

HYDROTHERMAL TREATMENT OF CCA- AND PENTA-TREATED WOOD¹

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ABSTRACT

Two of the three most commonly used wood preservatives in the United States are chromated copper arsenate (CCA) and oil-borne pentachlorophenol (penta). Both are excellent preservatives for extending the service life of exterior wood. Both also pose environmental problems associated with their disposal. This paper describes the treatment of two different groups of preservative-treated wood (CCA type C and oil-borne penta) in anaerobic supercritical water (SC) under acidic and basic conditions, respectively. A decommissioned (ca. 13 yr) southern pine (*Pinus* sp.) guard rail impregnated with CCA and a freshly treated penta-impregnated pole were examined. During SC treatments, wood particles were transformed (approx. 98% efficiency) into liquid and gaseous hydrocarbon (HC) phase. The metals recovered in the two liquid phases vs. total concentration in the wood were as follows: copper: 91% AQ; <1% HC, chromium: 28% AQ; 1.3% HC, and arsenic: 69% AQ; <1% HC. The penta wood yielded a similar hydrocarbon mixture, with the chlorinated phenols undergoing dechlorination and further reaction. The formation of phenolic condensation products such as chlorinated dibenzofurans and dioxins occurred under these conditions when the reaction was run in quartz-lined containers and metals were excluded from the reaction mixture. When iron (either from the reactor walls or added in quartz cells as iron particles) was present, these products were not observed.

Keywords: CCA, hazardous and solid wastes, PAHs, penta, preservative-treated wood, supercritical water, transformation/recovery/recycling.

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INTRODUCTION

Two of the three most commonly used wood preservatives in the United States are chromated copper arsenate (CCA) and oil-borne pentachlorophenol (penta). Both of these are highly effective preservatives for prolonging the service life of exterior wood.

CCA, which was introduced in 1933, contains copper, chromium, and arsenic. For the past two decades, CCA has emerged as the primary wood preservative for residential and commercial applications (Smith and Shiau 1998). In 1997, 10.5 million m³ (372.1 million ft³) was treated with waterborne preservatives, more than 98% with CCA. In 1997, approximately 66% of all the wood treated with CCA was lumber (Micklewright 1998). Cooper (1993) estimated that the future volumes of CCA-treated wood removed from service in the United States would rise from 35 million ft³ (1 million m³) in 1990 to 565 million ft³ (16 million m³) in 2020. This amount is likely to increase as a result of public concerns and existing and pending legislation concerning arsenic.

Penta, first produced in the 1930s, can be formulated with a variety of heavy or light organic solvents (Schultz and Nicholas 2003). It is currently used in about 10% of all treated wood in North America, primarily for utility poles (Micklewright 1998).

The increasing volume of treated wood products being decommissioned poses disposal problems. There is increasing public concern and restrictions on disposal because of potential adverse effects on human health and the environment. Typical waste disposal options such as landfilling or incineration are both environmentally unacceptable and expensive. Many treatment options addressing these concerns have been explored, including reuse, abatement, modification, recycling, retreatment, and destruction (Cooper 1993, 1994). Recycling of these preservatives is potentially economically feasible and offers an environmentally attractive option.

Supercritical (SC) water (>374°C/221 bar) under anoxic and reducing conditions has been used for a variety of synthetic (Junk and Catallo 1997; Jimeno *et al.* 1997; Junk *et al.* 1997a,

1997b) chemical transformation/recycling purposes (Catallo and Junk 2001; Catallo and Shupe 2002). The SC phase is one of the most energetic and chemically dynamic conditions known for aqueous systems, including a) liquid water under conditions normally observed, b) very high pressures and, c) superheated steam (Junk and Catallo 1997; Van Eldik and Hubbard 1997), as well as other supercritical fluids (e.g., CO₂; Van Eldik and Hubbard 1997).

Work with single compound standards (Junk and Catallo 1997), and related theoretical studies, suggests that reaction pathways involved in observed SC aqueous transformations are primarily ionic or concerted (e.g., via aryne species), rather than free radical in nature. Related work showed transformation product mixtures resulted from sonochemical treatment of target compounds (e.g., chlorinated phenols) resulted from radical reactions, and differed from those obtained under supercritical aqueous conditions (Goskonda *et al.* 2002). This is because the energies achieved in the cavitation zone of aqueous sonochemical systems far exceed those of the supercritical aqueous phase.

