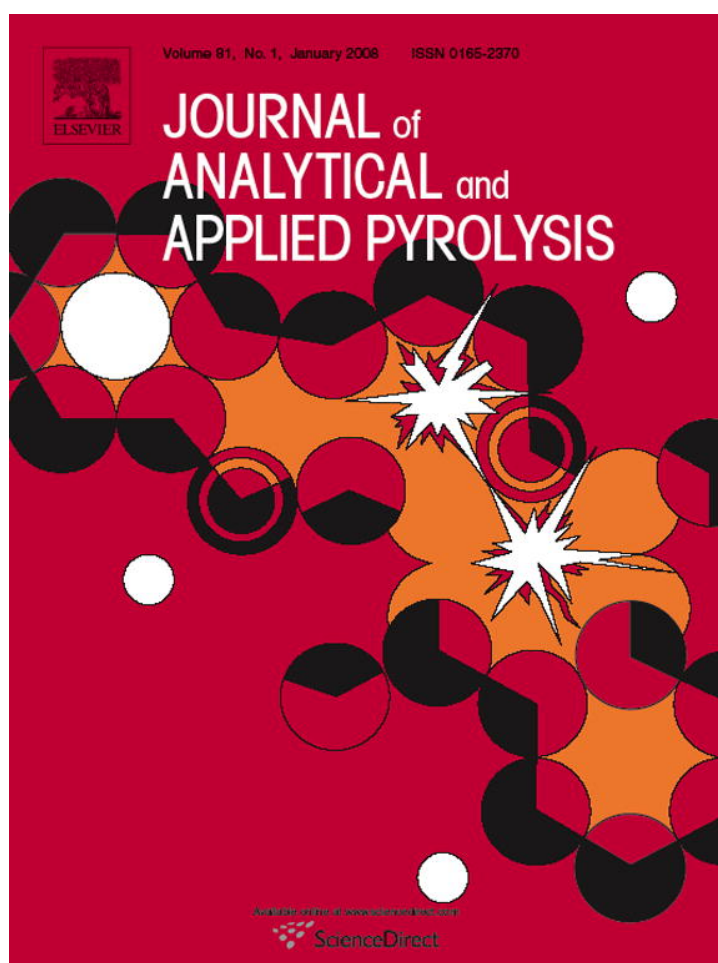


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Understanding the pyrolysis of CCA-treated wood Part I. Effect of metal ions

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Abstract

The influence of several inorganic compounds ($K_2Cr_2O_7$, CrO_3 and $CuSO_4$) on the pyrolysis of southern pine wood has been investigated. The wood powder was pre-treated with various inorganic compound solutions prior to the pyrolysis and the distribution and yields of the pyrolysis products were obtained by gas chromatography and quantitative ^{31}P nuclear magnetic resonance (NMR) analyses. Our experiments showed that $K_2Cr_2O_7$ and $CuSO_4$ salts promoted the formation of levoglucosan (LG). In particular, the former providing higher LG yields up to 26.7%. The CrO_3 treatment induced the production of low tar and high char yields, with a very low yield of LG and high yield of levoglucosone (LGO). The underlying reasoning behind these findings may be due to an acidic catalysis mechanism, which promotes cellulose depolymerization and dehydration processes. Due to acid-catalyzed lignin condensation reactions, the yield of lignin degradation products from the pyrolysis of pre-treated wood was found to dramatically decrease in comparison to untreated wood.

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1. Introduction

The effects of metal salts on the pyrolysis of wood and cellulose have been studied extensively. The initial motivation to investigate the influence of metals on wood has been focused on the development of flame-retardant compounds [1]. Many metal salts can be used to reduce the flammability and smoke generation of wood [2]. It was reported [3,4] that the presence of metal compounds generally promoted the formation of char as well as water and carbon dioxide, and decreased the yield of tar. It has been shown that the addition of different sodium salts substantially lowers the activation energy of overall thermal decomposition process; the amount of char is increased and the LG-forming reactions are suppressed [3,5–8].

