	3.2	4.4	8.1
Char	28.5	26.3	52.6	45.3	25.0	6.8	7.7	11.9
Total recovery	91.1	95.3	89.2	93.5	92.8	93.1	86.5	84.6

Table 11—Yields of tar compounds from pyrolysis of pre-treated wood (weight percentage based on water-free tar)

Compound name	Untreated	$K_2Cr_2O_7$	CrO_3	$CrO_3 + CuSO_4$	$CuSO_4$
Hydroxyacetaldehyde	3.07	0.51	0.14	0.14	0.64
Acetic acid	1.87	0.60	1.51	1.59	1.32
Hydroxyacetone	1.36	0.08	nd[a]	nd	0.25
2-Furaldehyde	0.34	0.32	0.23	0.22	0.32
Furfuryl alcohol	0.37	0.01	nd	nd	0.08
Furan-(5H)-2-one	1.10	0.11	0.26	0.27	0.16
Phenol	0.04	0.04	0.06	0.08	0.06
Guaiacol	0.41	0.30	0.19	0.22	0.35
p-Cresol	0.07	0.03	0.04	0.05	0.05
Levoglucosenone	0.19	0.98	2.69	2.51	0.43
4-Methyl guaiacol	0.65	0.29	0.08	0.09	0.45
2, 4-Dimethyl phenol	0.13	0.08	0.06	0.06	0.05
4-Ethyl-guaiacol	0.12	0.09	0.06	0.07	0.10
Eugenol	0.22	0.09	0.03	0.05	0.10
5-(hydroxy-methyl)-furaldehyde-(2)	0.99	1.10	0.54	0.57	0.88
Catechol	0.62	0.47	0.50	0.56	0.63
Isoeugenol	0.51	0.16	nd	nd	0.10
Vanillin	0.35	0.28	0.30	0.31	0.20
Acetoguaiacone	0.23	0.13	0.23	0.19	0.13
Guaiacyl acetone	0.45	0.19	0.09	0.13	0.14
Levoglucosan	4.86	26.73	0.60	2.38	14.34

[a] nd is not detected.

higher, respectively, than that from untreated wood. This is also in agreement with the similar results of commercially prepared CCA-treated wood. The LG yield from CCA-treated wood was around three times higher than that from untreated wood.

The amount of LGO from CrO_3-treated wood was 14 times higher than that from untreated wood. The pyrolysis of wood pretreated with $K_2Cr_2O_7$ solution can also produce an increased yield of LGO (up to 1%). In earlier tests, the amount of LGO from CCA-treated wood was 0.87%, which was also greater than that from untreated wood. The increased yield of LGO may be related to the acid conditions of the pretreated metal compound solutions. According to the waterborne preservatives standard, the pH of CCA-Type C preservative solutions shall be within 1.6–2.5 limits (AWPA1999). If a CCA-treating solution has a pH value outside the stated limits, it can be made to conform by adding CCA concentrate or chromic acid. The pH values of pretreated solutions are in the acidic range. CrO_3 solution is an especially strong acid solution. Based on a proposed mechanism for the acid-catalyzed transformation of LG to LGO (Halpern and others 1973), it is understandable that greater yield of LGO can be obtained from pyrolysis of wood pretreated with CrO_3 solution.

In contrast, the metal compounds treatment did not promote the formation of hydroxyacetaldehyde, hydroxyacetone,

furfuryl alcohol, and furan-(5H)-2-one. This is similar to the effect observed for the CCA treatment. The quantified pyrolysis tar products from pretreated MCC are listed in Table 12. As can be seen from this Table, the Cu and Cr treatment did not increase the yield of all of the cellulose degradation products, including LG. This shows that the catalysis of LG formation by metal ions may involve some interaction with lignin. Richards and Zheng (1991) noted previously that some transitional metal ions have the ability to form complexes with phenols and interact with lignin in wood, which decreases the interference by lignin in the conversion of cellulose to LG.

The functional group content of pyrolysis tar from pretreated wood is shown in Table 13. Pyrolysis tar from $K_2Cr_2O_7$-treated and $CuSO_4$-treated wood contained higher amounts of total aliphatic alcohols compared to the untreated wood, which was attributable to a large amount of LG produced from pretreated wood. CrO_3-treated wood produced few aliphatic alcohols, which was due to the conversion of LG to LGO in the acid conditions. From the amount of condensed and non-condensed phenols and total phenols, it can be seen that the thermal degradation of untreated wood produced a higher amount of phenols, especially non-condensed phenols. GC-FID analysis also confirmed the same results. The pyrolysis of CrO_3-treated wood produced fewer phenols. The total phenols content of tar from CrO_3-treated wood