Laboratory data show that reactions of biogenic matter in SC water and brines give rise to volatile and semivolatile hydrocarbon assemblages after reaction times of minutes to hours. All forms of biogenic matter tested (e.g., protein, lipid, starch, cellulose, chitin, diatom cells, spent bacterial cultures, DNA, lignin, sewage, sludge, wood, and humic acid) were transformed to complex volatile and semivolatile hydrocarbon mixtures under SC conditions. Product mixtures consistently contained assemblages of linear and branched hydrocarbons, cycloalkanes, monoaromatics (e.g., benzene, phenol), PAHs (e.g., naphthalene, phenanthrene), heteroarenes (e.g., dibenzofuran, dibenzodioxin) and their C₁-C₅ alkyl homologs. Other products included gases CO₂, CH₄, and other volatile hydrocarbons) and carbonized particulate residues in minor amounts. Recent work by the authors showed >98% transformation of creosote-impregnated wood chips to light semivolatile hydrocarbons completely recovered in the nonaqueous residues (Catallo and Shupe 2003).

MATERIALS AND METHODS

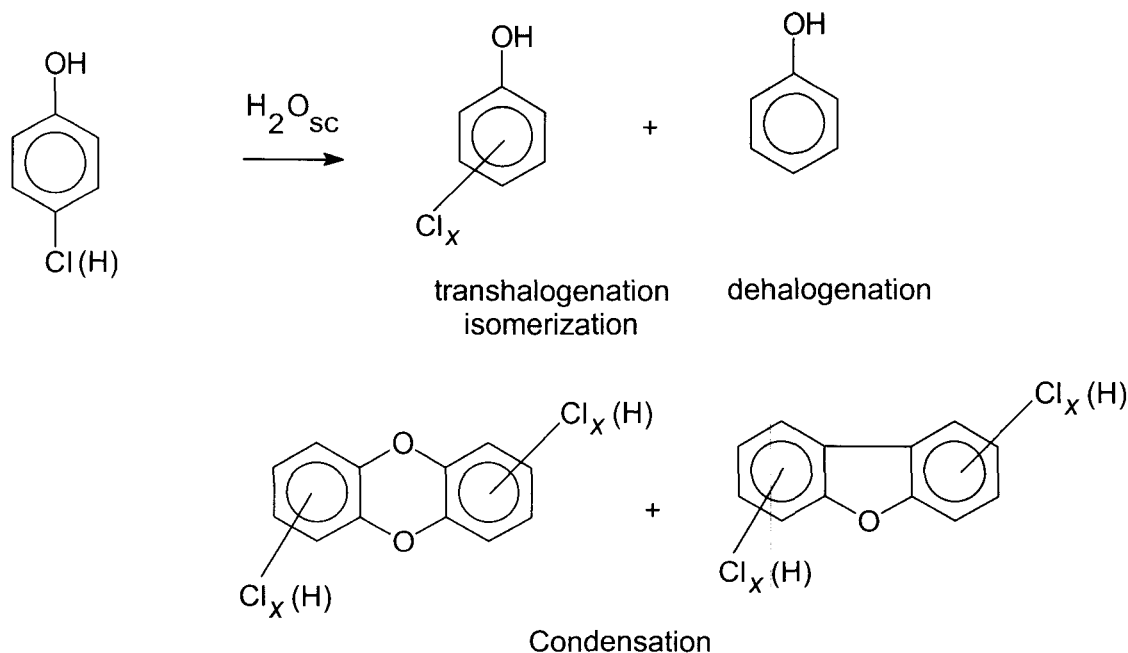
A representative decommissioned CCA type C-treated, southern yellow pine (*Pinus* sp.) highway guard rail was selected for this study. It had been in service in eastern Texas for 13 years and was decommissioned in 2000. It is highly likely that this wood was treated with a full cell process. At the time of treatment, the guard rails were required to have a retention of 0.40 pcf (6.4 kg/m³). It was common practice for guard rails destined for Texas to be treated to 0.50 pcf (8.0 kg/m³), as was the case here (Arnold 2002). A one-foot section above the ground, starting at the ground line, was removed. The assay zone used was 0.5 – 1.5 in. (1.27 – 3.81 cm) from the surface as specified in AWPA (2000) Standards C5 and C14. The actual retention was found to be 0.69 pcf (11 kg/m³) using inductively coupled plasma (ICAP) emission spectrometry as specified in AWPA (2000) Standard A21.

