

HYDROTHERMAL TREATMENT OF CREOSOTE-IMPREGNATED WOOD¹

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ABSTRACT

This paper describes the treatment of creosote-treated wood in anoxic supercritical water (SC). Decommissioned (ca. 15 yr) creosote-treated pine utility pole wood, which had been chipped was hydro-treated directly. During treatment, the creosote-derived hydrocarbon residues in the wood were nearly completely (>99%) recovered, and the wood itself was transformed into a mixture of hydrocarbons including substituted benzenes, phenolics, and light PAHs. These wood-derived transformation products served to reconstitute the "light end" of the creosote, which had been largely lost while in service. Thus, the hazardous waste (creosote hydrocarbon mixture) was recovered, and the solid waste (wood) was transformed into a complementary product mixture in a single pass. Solid residues after 12–20 h of treatment were <2% w/w.

Keywords: Creosote, hazardous and solid wastes, PAHs, supercritical water, transformation/recovery/recycling, utility poles, wood.

INTRODUCTION

Creosote, a high boiling fraction of coal or petroleum distillate, is widely used as a preservative for wood in utility structures, marine pilings, and other applications (Catallo and Gambrell 1987). In 1997, for example, some 2,758,061 m³ (97.4 × 10⁶ ft³) of wood was treated with 292,233,790 L (77.2 × 10⁶ gallons) of creosote along with 17,791,435 L (4.7 × 10⁶ gallons) of petroleum solvent (Micklewright 1998). It has been estimated that approximately 2 × 10⁶ m³ (70,629,333 ft³) of

creosote-treated wood is taken out of service each year in the United States and that total will grow to approximately 16 × 10⁶ m³ (565,034,668 ft³) in 2020 (Cooper 1994). Furthermore, it has been estimated that a total volume of 2.8 × 10⁶ m³ (100,000,000 ft³) of creosote-preserved wood is annually decommissioned (AWPI 1997).

Typically, waste wood products containing creosote are designated as dual solid (e.g., wood, other building material) and hazardous (chemical) waste material, frequently requiring special handling. This is because many of the residual aromatic hydrocarbons (AHs), polycyclic aromatic hydrocarbons (PAHs), and N-, O-, S-heterocycles (NOSHs) in the creosote are toxic and/or carcinogenic and mo-

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bile in the environment (Catallo 1996; Catallo and Gambrell 1987; Warshawsky 1992). For example, at a hazardous waste site, in which a creosote-treating facility was previously located, leachate and groundwater contained mutagenic PAHs, NOSHs, and related materials (Rostad et al. 1984).

Treatment approaches to decommissioned creosote-treated wood include incineration, land-filling, steam extraction (Roliadi 1997), and biological treatment (Portier et al. 1994). All of these approaches have had limited success in eliminating and/or recovering creosote. As a result, a need exists to provide more comprehensive treatments for creosote-impregnated materials.

Supercritical (SC) water ($>374^{\circ}\text{C}/221$ bar) under anoxic-reducing conditions can be used for a variety of synthetic purposes (Junk and Catallo 1997; Jimeno et al. 1997; Junk et al. 1997a, b) and chemical transformation (Catallo and Junk 2001) purposes. The SC phase is one of the most energetic and chemically dynamic conditions known for aqueous systems. For example, 3/8 in. stainless steel reactors rated far above $374^{\circ}\text{C}/221$ bar corrode and rupture after a few hours of exposure to neutral and basic SC water. Borosilicate glass, aluminum, and some plastics (e.g., teflon) dissolve or degrade rapidly under SC conditions. Further, organic chemicals of sparing water solubility at room temperature are rendered highly soluble in SC water and, thereby, are available for homogeneous and heterogeneous chemical reactions *in situ*. Of far greater interest than its corrosiveness and ability to solvate normally insoluble chemicals is that the SC phase vastly facilitates and promotes a wide range of organic chemical reactions such as trans- and de-halogenation, adduction, aromatic proton exchange, disproportionation, condensation, decarboxylation, and aromatization without added catalysts or reagents. The nature, rates, and yields of these reactions simply are not achieved in other aqueous systems including a) liquid water under conditions normally observed, b) very high pressures, c) superheated steam (Junk and Catallo 1997; Van

Eldik and Hubbard 1997), and other supercritical fluids (e.g., CO_2 ; Van Eldik and Hubbard 1997).