There are significant differences in the distribution and yields of phenolic compounds arising from the thermal decomposition of various lignocellulosic materials in the presence of different metal salts. In fact, several literature

accounts provide various approaches for the production of phenolic compounds in the presence of transition metals as catalysts [9–14]. For example, it has been reported that [9] the mixture of Cu(II) and Fe(III) salts improved the oxidative selectivity toward the production of vanillin and syringaldehyde during the alkaline oxidative degradation of lignin. Furthermore, Mn(III) cations have been reported to provide greater selectivity than Co(III) cation in relation to the conversion of lignin model compounds to benzoic acids and aromatic aldehydes via oxidative degradation [10,15].

In addition, some specific transition metals have been found to promote pyrolysis reactions. Cupric and ferrous ions have been reported to favor tar formation causing the formation of high yields of LG [16]. In particular, Dobelet et al. [17] showed that through the acidic catalysis mechanism, the 1,6-anhydrosaccharides content in volatile products and the LG/LGO ratio were governed by the iron concentration when the cellulose or decationized wood was pre-treated with iron(III) sulfate solution prior to the pyrolysis. At higher adsorbed iron concentration, the LGO content increased and the LG/LGO ratio decreased.

It is important to also note at this stage that the amounts of inorganic salts containing K, Ca and Mg in native wood are

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between 0.2 and 0.5% [18]. When these inorganic substances are removed from wood by acid washing prior to pyrolysis, the yield of LG can be drastically enhanced [16] and the yield of char can also be reduced [19].

In our earlier effort we have demonstrated that the chromated copper arsenate (CCA) treatment of wood has a significant effect on the amount of main carbohydrate degradation products [20]. 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 such effects, or the coordination of these two metal ions plays a key role to the pyrolysis process? In this paper, therefore, we discuss the influence of various inorganic compounds (CuSO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$ and CrO_3) on the pyrolysis of southern pine wood. These compounds are selected in accordance with the prescribed formulae used for waterborne CCA wood preservatives [21]. Our work is aided by the use of quantitative, ^{31}P NMR spectroscopy since it allows us to elucidate the structure and functional group distributions of pyrolysis tars emerging from control and pre-treated wood. Furthermore, thermogravimetric analytical (TGA) data of control and pre-treated wood samples are also provided.

2. Experimental

2.1. Initial materials

Southern pine wood was Wiley-milled repeatedly to small particles with particle sizes between 0.1 and 0.2 mm. The wood samples used in the pyrolysis experiments have been oven-dried. During the drying process, the wood samples were put in a vacuum oven at the temperature of 40 °C until a constant weight of wood samples was obtained. The moisture content of wood samples is 8%, a percentage obtained from the difference of mass before and after drying.

2.2. Pre-treatment with metal ions

The wood powder (12 g) was immersed in 0.05 M metal salt solution ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{K}_2\text{Cr}_2\text{O}_7$), CrO_3 acid solution or 0.05 M CrO_3 + 0.024 M $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ mixture, degassed in vacuum and eluted in a column with more solution (2 L) to create samples containing specific metal ions. The treated samples were then washed with deionized water to remove any of the metal ions which were not bound to the wood powder. After being washed by deionized water, the products were air dried. The pH values of the pre-treated solutions are listed in Table 1.

Table 1
pH values of the pre-treated solutions

Pre-treated solutions	pH value
$\text{K}_2\text{Cr}_2\text{O}_7$	3.9
CrO_3	1.8
CrO_3 + CuSO_4	1.8
CuSO_4	3.7

2.3. Pyrolysis

The pyrolysis of pre-treated wood samples was carried out under heat in a Kugelrohr short-path distillation apparatus [20]. The sample weight was 3 g for each trial. The vacuum pressure was controlled at 7 mmHg. The thermal treatment was carried out at 350 °C for 30 min. The end product—char was collected in the first flask, whereas the tar was condensed with ice water (0 °C) and collected for further analyses. The distillate was condensed with dry ice–acetone at –70 °C.

2.4. Analytical methods

2.4.1. 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 × 0.25 mm i.d. and 0.25 μm film thickness) and an isothermal temperature profile at 45 °C for the first 4 min, followed by a 3 °C/min temperature gradient to 270 °C and finally an isothermal period at 270 °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 °C, respectively. For the sample preparation, 70 mg of tar was weighed and dissolved in 5 mL of acetone. Fluoranthene was used as an internal standard. Detailed signal assignments of the emerging gas chromatograms of the obtained pyrolysis tars can be located in Ref. [20].