For penta, a representative freshly treated (target retention 0.45 pcf (7.2 kg/m³)) utility pole was selected and a 1-ft (30.5-cm) section was removed from the top end of the pole. The assay

zone selected for SC analysis was 0.5 – 2.0 in. (1.27 – 5.08 cm) from the surface as specified in AWPA (2000) Standard C4. The actual preservative retention of the pole was determined via X-ray spectroscopy to be 1.13 pcf (18.1 kg/m³) using AWPA Standard A9 (2000).

Both sample types were ground in a Wiley Mill and passed a 1-mm mesh screen. Weighed particle samples (1.00 g) were added to 65 mL i.v. high pressure corrosion-resistant autoclaves in the presence of deionized water. The pH was adjusted to 3.0–4.0 (CCA) and 10–11 (penta) using HNO₃ and NaOH, respectively. The suspensions were sparged with AR for 1 h to remove dissolved oxygen, sealed, and incubated at 400 ± 10°C with pressure of about 300 bar for 12 h including heat-up and cool-down (approximately 2 h each).

Quartz cells were used to study the effects of dissolved metals on the SC reaction products, particularly with respect to undesirable condensation reactions involving chlorinated phenols resulting in more toxic species, e.g., chlorinated dibenzo-p-dioxins, as is schematized below. These products have been observed when



chlorolignins and other halogenated organic chemicals are mineralized using highly oxidizing supercritical water (the so-called supercritical wet oxidation, or SWO) to treat pulp wastes and industrial byproducts. Aliquots of aqueous 4-chlorophenol (4CP) in distilled water at pH 10.0 were placed in the quartz reactors and sealed using a hydrogen-oxygen torch. These were put inside the high-temperature autoclaves, which were then amended with water so as to be volumetrically identical with the quartz reactors. Thus, the pressure/temperature profiles inside and outside the quartz reactors were equilibrated throughout the SC treatment, and they were able to survive intact.

Subsamples of each type of milled decommissioned wood were weighed into thimbles (Whatman, Springfield Mill, UK; 10 × 50 mm) and micro-Soxhlet extracted with dichloromethane (DCM) in order to obtain and quantify any semi-volatile organic residues present in the wood prior to treatment.

Organic chemical analysis

Following SC treatment, the contents of the reactors were vacuum-filtered using pre-weighed filters, and the filtrate phases were liquid-liquid extracted with DCM in separatory funnels. The organic phases were collected and dried over anhydrous sodium sulfate followed by gas chromatography-mass spectrometry (GC-MS) analyses:

GC-MS: Shimadzu QP500 GC-MS; DB 5 capillary column (30 m; 0.25 mm id; 0.25 μm film); injector 250°C; temperature program 50°C (4 min) ramp 4°C/min to 250°C (10 min); sampling rate 2 Hz and mass acquisition range 50–450 amu in the full scan mode. Analyte transfer to the mass spectrometer source was at 280°C. Target molecular ions spanned the inclusive molecular weight range between toluene and various possible polychlorinated dibenzofurans (e.g., hexachlorodibenzodioxin, 390 amu). Product identification was performed using: a) comparison of experimental data with authentic standards, b) interpretation of mass spectra (molecular ions, isotopic structures, and logical frag-

ment losses), and c) comparison of spectra with computerized libraries of mass spectra. Mass spectra were considered acceptable if there was a signal: noise ratio of >3 for the base peak of interest, and minimal background interference with respect to isotopic clusters and fragments. MS tuning (PFTBA) was performed at least once daily and all MS analyses for comparison were conducted under the same tune. Digital background subtraction and chromatographic overlay algorithms were used for further evaluation of GC-MS data from standards and extracts. The individual compound standards and mixtures thereof were made up as concentrated stocks in DCM using commercially available polycyclic aromatic hydrocarbons (PAHs) and N-, O-, and S-heterocycles (NOSHs) in the highest purities available (typically 99% or above). The nominal detection limits for extracts were: a) light semi-volatiles (92–178 amu) : 400 pg and b) heavier semi-volatiles (178–252 amu) : 600–800 pg.