Laboratory data show that reactions of biogenic matter in SC water and brines give rise to volatile and semivolatile hydrocarbon assemblages in a matter of minutes to hours. All forms of biogenic matter tested (protein, lipid, starch, cellulose, chitin, diatom cells, spent bacterial cultures, DNA, lignin, 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, pyrene), heteroarenes (e.g., dibenzofuran, dibenzodioxin, dibenzopyran), and their C_1 - C_5 alkyl homologs (includes mixtures of methyl and longer alkyl chain substituents). Other products included gases (CO_2 , CH_4), asphaltics, and minor amounts of carbonized particulate residues. The major variables tested thus far in SC treatments have been temperature and duration: rates of hydrocarbon formation and degree of mineralization and carbonization were higher at higher temperature or longer times. Other factors found to influence hydrocarbon concentration and composition in SC were (a) the elemental composition and molecular structure of the starting materials, and (b) the presence of coreactants in the reaction mixture, e.g., dissolved metals or reducing agents. The objective of this work was to study the effects of SC conditions on the recovery and transformation of hazardous and solid wastes in decommissioned utility pole wood.

MATERIALS AND METHODS

A representative decommissioned creosote-treated, southern yellow pine (*Pinus* sp.) utility pole was selected for this study. A one-foot section, starting at the ground line and proceeding vertically toward the top of the pole, was removed and reduced to particles in a Wiley Mill that passed a 1-mm mesh screen.

Weighed particle samples (2.5 g) were added to 65 mL i.v. high pressure autoclaves in the presence of water above pH 10. The suspension was sparged with Ar for 1 h, sealed and incubated at $400 \pm 10^\circ\text{C}/280$ bar for 15 h, including heat-up and cool-down. Fresh creosote was obtained commercially (Kopper Industries, Inc., Pittsburg, PA), diluted to appropriate levels using dry dichloromethane (DCM), and analyzed by gas chromatography-mass spectrometry (GC-MS; see below). **Caution: High temperatures and pressures. Corrosive.**

Subsamples of the milled decommissioned utility pole wood were weighed into cellulose thimbles (Whatman, Springfield Mill, UK; 10×50 mm) and micro-Soxhlet extracted with ether in order to obtain and analyze a sample of weathered creosote. The resulting extract was dried over anhydrous sodium sulfate.

Following SC treatment, the contents of the reactors were vacuum-filtered using pre-weighed membranes, and filtrates were liquid-liquid extracted with ether in separatory funnels. The ether phase was collected and dried with anhydrous sodium sulfate as above followed by GC-MS analyses.

CG-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 $4^\circ\text{C}/\text{min}$ to 250°C (10 min); sampling rate 2 Hz and mass acquisition range 50–300 amu in the full scan mode. Analyte transfer to the mass spectrometer source was at 280°C . Target ions spanned the inclusive molecular weight range between benzene (78 amu) and coronene (300 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 fragment 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 per-

formed 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. Semiquantitation was performed by comparison of molecular ion peak integrals in samples to external standard curves constructed using known amounts of PAH standards. Creosote compound recoveries also were determined using direct comparison of target analyte molecular ion peak integrals with those from deuterated PAH internal standards.