2.4.2. ^{31}P NMR analysis of tar

^{31}P NMR spectra were obtained on a Bruker 300 MHz NMR spectrometer. The preparation of solvents and derivatizing reagent can follow 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 100 μL internal standard (*N*-hydroxynaphthalimide) was then added, 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 yield of LGO in the tar was determined by ^{31}P NMR and the signals were assigned as per our earlier effort [20].

2.4.3. Metal analysis

The metal (Cr and Cu) content of pre-treated raw materials was determined by atomic absorption spectroscopy Perkin-Elmer 2380. Analytical wavelengths were 357.9 nm for Cr and 324.8 nm for Cu. The samples for metal analysis were prepared according to the reflux method provided by Helsen et al. [23]. This methodology causes the complete sample dissolution in nitric acid without loss of any material. 0.1 g of dried wood powder was placed into a conical flask equipped with a reflux condenser, followed by the addition of 10 mL of 65% HNO_3 . Then the flask was heated on a heating plate under reflux until the sample dissolved completely (approximately 2 h).

2.4.4. Thermogravimetric analysis

TGA was carried out using a TGA Q500 instrument. The wood powder sample, approximately 10–15 mg in weight, was introduced into a platinum sample pan and heated from room temperature to 600 °C at a heating rate of 50 °C/min under a nitrogen flow of 60 mL/min.

3. Results and discussion

3.1. Quantitative analysis of tar products

The contents of Cr and Cu in the pre-treated wood samples are listed in Table 2. Wood powder pre-treated with 0.05 M CuSO₄ solution contained 0.21% Cu ions, which was similar to the Cu concentration (0.27%) in the commercially prepared CCA-treated wood [20]. Thus, in our study, 0.05 M metal compound solutions were selected to pre-treat southern pine wood powder and the pyrolysis results were compared with those from commercially prepared CCA-treated wood. As can be seen from Table 2, the Cr concentration was 2.49% in the CrO₃-treated wood and 1.71% in the CrO₃ + CuSO₄-treated wood, which was higher than the Cu concentration in the pre-treated wood. This shows that the Cr ion is easily absorbed by the wood.

Yields of pyrolysis fractions (at 350 °C) of pre-treated wood are shown in Table 3. The total recovery (the sum of the yields of char, tar and distillate) from pyrolysis of pre-treated wood was around 90%. The yields of pyrolysis tar from K₂Cr₂O₇-treated wood and CuSO₄-treated wood were similar to that from untreated wood. Correspondingly, the yields of char from pre-treated wood were found to be close to that from untreated wood.

For CrO₃ and CrO₃ + CuSO₄-treated wood, however, the yields of pyrolysis fractions were quite different from those of

Table 2

Concentration of Cr and Cu in pre-treated wood

Pre-treated wood	Chromium (%)	Copper (%)
K ₂ Cr ₂ O ₇	0.23	–
CrO ₃	2.49	–
CrO ₃ + CuSO ₄	1.71	0.002
CuSO ₄	–	0.21

Table 3

Yields of pyrolysis fractions of pre-treated wood at 350 °C (wt.% based on water-free wood)

Fractions	Untreated	K ₂ Cr ₂ O ₇	CrO ₃	CrO ₃ + CuSO ₄	CuSO ₄
Char	28.5	26.3	52.6	45.3	25.0
Tar	59.6	58.5	22.6	32.2	59.1
Distillate	3.0	10.5	14.0	16.0	4.4
Total recovery	91.1	95.3	89.2	93.5	92.8

untreated wood. The yields of tar decreased drastically while the yields of char increased to around 50%. Chromic acid treatment has been used to improve wood surface properties. It has been reported that chromic acid-modified wood exhibits greatly improved water repellency, better mildew resistance and reduced extractives staining [24–26]. Chromic acid causes chemical changes in the surface of wood [27]. The fixation of chromium(VI) trioxide results from the formation of insoluble complex salts that coordinate with free hydroxyls in the carbohydrates and lignin [28–30]. Since these hydroxyls are unavailable to form hydrogen bonds with water, the wood has greater water repellency and dimensional stability [25]. 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