Table 12—Yields of tar compounds from pyrolysis of pre-treated MCC (weight percentage based on water-free tar)

Compound name	MCC	Cu-MCC	Cr-MCC
Hydroxyacetaldehyde	1.16	0.13	0.11
Acetic acid	1.05	0.28	0.23
Hydroxyacetone	0.59	0.05	0.04
2-Furaldehyde	0.76	0.10	0.14
Furfuryl alcohol	0.09	0.01	0.01
Furan-(5H)-2-one	0.44	0.11	0.08
Levoglucosenone	1.87	1.14	1.72
5-(hydroxy-methyl)-furaldehyde-(2)	1.04	0.31	0.26
Levoglucosan	40.59	34.16	29.81

Table 13—Functional group content of pyrolysis tar from pre-treated wood by quantitative ^{31}P NMR (mmol/g based on water-free tar)

Functional group	Integrated chemical shift range (ppm)	Untreated	$K_2Cr_2O_7$	CrO_3	$CrO_3 + CuSO_4$	$CuSO_4$
Aliphatic alcohols	149.6–145.0	7.08	11.03	2.00	3.39	8.72
Condensed phenols	143.8–140.2	0.94	0.96	0.72	0.89	0.76
Non-condensed phenols	140.2–137.4	1.67	0.91	0.56	0.79	0.86
Total phenols	143.8–137.4	2.61	1.87	1.28	1.68	1.82
Carboxylic acids	135.5–134.3	0.64	0.21	0.44	0.55	0.34

was 50% less than that from untreated wood. Because of the formation of complex structures between Cr and lignin, few lignin-derived products, especially non-condensed phenols, would be released during pyrolysis. The amount of total carboxylic acids of tar from untreated wood was also higher than those from pretreated wood.

4. Use of TGA to Follow the Thermal Decomposition of CCA-Treated Wood

TGA modeling of the thermal degradation of CCA-treated wood can provide an understanding of its fundamental thermal decomposition processes (Helsen and Van den Bulck 2000a,b; Kercher and Nagle 2001; Hirata and others 1993; Helsen and others 1999, 2003, 2004). Helsen and others (2000) applied TG analysis to study arsenic model compounds (pure arsenic oxides) and derived a kinetic scheme for the pyrolysis of CCA-treated wood (Helsen and Van den Bulck 2000a). Kercher and others (2001) created model systems with simple inorganic oxides to investigate the thermal decomposition of the inorganic compounds and complexes in CCA-treated wood. Kercher and others (2001) found that the thermal decomposition of inorganic oxides was strongly affected by the interaction with wood decomposition products. The highly reducing environment created by the inert pyrolysis of CCA-treated wood can cause arsenic volatilization below 400 °C and copper(II) oxide reduction at 305 °C.

In the present study, we provide a comprehensive thermo-gravimetric evaluation of CCA-treated wood samples. The

thermal decomposition behaviors of Southern Pine wood and its CCA-treated equivalent were investigated at different heating rates and atmospheric compositions. The pretreatment of CCA-treated wood with phosphoric acid was evaluated by TGA. The effect of individual metal ions on pyrolysis of untreated wood was also examined. Inert pyrolysis of wood powder was performed in nitrogen at heating rates of 5 and 50 °C/min. Combustion was carried out in air at heating rates of 5 and 50 °C/min.

The TGA curves of untreated wood in air and in nitrogen are shown in Figure 10. As can be seen from this figure, the weight fraction curves are very similar for the inert pyrolysis at fast and slow heating rates. These curves showed three key stages: low-temperature volatile loss, main pyrolysis, and carbonization. In the early stage, water began to volatilize and was completely gone at 150 °C. The majority of weight loss occurred in the main pyrolysis stage, which was observed between 200 and 350 °C at a heating rate of 5 °C/min (between 200 and 400 °C at a heating rate of 50 °C/min). The carbonization stage occurred at a temperature beyond 350 °C for 5 °C/min (400 °C for 50 °C/min), with the release of remaining volatiles from the solid pyrolysis product. Finally, the char yields for inert pyrolysis were very similar (~12%) at both fast and slow heating rates.