RESULTS AND DISCUSSION

Figure 1 shows a total ion chromatogram (TIC) of semivolatile AHs, PAHs, and NOSHs from a fresh creosote. Selected chemical structures are given in Fig. 2. The fresh creosote (Fig. 1) contains a complex array of aromatic and heterocyclic compounds spanning the molecular weight range 94 through 252 (i.e., phenol through the benzofluoranthene/benzopyrene isomers). Looking specifically at elution times less than 25 min (X-axis), there are substantial amounts of phenol, indene, naphthalene, quinoline, biphenyl, and their C_1 and C_2 alkyl homologs. Compounds eluting after 25 min included 3–5 ring PAHs and NOSH compounds such as fluorene, dibenzothiophene, dibenzofuran, phenanthrene, pyrene, carbazole, isomers of benzofluorene (216 amu), triphenylene/benzanthrance/chrysene (226 amu), and the 252 amu compounds mentioned above.

Figure 3 shows a TIC of weathered creosote recovered from the decommissioned wood pole material by solvent extraction. It can be seen that, with the exception of a chlorinated material around 7 min (i.e., tetrachloroethane) and a small residue of quinoline (129 amu), the light semivolatile components of the creosote (i.e., those compounds eluting before 25 min) in the decommissioned pole are absent. This is very clearly seen in the case of naphthalene, which is the most abundant light se-