Table 4

Yields of tar compounds from pyrolysis of pre-treated wood (wt.% based on water-free tar)

Compound name	Untreated	K ₂ Cr ₂ O ₇	CrO ₃	CrO ₃ + CuSO ₄	CuSO ₄
1. Hydroxyacetaldehyde	3.07	0.51	0.14	0.14	0.64
2. Acetic acid	1.87	0.60	1.51	1.59	1.32
3. Hydroxyacetone	1.36	0.08	nd ^a	nd	0.25
4. 2-Furaldehyde	0.34	0.32	0.23	0.22	0.32
5. Furfuryl alcohol	0.37	0.01	nd	nd	0.08
6. Furan-(5H)-2-one	1.10	0.11	0.26	0.27	0.16
7. Phenol	0.04	0.04	0.06	0.08	0.06
8. Guaiacol	0.41	0.30	0.19	0.22	0.35
9. <i>p</i> -Cresol	0.07	0.03	0.04	0.05	0.05
10. Levoglucosenone	0.19	0.98	2.69	2.51	0.43
11. 4-Methyl guaiacol	0.65	0.29	0.08	0.09	0.45
12. 2,4-Dimethyl phenol	0.13	0.08	0.06	0.06	0.05
13. 4-Ethyl-guaiacol	0.12	0.09	0.06	0.07	0.10
14. Eugenol	0.22	0.09	0.03	0.05	0.10
15. 5-(Hydroxy-methyl)-furaldehyde-(2)	0.99	1.10	0.54	0.57	0.88
16. Catechol	0.62	0.47	0.50	0.56	0.63
17. Isoeugenol	0.51	0.16	nd	nd	0.10
18. Vanillin	0.35	0.28	0.30	0.31	0.20
19. Acetoguaiacone	0.23	0.13	0.23	0.19	0.13
20. Guaiacyl acetone	0.45	0.19	0.09	0.13	0.14
21. Levoglucosan	4.86	26.73	0.60	2.38	14.34

^a Not detected.

Table 5

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	$\text{K}_2\text{Cr}_2\text{O}_7$	CrO_3	$\text{CrO}_3 + \text{CuSO}_4$	CuSO_4
Aliphatic alcohols	149.6–145.0	7.08	11.03	2.00	3.39	8.72
Condensed phenols	143.8–140.2 (except peak at 141.3 ppm)	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

volatile products. Thus, in our trial, the yields of tar decreased while the yields of char increased.

The quantified pyrolysis tar products from untreated wood and its metal ion pre-treated wood counterpart are listed in Table 4. As can be seen from this table, the quantitative analysis of tar compounds showed a significant difference between untreated and pre-treated wood. A large amount of tar fraction comes from carbohydrate thermal degradation. The yield of carbohydrate degradation products varied considerably with treatment of different metal ions. The amount of LG increased drastically when wood samples were treated by CuSO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ solution, which was around three and five times 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 [20].

The amount of LGO from CrO_3 -treated wood was 14 times higher than that from untreated wood. The pyrolysis of wood pre-treated with $\text{K}_2\text{Cr}_2\text{O}_7$ solution can also get a high yield of LGO up to 1%. In the previous study, the amount of LGO from CCA-treated wood was 0.87% [20], which was also higher than that from untreated wood.

The obtained high yields of LG and LGO are related to the acid conditions of pre-treated 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 [21]. If a CCA treating solution has a pH value outside the stated limits, it can be made conforming by the addition of CCA concentrate or chromic acid. As can be seen from Table 1, all the pH values of pre-treated solutions are in the acidic range. CrO_3 solution is an especially strong acid solution. Under such acid catalysis conditions, high yields of LG and LGO can be obtained via cellulose depolymerization and dehydration processes. Dobelet et al. [17] have also reported that the introduction of iron(III) (by adsorption of $\text{Fe}_2(\text{SO}_4)_3$), increased the content of 1,6-anhydrosaccharides in the volatile products and this was rationalized on the basis of acid catalyzed cellulose depolymerization and dehydration proceeding with the combined action of sulfate ions under pyrolysis conditions.