In an air atmosphere, the initial weight loss of untreated wood was the same as in nitrogen up through 200 °C. Compared to decomposition of untreated wood in nitrogen
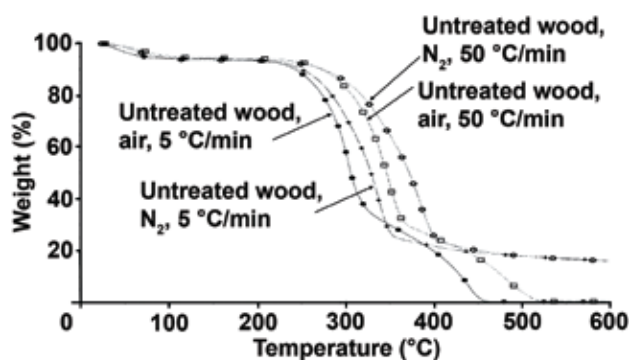
Figure 10—Thermogravimetric analysis (TGA) of untreated wood in air and in nitrogen at 5 and 50 °C/min.
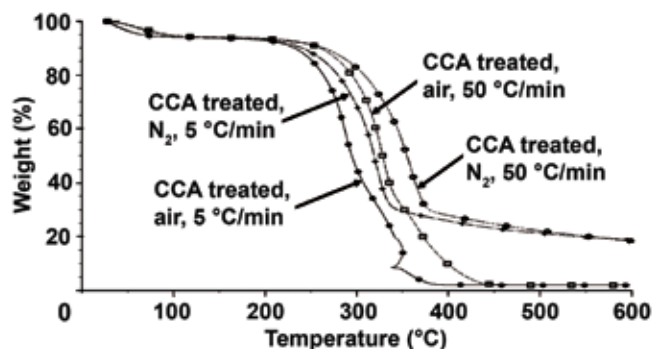

Figure 11—Thermogravimetric analysis (TGA) of CCA-treated wood in air and in nitrogen at 5 and 50 °C/min.

at 5 °C/min, the main weight loss step occurred at lower temperatures in air with the same heating rate. The same phenomenon also occurred at 50 °C/min. These results show that wood decomposition is accelerated by oxygen. Char produced after the main thermal degradation stage can be further oxidized. Finally, the char yields for combustion TGA experiments were the same (almost 0) at both fast and slow heating rates.

The experimental behavior of the CCA-treated wood in air and in nitrogen was similar to that found for untreated wood (Fig. 11). The treated wood also went through the three stages. In air, final char yields of fast and slow combustion were around 2%. This implied that some metals were left on the pan after the TGA run. Hirata and others (1993) have pointed out that almost all the chromium and copper stayed in the residue char, whereas arsenic volatilized into the gas phase. The evolved amount of arsenic increased with increasing temperature. Kercher and Nagle (2001) also showed that As_2O_5 began to volatilize at 600 °C in air or in nitrogen. The thermal decomposition of CuO can lead to the formation of Cu_2O at 800 °C. Cr_2O_3 was very stable and only underwent minor reactions in the TGA experiments.

Overall, we found that the temperature at the beginning of the main combustion for CCA-treated wood was around

150 °C at a heating rate of 50 °C/min, which was less than that for the untreated wood. After the initial weight loss step, the CCA components accelerated combustion. The temperature corresponding to the maximum rate of weight loss (T_{peak}) was around 328 °C for the CCA-treated wood sample, which was less than that for untreated wood ($T_{peak} = 348$ °C). The copper and chromium compounds can behave as accelerators to degrade wood samples at lower temperatures (Osawa 1988). The CCA treatment resulted in a weight loss rate of 1.4%, which was greater that of untreated wood (1.2%). For char oxidation, T_{peak} was around 367 °C for the CCA sample, which was much lower than the value for the untreated wood ($T_{peak} = 480$ °C). Thus, CCA accelerated not only the decomposition of cellulose but also char oxidation.
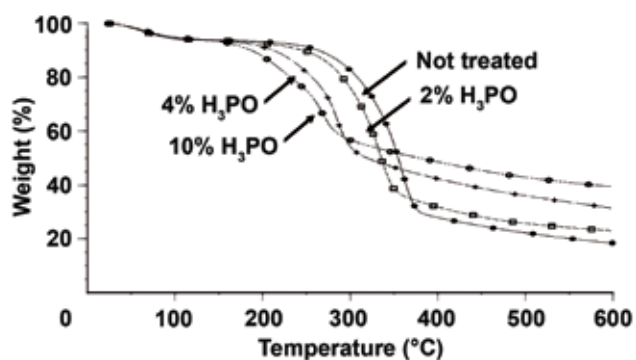
For nitrogen at 50 °C/min, the initial weight loss from the CCA-treated wood was the same as that from the untreated wood up through 250 °C. This temperature was higher than the value obtained in air, showing again that wood decomposition is accelerated by oxygen. The maximum rate of weight loss occurred at the temperature of 359° C for the CCA-treated wood, whereas that value for untreated wood was 385 °C. As a whole, these results indicate that the CCA components promote the thermal degradation of wood in nitrogen. We observed that untreated wood had a shoulder located at the lower temperature region of the differential thermogravimetry (DTG) curve (data not shown). This lower temperature shoulder is associated with the decomposition of hemicellulose and the higher temperature peak is associated with the decomposition of cellulose (Grønli 1996). For the CCA-treated wood, the shoulder at the low-temperature region of the DTG curve has disappeared because the decomposition of hemicellulose and cellulose occurs in a narrower temperature range and both ranges overlap, resulting in a more peaked DTG curve due to the presence of CCA (Helsen and others 1999).

