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Liquefaction of CCA-treated wood and elimination of metals from the solvent by precipitation

Lianzhen Lin and Chung-Yun Hse*

USDA Forest Service, Southern Research Station, Pineville, LA, USA

*Corresponding author.
USDA Forest service, Southern Research Station, Pineville, LA, USA
E-mail: chse@fs.fed.us

Abstract

Spent chromated copper arsenate (CCA)-treated wood was liquefied in polyethylene glycol 400/glycerin (2:1 w/w). Sulfuric acid (95–98%) and ferrous salts ($FeSO_4 \cdot 7H_2O$ or $FeCl_2 \cdot 4H_2O$) were used as catalysts and additives, respectively. The resulting liquefied CCA-treated wood was diluted with aqueous solvents and was then mixed with complexion/precipitation agents, followed by precipitation or filtration to remove the toxic metal-bearing sediment. As a result, more than 90% of Cu, Cr or As was removed.

Keywords: chromated copper arsenate; detoxification; inductively coupled plasma; recycling; treated wood; wood liquefaction.

Introduction

The economic and ecological aspects of treated woods have been discussed by Eisler (2002) and Falk (1997), respectively. In the majority of cases chromated copper arsenate (CCA) is used for wood protection. Disposal of this spent CCA-treated wood has increasingly become a major concern. Popular waste disposal options for spent preserved wood, such as burning and land filling, are costly or even impractical because of increasingly strict regulatory requirements. Burning of preservative-treated wood waste emits highly toxic arsenic into the environment (Dobbs and Grant 1978; Hirata et al. 1993; McMahon et al. 1986). Recycling of the preserved wood and removal of the toxic preservatives from preservative-treated wood is of great importance. Research has been carried out in this area, focusing on direct recycling of preserved wood into composite manufacturing (Mengeloglu and Gardner 2000; Munson and Kamdem 1998; Vick et al. 1996), CCA removal from spent CCA-treated wood by low-temperature pyrolysis (Helsen and Van den Bulk 2000), solvent extraction (Cooper 1991; Honda et al. 1991), biological remediation (Clausen 1997; Legay and Labat 1997; Leithoff and Peek 1997; Stephan and Peek 1992), and dual treatment processes involving biological remediation and chemical extraction (Clausen and Smith 1998).

Research at our laboratory has been focused on a recycling system based on wood liquefaction technology. The principal goals of our research are: (1) eliminating CCA from treated wood; (2) utilizing CCA-free liquefied wood as bio-based chemicals for the preparation of resin or plastic; and (3) achieving zero discharge of CCA into the waste stream.

In this study, we describe the liquefaction of CCA-treated wood and the precipitation of metals from the resulting liquid.

Experimental

Materials

Recycled CCA-treated southern pine (*Pinus* sp.) wood was obtained from Arnold Forest Products Co. of Shreveport, Louisiana. The wood was reduced to sawdust at the Southern Research Station, Pineville, Louisiana. After screening through a 20-mesh sieve, the oven-dried sawdust was used without further treatment. The residual preservative in the wood was determined by means of inductively coupled plasma (ICP) spectroscopy. The CCA contents in the sawdust as determined were 2261±90 ppm of Cu, 3400±110 ppm of Cr, and 3290±150 ppm of As.

Chemicals

A mixed solvent of polyethylene glycol 400/glycerin (2:1 w/w) was used for all liquefaction. Sulfuric acid (assay 95–98%) was used as a catalyst and ferrous salts ($FeSO_4 \cdot 7H_2O$ or $FeCl_2 \cdot 4H_2O$) were used as additives. All chemicals were reagent grade.

Liquefaction of wood

The conditions used for liquefaction were: reaction temperature, 150°C; reaction time, 120 min; solvent/wood ratio, 3:1 (w/w); salt additive/wood ratio, 2–20:100 (w/w); and catalyst/solvent ratio, 3:100 (w/w).

The liquefaction solvent (PEG/glycerin), catalyst, and salt additive were weighed into a beaker and then mixed until the catalyst and salt additive were uniformly dispersed in the solvent. A CCA-treated wood sample was introduced and mixed with the liquefaction solvent. The thoroughly mixed ingredients were placed in a Paar reactor equipped with a stirring system at a reactor temperature of 150°C. After a 120-min reaction time the reactor was cooled to ambient temperature. The liquefied wood solution was transferred into a container and stored at room temperature.