Metals analyses

Metal reactors were acid-extracted before and after SC treatment in order to: a) quantify any extractable traces of CCA from the metal matrix, and b) determine post-treatment adsorption/sequestration of CCA. All solutions, glassware, method blanks, and post-SC treatment samples were processed and analyzed using standard approaches for metal analysis (e.g., Catallo et al. 1995). All glassware was cleaned with soap and water, rinsed 10 times with tap water, soaked in a 4N HNO₃ acid bath overnight, and rinsed 5 times with deionized water. Method blanks were prepared and analyzed for the aqueous phases (AQ), organic phases (HC), and analytical dilution water. The aqueous phases from the SC treatments were treated with 5 mL of trace metal grade HNO₃ and left covered for 48 h. This extract was rinsed into a 100 mL Pyrex digestion tube and heated to 90°C for several hours. The temperature was increased to 120°C until volume was reduced to 1.5 mL. This was diluted with deionized water to 50 mL total volume and analyzed directly. The organic phase was evaporated to near-dryness, followed by addition of 5

mL of HNO_3 . This was refluxed at 120°C for several hours so as to solubilize metals and eliminate organic matter. Then the reflux was discontinued and the extract was heated at the same temperature until volume was reduced to 1.5 mL. This was diluted to 50 mL final volume as above and analyzed. Samples method blanks and acid rinses of the reactor vessel were then analyzed for copper, chromium, and arsenic using inductively coupled argon plasma emission spectrometry (ICAP). Metals concentrations in each phase are presented as means (μg or ppm) and standard errors of duplicate runs.

RESULTS AND DISCUSSION

Figure 1 shows a total ion chromatogram (TIC) from GC-MS analysis of semivolatile or-

ganic chemicals from the CCA-treated wood before (A) and after (B) hydrothermal treatment. It can be seen that no semivolatile compounds are detected in the range of interest in the pretreatment organic extracts as indicated by GC-MS (Fig. 1A). After hydrothermal treatment, the resulting organic phase (Fig. 1B) contained a complex array of semivolatile aromatic and heterocyclic compounds spanning the molecular weight range of 92 (toluene) to 226 (chrysene and its isomers). The efficiency of wood degradation was about 98–99% based on measurements of difference between wood mass introduced to the reactors and that recovered post-treatment on the filters. Even though this wood was transformed under acidic SC conditions, the product profile is similar to that observed under basic conditions using creosote-