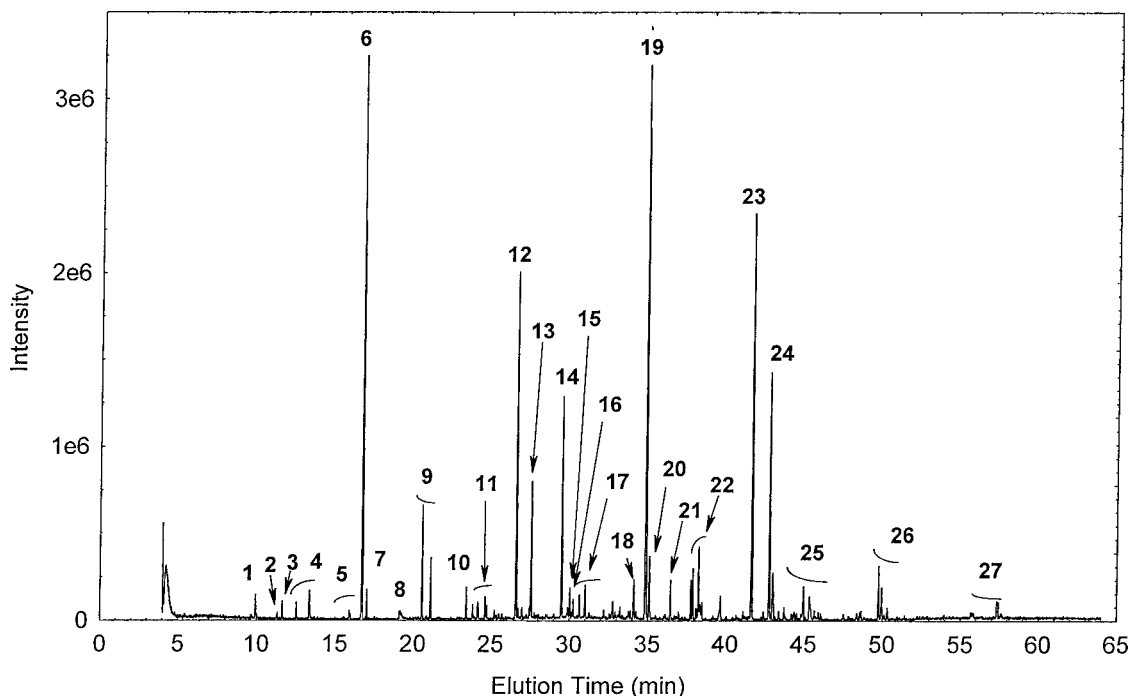


FIG. 1. Total ion chromatogram (TIC) of fresh creosote. Compounds: 1. Phenol. 2. 2,3-Dihydro-1H-indene. 3. 1-H-Indene. 4. C₁ Phenols (2 isomers). 5. C₂-Phenols (3 isomers). 6. Naphthalene. 7. Benzo(b)thiophene. 8. Quinoline. 9. C₁-Naphthalenes. 10. Biphenyl. 11. C₂-Naphthalenes (4 isomers). 12. Acenaphthylene. 13. Dibenzofuran. 14. Fluorene. 15. C₃-Naphthalenes (3 isomers). 16. C₁-Biphenyl. 17. C₁-Dibenzofurans (2 isomers). 18. Dibenzothiophene. 19. Phenanthrene. 20. Anthracene. 21. Carbazole. 22. C₁-Phenanthrenes (4 isomers). 23. Fluoranthene. 24. Pyrene. 25. Benzofluorenes (3 isomers). 26. Triphenylene/Benzanthracene/Chrysene (2 isomers). 27. Benzofluoranthenes/Benzopyrenes (m/z 252; 4 isomers).

semivolatile compound in the fresh creosote (Fig. 1) but is absent from the weathered material. Other compounds found in the fresh but not in the weathered creosote included phenol, benzothiophene, and biphenyl and several of their alkyl homologs. The loss of the light semivolatile aromatic and heterocyclic compounds likely reflects leaching or degradation *in situ*, and this would reduce preservative efficacy. Nevertheless, toxic and carcinogenic compounds remain in the wood after decommissioning, as evidenced by the compounds that eluted after 25 min including dibenzofuran, phenanthrene, fluoranthene/pyrene, and the benzofluoranthenes. Interestingly, the ratios of these compounds to one another are close to those observed in the fresh creosote, illustrating the lack of pronounced weathering

of these relatively nonvolatile and water-insoluble chemicals.

Figure 4 shows a TIC of the nonpolar liquid residue generated by a 15-h SC treatment of the decommissioned utility pole wood. The wood particle mass subjected to SC treatment was 98–99% (w/w) degraded and transformed to semivolatile hydrocarbons (e.g., benzene, phenol, indene, and their alkyl homologs). Thus, the resulting post-SC treatment mixture was no longer a suspension of particles, but rather a biphasic system of polar (water) and nonpolar (oil) liquids with the solid residue almost completely transformed with 1–2% of the original wood mass remaining as carbonized particles. In addition to monoaromatic compounds, and their alkyl homologs, the SC treatment of the decommissioned pole re-