TGA of Untreated Wood and CCA-Treated Wood Pretreated with H_3PO_4

TGA revealed that the impregnation of wood in phosphoric acid altered the pyrolysis mechanisms. Pyrolysis proceeded via predominant dehydration reactions leading to the decrease of the amount of volatile products. The onset temperatures and the temperatures corresponding to the maximum weight loss also decreased, which indicated that phosphoric acid accelerated the pyrolysis process (Table 14). As can be seen in Figure 12, the curves were shifted to lower temperatures when the amount of phosphoric acid was increased. The final char yields were also increased with the addition of phosphoric acid. These results are consistent with the observed effect of phosphoric acid as a flame retardant. It is known that phosphoric acid can improve the fire retardancy of wood by lowering its weight loss rate and increasing its char yield (Shafizadeh and others 1975).

Table 14—Characteristics of untreated wood and CCA-treated wood thermodestruction in the presence of H₃PO₄

Sample	H_3PO_4 %	Initial temperature of mass loss (°C)	Temperature of maximal rate of mass loss (°C)	Mass loss up to 500 °C (%)
Untreated wood	—	250	386	82
	2	200	298	68
	4	170	276	62
	10	150	271	59
CCA-treated wood	—	250	359	78
	2	200	334	74
	4	175	286	64
	10	150	269	57

Figure 12—Thermogravimetric analysis (TGA) of CCA-treated wood pretreated with H₃PO₄ in nitrogen at 50 °C/min.
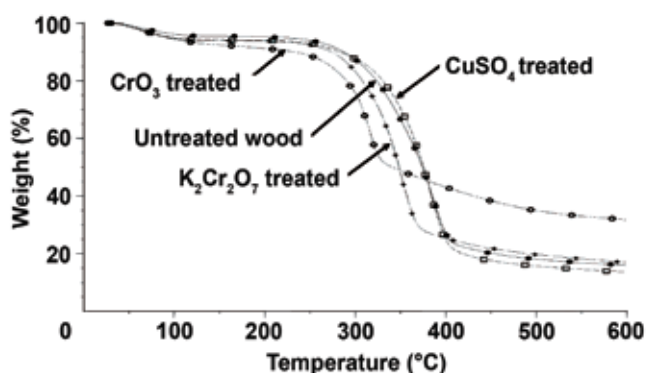
Figure 13—Thermogravimetric analysis (TGA) of untreated wood pretreated with metal compounds in nitrogen at 50 °C/min.

TGA of Untreated Wood Pretreated with Metal Compounds

Figure 13 shows the pyrolysis behavior of untreated wood pretreated with metal compounds and indicates the parameters (DTG max, initial temperature of mass loss, initial and final char yield) recorded in Table 15. As can be seen from this figure, the TGA curves of treated samples were shifted to the lower temperatures regions. Table 15 shows that the metal-compound-treated woods had lower DTG maxima than the untreated wood. This effect was most apparent with the CrO₃-treated wood. Moreover, this wood sample produced the highest yield of initial char (49% at 345 °C), which can further degrade slowly at higher temperatures, the yield decreasing to 32% at 600 °C. The same phenomenon also occurred for the K₂Cr₂O₇-treated wood, with the high yield of initial char and the subsequent slow pyrolysis of this char. The kinetic thermo-analytical studies with fire retardants and inorganic salts also obtained similar results. The pyrolysis processes showed apparent changes in the higher rate of volatilization at the lower temperatures and the increase of residual char yield (Shafizadeh 1968). Richards and Zheng (1991), also observed effects similar to those observed in this study when they investigated ion exchanged and sorbed-salts wood samples. Their study reported that ferrous wood showed the most dramatic effect of the lowest breakthrough temperature and DTG maximum of the samples studied.

Conclusions

CCA treatment of wood had a notable effect on the characteristics of carbohydrate-derived degradation products of tar. Pyrolysis tar from CCA-treated wood contained greater proportions of aliphatic alcohols and lesser quantities of phenolic compounds than did untreated wood. In particular, yields of the important pharmaceutical precursors levoglucosan and levoglucosenone were elevated by 3 and 4.5 times, respectively, than untreated wood. A kinetic study of the pyrolysis of CCA-treated wood by thermogravimetric analysis also demonstrated that CCA components have a significant influence on thermal decomposition behavior of CCA-treated wood. The CCA treatment lowered the beginning temperature for the main combustion period, accelerated combustion after the initial weight loss step, and accelerated oxidation of char.