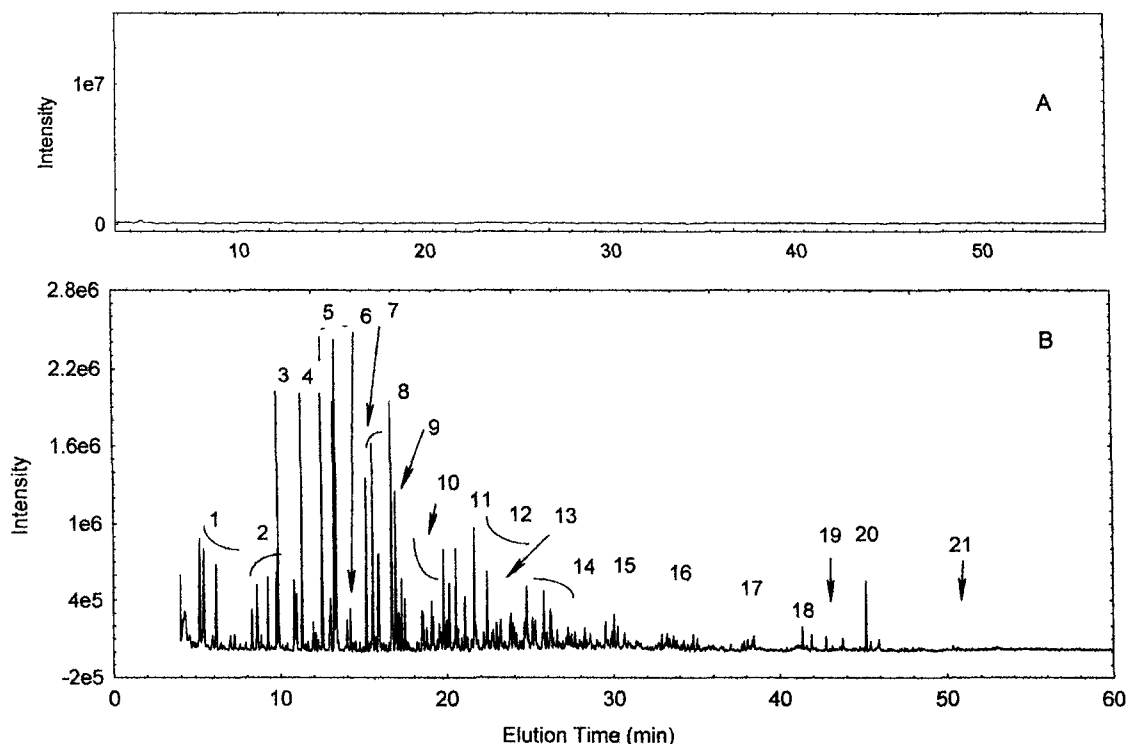


FIG. 1. Total ion chromatogram (TIC) of A. DCM Extract of CCA-impregnated wood (no analytes detected). B. DCM extract of the CCA-impregnated wood after SC treatment. Compounds: 1. C_2 -Benzenes (3 isomer). 2. C_3 -Benzenes (5 isomers). 3. Phenol. 4. Indane. 5. C_1 -Phenols (2 isomers). 6. C_4 -Benzenes (6 isomers). 7. C_1 -Indanes (2 isomers). 8. C_2 -Phenols (3 isomers). 9. Naphthalene. 10. C_5 -Benzenes (4 isomers). 11. C_3 -Phenols. 12. C_1 -Naphthalenes (2 isomers). 13. Hydroxyindane. 14. C_4 -Phenols. 15. C_1 -Biphenyls. 16. Phenanthrene/anthracene. 17. C_1 -Phenanthrenes/anthracenes (5 isomers). 18. C_2 -Phenanthrenes (3 isomers). 19. C_3 -Phenanthrenes. 20. C_4 -phenantrene (1 isomer). 21. Triphenylene/Benzanthracene/Chrysene (2 isomers).

impregnated *Pinus* sp. (Catallo and Shupe 2003; Catallo and Junk 2001), and other wood types including Chinese tallow tree (*Sapium* sp.) (Catallo and Shupe 2002). These similarities include the presence of highly substituted benzenes (i.e., up to C₅) phenols (up to C₃), and light PAHs (i.e., indanes and naphthalenes with up to C₂). There are, however, also significant differences between the basic and acidic SC semi-volatile wood-derived product mixtures. For example, the acidic treatments provide for increased alkyl substitution of several aromatic compounds, particularly the phenols and three ring PAHs (e.g., C₄ phenols and C₄ phenanthrenes, which were observed here for the first time in substantial amounts). Also, the acidic SC conditions had an apparent inhibitory effect on the generation of PAH ring systems larger than phenanthrene vs. the basic conditions (e.g., see Fig. 3 below, Catallo and Shupe 2003), where systems up to five fused rings were detected.