Residue determination

A 50-g sample of the liquefied wood was dissolved in 250 ml of acetone/water (4:1 v/v) under stirring, and then the solution was filtered through a glass fiber filter (0.45 μm), which was then washed with the same solvent until the filtrate was clear. The residue remaining on the filter was dried in an oven at 100°C to a constant weight.

Table 1 Relationship between liquefaction conditions[a] and percentage of unliquefied residue.

Sample	Acid (%)[b]		Ferrous ions (molar ratio)[d]		Unliquefied residue (%)
	H_2SO_4	H_3PO_4	$FeSO_4 \cdot 7H_2O$[c]	$FeCl_2 \cdot 4H_2O$[c]	
A	3				0.54
B	3		2.48		2.8
C	3		4.97		5.1
D	2		2.48		4.7
E	2		4.97		6.3
F	3			5.21	3.0
G	2	1			0.95

[a] Liquefaction temperature 150°C, time 90 min, solvent/wood ratio 3:1.

[b] Based on the weight of polyol.

[c] Based on the weight of wood.

[d] Molar ratio of ferrous ions to all the heavy metals.

Detoxification

A typical batch experiment for removal of CCA from liquefied wood was carried out as follows. A 50-g sample of the liquefied wood was redissolved in 300 ml of acetone/deionized water (4:1 v/v) solution; 2 g of $Ca(OH)_2$ was added under stirring to precipitate the heavy metals. Stirring was continued for 1–2 h and then the mixture was centrifuged (6000 rpm, 6842×*g*). The supernatant was concentrated in an evaporator and the CCA-containing residue was dried in an oven at 100°C for 10 h and weighed.

Determination of copper, chromium, and arsenic

Solid wood residue digestion was carried out according to AWPA Standard A7-93 (American Wood-Preservers' Association 1995a) previously employed in our laboratory for wet chemistry analyses. In short, the procedure requires accurate weighing of a sample of CCA-containing solid residue into a 100-ml test tube. For each gram of solid residue, 15 ml of nitric acid is added. A digestion blank is also prepared along with the samples. Test tubes are placed in an aluminum heating block and warmed slowly. The temperature is increased to 120–130°C after the initial reaction producing brown fumes subsides. The temperature is maintained until a transparent liquid is obtained. This is cooled to room temperature and 5 ml of hydrogen peroxide is added drop-wise. If the solution is not clear after this treatment, the temperature is increased and another 5 ml of hydrogen peroxide is added drop-wise. Heating is continued until approximately 1 ml of sample solution is left in the test tube. The sample is carefully transferred into a 25-ml volumetric flask and then diluted with deionized water to make up 25 ml of solution ready for quantitative elemental analysis of Cu, Cr, and As.

Quantitative elemental analysis of Cu, Cr, and As was conducted according to AWPA Standard A21-00 (American Wood-Preservers' Association 1995b). The standard describes an inductively coupled plasma emission (ICP) spectrometric method for the analysis of treated wood and treating solutions. Using a computer-controlled spectrometer, emission is calibrated to display concentration directly.

Table 2 Effect of treatment conditions on the removal of Cu, Cr, and As in spent CCA-treated wood.

Liquefied wood	Additive	pH	Cu (%)	Cr (%)	As (%)
A	None	8.4	28.2	79.4	76.0
B	$FeSO_4 \cdot 7H_2O$	8.5	91.6	94.0	98.4
C	$FeSO_4 \cdot 7H_2O$	8.2	99.8	99.3	98.9
D	$FeSO_4 \cdot 7H_2O$	7.9	90.1	91.5	96.3
E	$FeSO_4 \cdot 7H_2O$	8.3	92.0	92.1	97.1
F	$FeCl_2 \cdot 4H_2O$	7.5	80.0	95.0	90.5
G	H_3PO_4	9.9	93.6	100	99

The pH was adjusted by adding $Ca(OH)_2$.