Treatment of the wood with combinations of chromium and copper salts provided some insight into the mechanisms of CCA's effects on pyrolysis products. The yields of pyrolysis

Table 15—Thermogravimetric analysis of wood and MCC[a] sorbed with salt solutions

Sample	DTG[b] max (°C)	Initial temperature of mass loss (°C)	Initial char		Final char yield (%) at 600 °C
			Temp (°C)	Yield (%)	
Untreated wood	386	250	418	23	16
CuSO₄	383	236	438	18	14
K₂Cr₂O₇	351	231	396	26	17
CrO₃	315	194	345	49	32

[a] Microcrystalline cellulose.
[b] Differential thermogravimetry.

tar and char from $K_2Cr_2O_7$-treated wood and $CuSO_4$-treated wood were similar to that from untreated wood. For CrO_3- and $CrO_3 + CuSO_4$-treated wood, however, the char yields were quite different. The yields of tar decreased substantially while the yields of char increased to around 50%. Treatment with $K_2Cr_2O_7$ and $CuSO_4$ salts promoted the formation of levoglucosan, whereas CrO_3 treatment favored the formation of levoglucosenone. It appears likely that the strong acidity of the CrO_3 solution used in the study and in commercial CCA formulations plays a key role in the increased yield of levoglucosenone in the pyrolysis tar.

Treatment with phosphoric acid resulted in a considerable change in the thermal decomposition mechanism as demonstrated by a decrease in tar component and increase in char component for both untreated and treated wood. Phosphoric acid also appears to be an efficient catalyst for levoglucosenone formation. Pyrolysis of both untreated and CCA-treated wood in the presence of phosphoric acid gave rise to substantially higher yields of levoglucosenone, demonstrating the potential for a new pathway in the rational use of CCA-treated wood waste. The results of this study indicate that low-temperature pyrolysis, with the potential for recovery of a range of useful chemicals, may offer a feasible option for management of waste CCA-treated wood.

References

Akim, E. 1984. Khimiya Drevesiny. (Wood Chemistry). 4:3–17.

AWPA. 1999. AWPA book of standards. Birmingham, AL: American Wood-Preservers' Association. p. 11.

AWPA. 2007. Standard for waterborne preservatives; book of standards. Birmingham, AL: American Wood-Preservers' Association. [Pages Unknown]

Bravar, M.; Rek, V.; Kostelac-Biffl, R. 1973. Effect of ultraviolet irradiation on photooxidation and crosslinking reactions in a poly(vinylalcohol)-ammonium dichromate system. Journal of Polymer Science. 40:19–31.

Cooper, P.A. 1991. Leaching of CCA from treated wood: pH effects. Forest Products Journal. 41(1):30–32.

DeGroot, W.F.; Shafizadeh, F. 1984. The influence of exchangeable cations on the carbonization of biomass. Journal of Analytical and Applied Pyrolysis. 6(3):217–232.

DiCosimo, R.; Szabo, H.C. 1988. Oxidation of lignin model compounds using single-electron-transfer catalysts. Journal of Organic Chemistry. 53(8):1673–1679.

Dobbs, A.J.; Phil, D.; Grant, C. 1978. The volatilization of arsenic on burning copper-chromium-arsenic (CCA) treated wood. Holzforschung. 32(1):32–35.

Dobele, G.; Rossinskaja, G.; Telysheva, G.; Meier, D.; Faix, O. 1999. Cellulose dehydration and depolymerization reactions during pyrolysis in the presence of phosphoric acid. Journal of Analytical and Applied Pyrolysis. 49:307–317.

Dobele, G.; Meier, D.; Faix, O.; Radtke, S.; Rossinskaja, G.; Telysheva, G. 2001. Volatile products of catalytic flash pyrolysis of celluloses. Journal of Analytical and Applied Pyrolysis. 58–59:453–463.

Dobele, G.; Dizhbite, T.; Rossinskaja, G.; Telysheva, G.; Meier, D.; Radtke, S.; Faix, O. 2003. Pretreatment of biomass with phosphoric acid prior to fast pyrolysis: a promising method for obtaining 1, 6-anhydrosaccharides in high yields. Journal of Analytical and Applied Pyrolysis. 68–69:197–211.

Duncalf, B.; Dunn, A.S. 1964. Light-sensitized crosslinking of polyvinyl alcohol by chromium compounds. Journal of Applied Polymer Science. 8(4):1763–1776.