Table 1 gives metals concentration data for CCA in each phase recovered (AQ, HC, and the first post-treatment reactor extract), as well as percent total encountered in each phase. It can be seen that very little of the metal mass partitioned with the HC phase under these conditions, and that, with respect to liquids recovered from the reactors, the overwhelming majority of metals were found in the acidic AQ vs. the HC. In the case particularly of Cr and also of As, significant residues of these materials remained adsorbed to the reactor surfaces, as determined by repeated post-treatment acidic extraction of the reactors followed by ICAP analysis. It was found that Cr

and, to a lesser extent As, were tightly associated with the reactor walls. Loss of As as the AsH₃ (arsene) gas also is highly likely under acidic conditions, and this gas can be scrubbed and recovered in large-volume treatment operations. Further, the coprecipitation and/or deposition of Cr and As on the reactor surfaces could be ameliorated by using an unreactive or easily replaceable liner in the hot zone of the reactor. Appropriated materials for this purpose are quartz and garnet, with borosilicate glass only stable for short periods in the presence of SC water. Previous SC experiments examining the behavior of CCA-treated wood under basic pH conditions showed that more metal mass occurred in the HC phase, and it could be extracted reasonably well by acidic water post-treatment. It was also found that basic SC conditions enhanced the deposition of the metals *in situ*. Aqueous recoveries of all metals after treatment by acidic washing were typically below 40% of total. Acidic SC conditions lessened the scaling problem. These data suggest that more highly acidic conditions could further decrease metal deposition or reactor walls and increase their partitioning with the AQ phase. For pH < 2, SC water experiments, special alloys are needed for reactors. We currently are evaluating Ta/W and Ta/Nb for treatment stability, lifespan, and appropriate machinability.