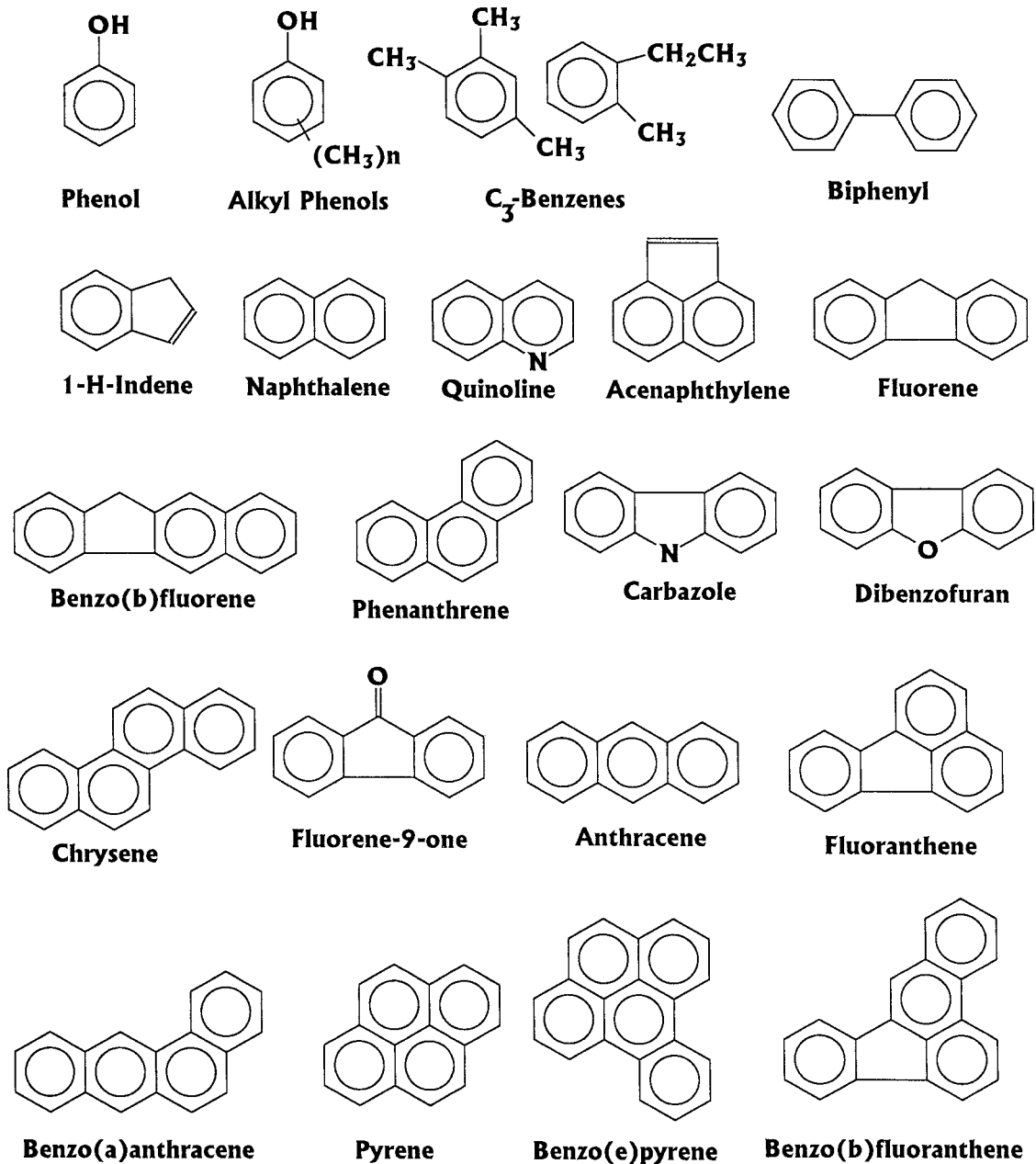


FIG. 2. Chemical structures of selected AHs, PAHs, and NOSHS identified in creosote and SC treated utility pole wood.

placed substantial amounts of phenol and naphthalene and their C_1 and C_2 alkyl homologs. It was shown above that these compounds are prominent in fresh creosote but are depleted during service. Further, the chlori-

nated compound found in the weathered creosote (Fig. 3, compound 1) was degraded, and the PAH and NOSH compounds eluting after 25 min in the SC treatment were virtually identical to the fresh and weathered creosote