EPA. 2003. Response to requests to cancel certain chromated copper arsenate (CCA) wood preservative products and amendments to terminate certain uses of other CCA products: 68 FR 17366-17372. Federal Register Environmental Documents. Washington, D.C.: U.S. Environmental Protection Agency. http://www.epa.gov/EPA-PEST/2003/April/Day-09/p8372.htm.

Evans, J.J.; Milne, T.A.; Soltys, M.N. 1986. Direct mass-spectrometric studies of the pyrolysis of carbonaceous fuels: III. primary pyrolysis of lignin. Journal of Analytical and Applied Pyrolysis. 9(3):207–236.

Feist, W.C. 1983. Protection of wood surfaces with chromium trioxide. Research Paper FPL–RP–339. Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory: 11 p.

Fengel, D.; Wegener, G. 1984. Wood: chemistry, ultrastructure, reactions. New York: Walter de Gruyter: Chapter 3:34.

Fung, D.P.C.; Tsuchiya, Y.; Sumi, K. 1972. Thermal degradation of cellulose and levoglucosan - the effect of inorganic salts. Wood and Fiber Science Journal. 5(1):38–43.

Grønli, M.G. 1996. A theoretical and experimental study of the thermal degradation of biomass. Doktor Ingeniørachandling NTNU. ITEV-rapport 1996:03. p. 115.

Halpern, Y.; Patai, S. 1969. Pyrolytic reactions of carbohydrates. Part VI. Isothermal decomposition of cellulose in vacuo in the presence of additives. Israel Journal of Chemistry. 7:685.

Halpern, Y.; Riffer, R.; Broido, A. 1973. Levoglucosenone (1,6-anhydro-3,4-dideoxy-. DELTA.3-.beta.-D-pyranosen-2-one). A major product of the acid-catalyzed pyrolysis of cellulose and related carbohydrates. Journal of Organic Chemistry. 38(2):204–209.

Helsen, L.; Van den Bulck, E. 1997. Release of metals during the pyrolysis of preservative impregnated wood: pyrolysis of CCA-treated wood. Developments in Thermochemical Biomass Conversion. 1:220–228.

Helsen, L.; Van den Bulck E. 1998. The microdistribution of copper, chromium and arsenic in CCA treated wood and its pyrolysis residue using energy dispersive x-ray analysis in scanning electron microscopy. Holzforschung. 52(6):607–614.

Helsen, L.; Van den Bulck, E. 2000a. Kinetics of the low-temperature pyrolysis of chromated copper arsenate-treated wood. Journal of Analytical Applied Pyrolysis. 53(1):51–79.

Helsen, L.; Van den Bulck, E. 2000b. Metal behavior during the low-temperature pyrolysis of chromated copper arsenate-treated wood waste. Environmental Science Technology. 34:2931–2938.

Helsen, L.; Van den Bulck, E. 2003. Metal retention in the solid residue after low-temperature pyrolysis of chromated copper arsenate (CCA)-treated wood. Environmental Engineering Science. 20(6):569–580.

Helsen, L.; Van den Bulck, E. 2005. Review of disposal technologies for chromated copper arsenate (CCA) treated wood waste, with detailed analyses of thermochemical conversion processes. Environmental Pollution. 134:301–314.

Helsen, L.; Van den Bulck, E.; Van den Broeck, K.; Vandecasteele, C. 1997. Low-temperature pyrolysis of CCA-treated wood waste: chemical determination and statistical analysis of metal input and output; mass balances. Waste Management. 17(1):79–86.

Helsen, L.; Van den Bulck, E.; Hery, J.S. 1998. Total recycling of CCA treated wood waste by low-temperature pyrolysis. Waste Management. 18:571–578.

Helsen, L.; Van den Bulck, E.; Mullens, S.; Mullens, J. 1999. Low-temperature pyrolysis of CCA-treated wood: thermogravimetric analysis. Journal of Analytical Applied Pyrolysis. 52:65–86.

Helsen, L.; Van den Bulck, E.; Van Bael, M.K.; Mullens, J. 2003. Arsenic release during pyrolysis of CCA treated wood waste: current state of knowledge. Journal of Analytical Applied Pyrolysis. 68–69:613–633.

Helsen, L.; Van den Bulck, E.; Van Bael, M.K.; Vanhoyland, G.; Mullens, J. 2004. Thermal behaviour of arsenic oxides (As2O5 and As2O3) and the influence of reducing agents (glucose and activated carbon). Thermochimica Acta. 414:145–153.

Hirata, T.; Inoue, M.; Fukui, Y. 1993. Pyrolysis and combustion toxicity of wood treated with CCA. Wood Science and Technology. 27:35–47.