As mentioned above, a problem was encountered with hydrothermal treatment of phenolic materials. Under appropriate conditions, individual compounds can combine to form byproducts, including the dibenzofurans, dibenzopyrans

TABLE 1. Concentrations of CCA metals in pre-treatment wood chip extracts and the post treatment aqueous (AQ) and hydrocarbon (HC) samples.

Element	Pretreatment ¹	Aqueous post treatment ²	Hydrocarbon post treatment ³	Reactor wall recovery ⁴	Total	%Mass Recovered ⁵
Cu	1064 (33) ^b	968 (24)	10 (0.6)	88.0 (3.0)	1066	100.2
Cr	1644 (37)	460 (32)	21 (0.3)	0.24 (0.06)	481	29.3
As	1458 (38)	1006 (20)	10 (0.26)	5.0 (0.3)	1021	70.0

¹Micrograms metal per gram wood by acidic extraction followed by ICAP analysis.

^{2,3}Micrograms metal (total) in the liquid phases.

⁴Total micrograms metal recovered in one extraction of the reactor vessel after SC treatment.

⁵Percent of total metals readily recovered in both liquid phases and the first post-treatment reactor extraction.

^bData are means and ranges (in parentheses) of duplicate analyses.

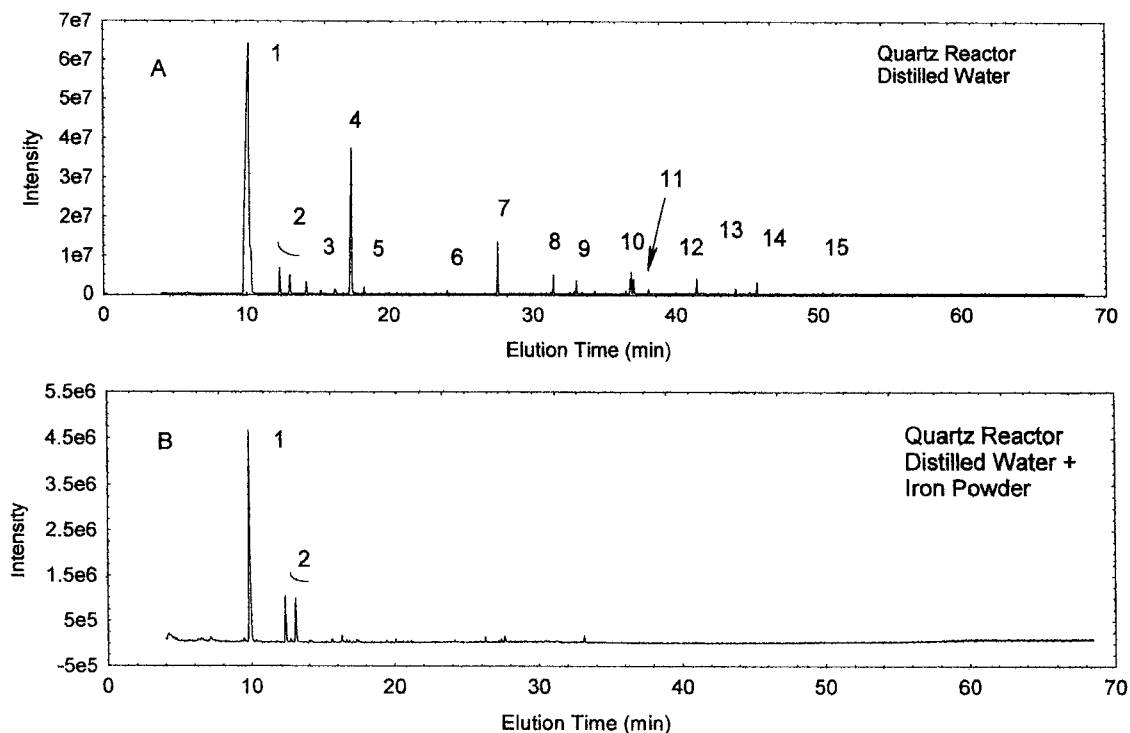


FIG. 2. A. Total ion chromatogram of 4-chlorophenol after SC treatment in a quartz reactor. B. The same as (A) but with an excess of (3 mg) of iron powder. 1. Phenol 2. C₁-Phenols (2 isomers). 3. Benzofuran and C₂-Phenols (2 isomers). 4. 4-Chlorophenol (educt). 5. C₃-Phenol. 6. Diphenyl ether. 7. Dibenzofuran. 8. Xanthene. 9. Monochlorinated unknown. (3 isomers, mass 202/204). 10. 9H-Xanthene-one. 11. Dibenzodioxin. 12. Dichlorodibenzofuran. 13. Monochlorinated unknown. (mass 230/232). 14. Dichlorodibenzodioxin. 15. Dichloroxanthene.

(xanthenes), and dibenzodioxin. If chlorinated phenolics are involved, the situation can be unfavorable because of the generation of chlorinated dibenzodioxins and dibenzofurans, many of which are known or suspected mutagens/carcinogens. Figure 2A shows this effect using 4-chlorophenol (4CP) as the educt: clearly, when run under SC conditions in pure water with no contact with reactor walls (i.e., the reaction is run in the quartz cells in isolation from metal surfaces and dissolved metal ions), 4CP partially reacts with itself to form chlorinated dibenzofurans, dioxins, and related materials. Addition of iron particles to the quartz reactor significantly decreased these reactions (Fig. 2B). This mimics the state of affairs encountered under SC conditions using metal reactors because leached and surface iron is part of the SC reaction system: as

illustrated here, it enhances dechlorination and decreases condensation of phenolics to polycyclic O-containing heterocycles.

Figure 3 shows the pretreatment solvent extract from the penta wood chips (A), and the post-treatment hydrocarbon mixture containing no detectable penta (B). The level of penta detected in extracts of the pre-treatment wood was on the order of 1,000 ppm. After treatment, no penta is detected (detection limit ca. 500 pg), and the resulting liquid hydrocarbon mixture is similar to the CCA-impregnated wood in many respects. Indeed, no chlorinated chemicals were detected in this hydrocarbon mixture. Anoxic SC water treatment of penta-impregnated wood offers: 1) reduction of waste penta concentration by at least 3.5 orders of magnitude vs. untreated wood, 2) the concomitant generation of a usable