In contrast, the metal ions treatment did not promote the formation of hydroxyacetaldehyde, hydroxyacetone, furfuryl alcohol and furan-(5H)-2-one, which was the same as the CCA treatment did.

The metal ion pre-treatment presents a significant effect on lignin decomposition, as shown in Table 4. The yield of main lignin degradation products such as isoeugenol, eugenol, guaiacol and 4-methyl-guaiacol decreased drastically in this

experiment. This could be attributed to related acid-catalyzed lignin condensation reactions.

The functional group content of pyrolysis tar from pre-treated wood is shown in Table 5. Pyrolysis tar from $\text{K}_2\text{Cr}_2\text{O}_7$ - 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 pre-treated wood. CrO_3 -treated wood induced the formation of less aliphatic alcohol functionalities which was due to the documented higher yields of LGO. From the amount of condensed, 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 was 50% less than that from untreated wood. Because of the acid-catalyzed lignin condensation reactions, not many lignin degradation products would be released during pyrolysis, especially non-condensed phenols. The amount of total carboxylic acids of tar from untreated wood was also higher than those from pre-treated wood.

3.2. TGA of wood samples pre-treated with metal ions

Fig. 1 shows the pyrolysis behavior of wood samples pre-treated with metal ions while the various thermal decomposition parameters (initial temperature of weight loss, temperature of maximal rate of weight loss and final char yield) are shown in Table 6. As can be seen from Fig. 1, the TGA curves of treated samples were shifted to lower temperatures. Table 6 shows that the treated samples with the various metal ions showed lower decomposition temperatures corresponding to the initial and

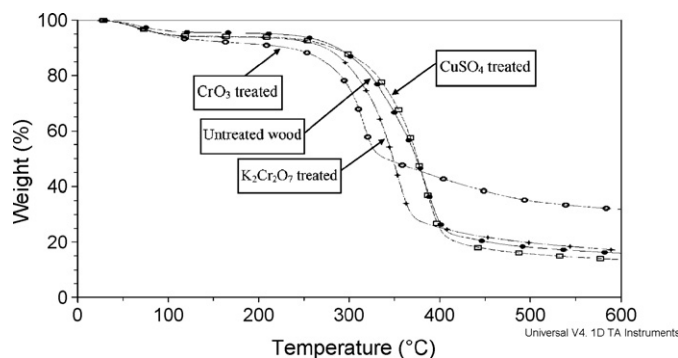


Fig. 1. TGA of wood samples pre-treated with metal ions in nitrogen at 50 °C/min.

Table 6
Thermogravimetric analysis of wood sorbed with salt solutions

Sample	Initial temperature of weight loss (°C)	Temperature of maximal rate of weight loss (°C)	Final char yield % (600 °C)
Untreated wood	250	386	16
CuSO ₄	236	383	14
K ₂ Cr ₂ O ₇	231	351	17
CrO ₃	194	315	32

maximum weight loss, compared to the untreated wood. In particular, the CrO₃-treated wood exhibited the most significant effect. This wood sample decomposed fast at lower temperatures, followed by a slower thermal decomposition at higher temperature offering a high final char yield of 32% at 600 °C. The same phenomenon was also apparent for the K₂Cr₂O₇-treated wood but to a smaller extent. Richards and Zheng [16] have also obtained similar data during their investigation of the influence of metal ions and of salts on wood pyrolysis products. Ferrous ions in wood were shown to have the most dramatic effect.

4. Conclusion

Treating wood with metal ions was found to have a significant effect on its degradation products. K₂Cr₂O₇ and CuSO₄ salts promoted the formation of LG. More specifically, K₂Cr₂O₇ gave a high yield of LG (26.7%). The CrO₃ treatment induced the production of low tar and high char yields, with a very low yield of LG and high yield of LGO. Due to the acid-catalyzed lignin condensation reactions, the yield of lignin degradation products from pre-treated wood dramatically decreased compared to untreated wood.

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