Honda, A.; Kanjo, Y.; Kimoto, A.; Koshii, K.; Kashiwazaki, S. 1991. Recovery of copper, chromium, and arsenic compounds from the waste preservative-treated wood. Doc. No. IRG/WP/3651. Internal research group on wood preservation: Kyoto, Japan 22nd annual meeting. Stockholm, Sweden: IRG Secretariat.

Jain, R.K.; Lal, K.; Bhatnagar, H.L. 1987. Thermal, morphological and spectroscopic studies on cellulose modified with phosphorus, nitrogen, sulphur and halogens. Journal of Applied Polymer Science. 33(2):247–282.

Kakitani, T.; Hata, T.; Kajimoto, T.; Imamura, Y. 2004. Effect of pyrolysis on solvent extractability of toxic metals from chromated copper arsenate (CCA)-treated wood. Journal of Hazardous Materials. B109:53–57.

Kaur, B.; Gur, I.S.; Bhatnagar, H.L. 1986. Studies on thermal degradation of cellulose and cellulose phosphoramides. Journal of Applied Polymer Science. 31(2):667–683.

Kaur, B.; Gur, I.S.; Bhatnagar, H.L. 1987a. Thermal degradation studies of cellulose phosphates and cellulose thiophosphates. Angewandte Makromolekulare Chemie. 147(1):157–183.

Kaur, B.; Jain, R.K.; Gur, I.S.; Bhatnagar, H.L.; Schulten, H.R. 1987b. Studies on the flame-retardant properties of transition metal complexes of cellulose ammonium phosphate. Journal of Analytic and Applied Pyrolysis. 11:465–498.

Kennedy, J.F.; Phillips, G.O.; Williams, P.A., Eds. 1996. The chemistry and processing of wood and plant fibrous materials. Abington, Cambridge, England: Woodhead: 345–350.

Kercher, A.K.; Nagle, D.C. 2001. TGA modeling of the thermal decomposition of CCA treated lumber waste. Wood Science and Technology. 35(4):325–341.

Kishore, K.; Mohandas, K. 1982. Action of phosphorus compounds on fire-retardancy of cellulosic materials: a review. Fire Mater. 6(2):54–58.

Knzi, K.M.F.; Cooper, P.A. 1998. Solvent extraction of CCA-C from out-of-service wood. Doc. No. IRG/WP/98-50107. Stockholm, Sweden Internal research group on wood preservation.

Kuroda, K.I.; Inoue, Y.; Sakai, K. 1990. Analysis of lignin by pyrolysis-gas chromatography. I. Effect of inorganic substances on guaiacol-derivative yield from softwoods and their lignins. Journal of Analytic and Applied Pyrolysis. 18(1):59–69.

Lebow, S.T. 1996. Leaching of wood preservative components and their mobility in the environment-summary of pertinent literature. General Technical Report FPL–GTR–93. Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory. 36 p.

Lebow, S.T. 2004. Alternatives to chromated copper arsenate for residential construction. Research Paper FPL–RP–618. Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory. 9 p.

Madorsky, S.L.; Hart, V.E.; Straus, S. 1956. Pyrolysis of cellulose in a vacuum. Journal of Research of the National Bureau of Standards. 56:343–354.

Marutzky, R. 1990. Entsorgung von mit holzschutzmitteln behandelten hölzern; möglichkeiten und probleme. Holz roh werkst. 48:19–24.

Müller-Hagedorn, M.; Bockhorn, H.; Krebs, L.; Müller, U. 2003. A comparative kinetic study on the pyrolysis of three different wood species. Journal of Analytic and Applied Pyrolysis. 68–69:231–249.

Osawa, Z. 1988. Role of metals and metal-deactivators in polymer degradation. Polymer Degradation and Stability. 20:203–236.

Pasek, E.A.; McIntyre, C.R. 1993. Treatment and recycle of CCA hazardous waste. Doc. No. IRG/WP 93-50007. Internal research group on wood preservation, Stockholm, Sweden.

Piskorz, J.; Radlein, D. St. A.G.; Scott, D.S.; Czernick, S. 1989. Pretreatment of wood and cellulose for production of sugars by fast pyrolysis. Journal of Analytic and Applied Pyrolysis. 16(2):127–142.

Rak, J. 1975. New evaluation of water repellency of wood by contact angle. Wood and Fiber Science. 7(1):16–24.

Richards, G.N.; Zheng, G. 1991. Influence of metal ions and of salts on products from pyrolysis of wood: applications to thermochemical processing of newsprint and biomass. Journal of Analytic and Applied Pyrolysis. (21):133–146.