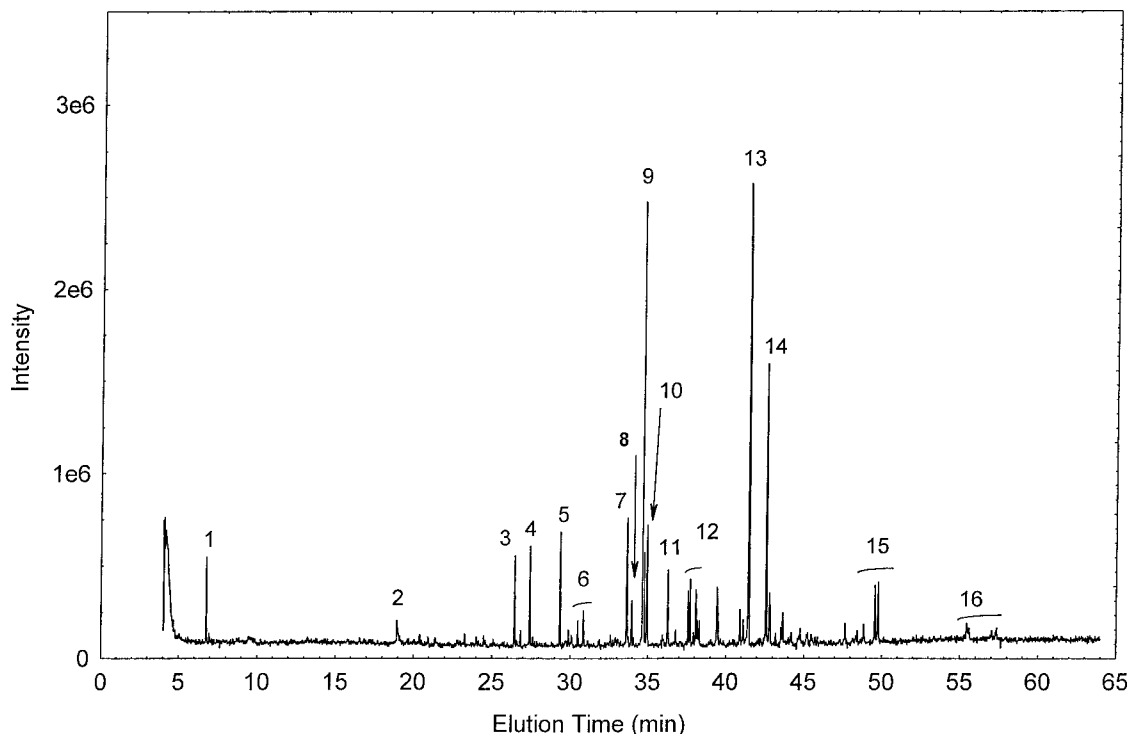


FIG. 3. Total ion chromatogram (TIC) of weathered creosote extracted from decommissioned utility pole wood. Compounds: 1. Tetrachloroethane (1 isomer). 2. Quinoline. 3. Acenaphthylene. 4. Dibenzofuran. 5. Fluorene. 6. C₁-Dibenzofurans (2 isomers). 7. Fluorene-9-one. 8. Dibenzothiophene. 9. Phenanthrene. 10. Anthracene. 11. Carbazole. 12. C₁-Phenanthrenes (4 isomers). 13. Fluoranthene. 14. Pyrene. 15. Triphenylene/Benzanthracene/Chrysene (2 isomers). 16. Benzo[a]fluoranthene/Benzopyrenes (m/z 252; 4 isomers).

samples. Thus, the residual creosote in the pole wood was recovered (>99% versus internal standards).

The use of SC water under oxidative 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/reductive SC conditions for simultaneous synthesis and recovery of wastes has not been examined. The current approach can employ existing pilot scale flow-trough systems with slight modifications, and with no increased input of energy, and it results in the reconstitution and recovery of a usable product. Clearly, this has the dual advantage of not increasing atmospheric CO₂, and reducing the need for new coal mining and production of

coal chemicals for the purposes of wood preservation.

CONCLUSIONS

The objective was to study the effects of SC conditions on the recovery and transformation of hazardous and solid wastes in decommissioned utility pole wood. The findings are quite encouraging and indicate that decommissioned creosote-treated wood can be chemically converted, using environmentally friendly chemical processes, into a mixture that is similar to fresh creosote. In essence, a closed-loop system is technically feasible. Further research is needed to determine the efficacy of the reconstituted and recovered creosote.