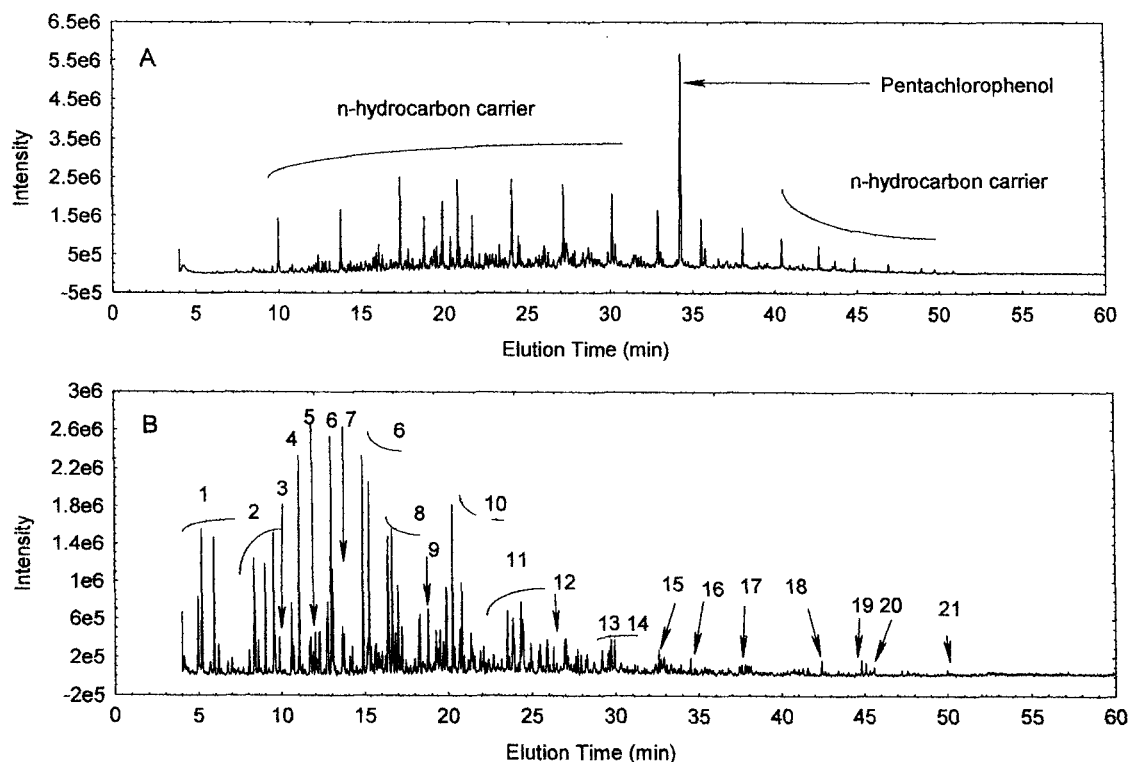


FIG. 3. Total ion chromatogram from GC-MS analysis. A. Penta-impregnated wood extract in DCM (no SC treatment). B. Liquid/liquid extract of aqueous and hydrocarbon phases resulting from SC treatment of penta wood chips. Compounds: 1. C_2 -Benzenes (3 isomers). 2. C_3 -Benzenes (5 isomers). 3. Phenol. 4. Indane. 5. C_1 -Phenols (2 isomers). 6. C_4 -Benzenes (5 isomers). 7. C_1 -Indanes (4 isomers). 8. C_2 -Indanes (6 isomers). 9. Naphthalene. 10. C_1 Tetralins. 11. C_1 -Naphthalenes (2 isomers). 12. C_2 -Naphthalenes (5 isomers). 13. Acenaphthalene. 14. C_3 -Naphthalenes. 15. Fluorene. 16. C_1 -Biphenyl. 17. C_1 -Phenanthrenes (4 isomers). 18. Pyrene. 19. C_1 Pyrenes (2 isomers). 20. Terphenyl. 21. Triphenylene-/chrysene/benzanthracene (2 isomers).

hydrocarbon product, and 3) the elimination of high volume treated wood waste.

CONCLUSIONS

The objective of this study was to evaluate the effects of SC conditions on the recovery and transformation of preservatives in decommissioned wood and the transformation of this wood into usable hydrocarbon mixtures. The findings indicated that decommissioned CCA- and penta-treated wood can be chemically converted, using environmentally benign chemical processes, into a mixture of hydrocarbons that can be used or sold. Thus, the hazardous waste (preservatives) was recovered (CCA) or degraded (penta), and

the solid waste (wood) was transformed into a complimentary product mixture in a single pass.

The major advantage of these findings is that there is no substantial solid or water-soluble residue from this process. In any case, the process water can be recycled. Based in these results, it would seem that the waste problem associated with decommissioned CCA- and penta-treated wood products can be addressed in environmentally friendly ways. This approach has attainable end points: 1) recovery and/or transformation of chemical wastes, 2) significant reduction of the volume of decommissioned treated wood targeted for landfills or other treatment systems (e.g., incineration), and 3) the generation of a value-added hydrocarbon mixture.

The use of SC water under highly oxidizing conditions (the so-called "supercritical wet oxidation or SWO" technology) for mineralization of pollutant wastes to CO₂ and water is well established (Mizuno et al. 2000), but the use of anoxic and reductive SC conditions for simultaneous synthesis and recovery of wastes has been examined only very recently (Catallo and Junk 2001; Catallo and Shupe 2003). The current approach can employ existing pilot scale flow-through systems with modifications, and recycling of preservatives recovered reduces the need for new production of these chemicals. In the current context, two areas of further work present themselves, particularly with respect to high volume treatment applications: 1) even trace levels of chlorinated byproducts may accumulate to unacceptable levels and this needs to be addressed, and 2) the generation of volatile arsenic species must be accommodated by scrubbing to capture any fugitive emissions.

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