Richards, G. N.; Shafizadeh, F.; Stevenson, T.T. 1983. Influence of sodium chloride on volatile products formed by pyrolysis of cellulose: indentification of hydroxybenzenes and 1-hydroxy-2-propanone as major products. Carbohydrate Research. 117:322–327.

Ripley, R.A.; Fung, D.P.C. 1971. Flash pyrolysis of aspen and black spruce lignins—the effect of inorganic salts. Wood and Fiber Science Journal. 4(1):25–31.

Shafizadeh, F. 1968. Pyrolysis and combustion of cellulosic materials. In: Wolfrom, M.L.; Tipson, R.S. (Eds.), advances in carbohydrate chemistry. New York: Academic Press. 23(1968):419–475.

Shafizadeh, F.; Chin, P.S.; DeGroot, W.F. 1975. Mechanistic evaluation of flame retardants. Journal of Fire Retardant Chemistry. 2:195.

Shafizadeh, F.; Lai, Y.Z.; McIntyre, C.R. 1978. Thermal degradation of 6-chlorocellulose and cellulose-zinc chloride mixture. Journal of Analytic and Applied Pyrolysis. 22(5):1183–1193.

Shafizadeh, F.; Furneaux, R.H.; Cochran, T.G.; Scholl, J.P.; Sakai, Y. 1979a. Production of levoglucosan and glucose from pyrolysis of cellulosic materials. Journal of Analytic and Applied Pyrolysis. 23(12):3525–3539.

Shafizadeh, F.; Furneaux, R.H.; Stevenson, T.T. 1979b. Some reactions of levoglucosenone. Carbohydrate Research. 71(1):169–191.

Solo-Gabriele, H.; Kormienko, M.; Gary, Kevin; Townsend, Timothy; Stook, Kristin; Tolaymat, Thabet. 2000. Alternative chemicals and improved disposal-end management practices for CCA-treated wood. Report to Florida center for solid and hazardous waste management http://www.ccaresearch.org/solo_00-08.pdf.

Stephan, I.; Nimz, H.H.; Peek, R.D. 1993. Detoxification of salt-impregnated wood by organic acids in a pulping process. Doc. No. IRG/WP 93-50012. Internal research group on wood preservation. Stockholm, Sweden.

Taylor, A.; Cooper, P.A.; Ung, Y.T. 2001. Effects of deck washes and brighteners on the leaching of CCA components. Forest Products Journal. 51(2):69–72.

Van Nice, H.L.; Farlee, R. 1976. A study of the photochemical reaction between poly (using alcohol) and chromate ion in aqueous solution. Proceedings: Meeting of the society of plastic engineers, inc. Ellenville, New York: p. 53.

Watson, P.A.; Wright, L.J.; Fullerton, T.J. 1993a. Reactions of metal ion complexes with lignin model compounds. part I. co (TSPP) as a single electron transfer catalyst and implications for the mechanism of AQ pulping. Journal of Wood Chemistry and Technology. 13(3):371–389.

Watson, P.A.; Wright, L.J.; Fullerton, T.J. 1993b. Reactions of metal ion complexes with lignin model compounds. part II. fe (TSPC) catalyzed formation of oxidized products in the absence of oxygen. Journal of Wood Chemistry and Technology. 13(3):391–409.

Watson, P.A.; Wright, L.J.; Fullerton, T.J. 1993c. Reactions of metal ion complexes with lignin model compounds. part

III. rh (TSPP) catalyzed formation of guaiacol from β-aryl ethers in exceptionally high yield. Journal of Wood Chemistry and Technology. 13(3):411–428.

Wehlte, S.; Meier, D.; Moltran, J.; Faix O. 1997. The impact of wood preservatives on the flash pyrolysis of biomass. In: developments in thermochemical biomass conversion, (Ed. by A.V. Bridgwater and D.G.B. Boocock), pp. 206–219. Chapman & Hall, London.

Wilkins, E.; Murray, F. 1980. Toxicity of emissions from combustion and pyrolysis of wood. Wood Science and Technology. 14(4):281–288.

Williams, R.S.; Feist, W.C. 1984. Application of ESCA to evaluate wood and cellulose surfaces modified by aqueous chromium trioxide treatment. Colloids and Surface. 9(3):253–271.

Williams, R.S.; Feist, W.C. 1985. Wood modified by inorganic salts: mechanism and properties. I. weathering rate, water repellency, and dimensional stability of wood modified with chromium (III) nitrate versus chromic acid. Wood and Fiber Science. 17(2):184–198.

Wu, G.; Heitz, M.; Chornet, E. 1994. Improved alkaline oxidation process for the production of aldehydes (vanillin and syringaldehyde) from steam-explosion hardwood lignin. Industrial and Engineering Chemistry Research. 33:718–723.