This research has shown that during SC

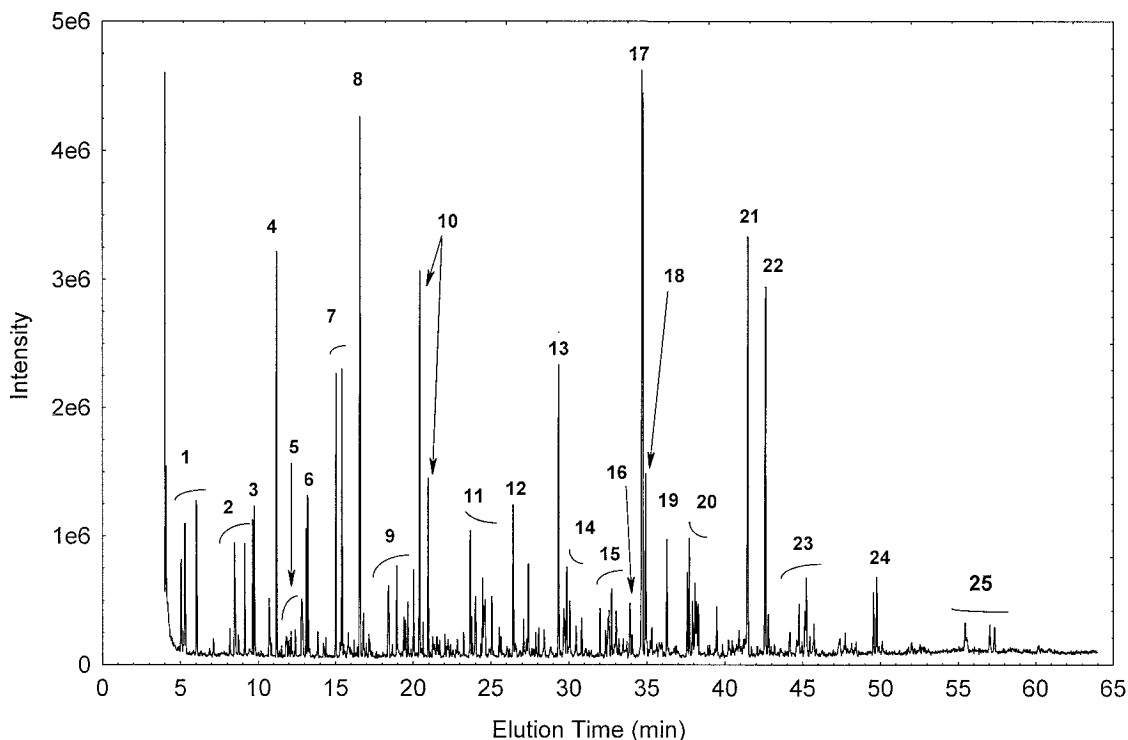


FIG. 4. Total ion chromatogram (TIC) of decommissioned utility pole wood after treatment (12 h) in SC water. Compounds: 1. C₂-Benzenes (3 isomers). 2. C₂-Benzenes (5 isomers). 3. Phenol. 4. 1-H-Indene. 5. C₄-Benzenes (4 isomers). 6. C₁-Phenols. 7. C₁-Indene. 8. Naphthalene. 9. C₂-Indenes (3 isomers). 10. C₁-Naphthalenes (2 isomers). 11. C₂-Naphthalenes (4 isomers). 12. Acenaphthylene. 13. Fluorene. 14. C₁-Biphenyls (2 isomers). 15. C₁-Fluorenes. 16. Dibenzothiophene. 17. Phenanthrene. 18. Anthracene. 19. Carbazole. 20. C₁-Phenanthrenes (4 isomers). 21. Fluoranthene. 22. Pyrene. 23. Benzofluorenes (3 isomers). 24. Triphenylene/Benzanthracene/Chrysene (2 isomers). 25. Benzofluoranthenes/Benzopyrenes (m/z 252; 4 isomers).

treatment, the creosote-derived hydrocarbon residues in the wood were recovered and the wood itself was transformed into a mixture of semivolatile hydrocarbons including substituted benzenes, phenols, and light PAHs. These wood-derived transformation products served to reconstitute the chemical "light end" of the creosote, which had been largely lost through volatilization, photolysis, and solubilization when in service. Thus, the hazardous waste (creosote hydrocarbon mixture) was recovered, and the solid waste (wood) was transformed into a complementary product mixture in one pass.

The major advantage of these findings is that there is no substantial solid residue from this process, and the water can be recycled.

Based on these results, it would seem that with a modest investment of equipment and energy, the waste problem associated with decommissioned CB- and creosote-treated wood products now has a new more environmentally friendly option. The new system has attainable end points: (1) complete recovery of chemical wastes, and (2) significant reduction of the volume of decommissioned creosote-treated wood targeted for landfills or treatment systems (e.g., incineration).

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