Results and discussion

The liquefaction results are shown in Table 1. The unliquefied residue was used as a factor to estimate the liquefaction rate of wood. It can be seen that all the unliquefied residues obtained under the study conditions are below 7%. The addition of ferrous ions affected the liquefaction rate to a small extent, while the addition of phosphoric acid improved the liquefaction rate.

The liquefied CCA wood samples were subjected to detoxification treatment as described in the Experimental section, and the results are shown in Table 2. Approximately 90% of the metals could be removed when ferrous salt or phosphoric acid was present during the liquefaction. Without additives, the removal rates were particularly low for copper. Accordingly, the addition of ferrous salts or phosphoric acid in the liquefaction resulted in an obvious improvement of the removal rate. In sample F, for which the ferrous salt used was $FeCl_2 \cdot 4H_2O$, the removal rate was low compared to samples B, C, D, and E, for which $FeSO_4 \cdot 7H_2O$ was used. This may be due to the fact that the additional amount of $Ca(OH)_2$ was not enough to precipitate all the metal ions, as indicated by the lower pH of the solution compared to the other samples. Sample A was obtained by a process similar to traditional wastewater treatment. However, most of the copper could not be removed by this method, suggesting that copper hardly formed insoluble copper hydroxide during the post-treatment.

It has been known that the major components of cured CCA-treated wood are $CrAsO_4$-lignin complexes, $CuCrO_4$-lignin complexes, Cu^{2+}-lignin and Cu^{2+}-cellulose complexes, and $Cr(OH)_3$ precipitates. In other words, the primary form of arsenic in the treated wood is in water-insoluble $CrAsO_4$ and most of chromium is also in the form of $CrAsO_4$, possibly with small amounts of Cr (VI)-lignin complexes, whereas copper is primarily in the form of Cu^{2+}-lignin and Cu^{2+}-cellulose complexes, with some $CuCrO_4$-lignin complexes (Hingston et al. 2001). During liquefaction, these complexes are either released from the decomposed lignin and cellulose or still remain as the complexes or chelates with decomposed lignin and cellulose (organic matter or organic acids). It is obvious that $CrAsO_4$ or its chelates, which are insoluble in aqueous solvents, can be removed effectively by liquefaction followed by precipitation.

According to traditional wastewater treatment, water-soluble metal ions such as Cu^{2+} can be rendered insoluble as heavy metal hydroxides by shifting the pH of the solution towards the alkaline range with a metal hydroxide such as calcium hydroxide. The metal hydroxide precipitates also act as a co-precipitant to accelerate the sedimentation of precipitated particles. However, sample A in Table 2 demonstrates that copper is difficult to remove using a simple post-treatment. This result is probably attributable to the fact that various organic acids can be produced during liquefaction due to extensive decomposition of lignin, cellulose, and hemicellulose (Pu and Shiraishi 1994). Copper has a strong tendency to form water-soluble chelates with organic acids (Hingston et al. 2001; Cooper and Ung 1992; Warner and Solomon 1990) and it is usually difficult to release it from chelates or solidify it as copper hydroxides due to their strong affinity to the chelates. Therefore, chemicals are necessary that can break the chelate-copper bond and form a stable, insoluble compound or complex of copper. The addition of substances that exert a stronger attraction for the chelate than the copper ion may also be helpful to free the heavy metal for precipitation as an insoluble hydroxide. In samples B–F, ferrous ions play such a role in releasing the copper by bonding the chelating agents (such as organic acids). In sample G, phosphoric acid may have broken the copper-chelate bond and formed a stable, insoluble complex as copper phosphate. Therefore, the removal rates for samples B–G were significantly improved compared to that of sample A, for which no ferrous ion or phosphoric acid was present.

As for Cr(VI), its content in the cured CCA-treated wood was lower than 10% and hexavalent chromium can be difficult to remove if it is not reduced to Cr(III). In the presence of ferrous ions during liquefaction, Cr(VI) could be reduced to Cr(III) and the latter can be removed by precipitation as $Cr(OH)_3$. Without ferrous ions, CrO_4^{2-} can form $CaCrO_4$, which is hardly soluble in aqueous solvents.

Based on the above results and analysis, we propose the following removal mechanisms for Cr, Cu and As.

Conclusions

The presence of reducing agents in the liquefaction of spent CCA-treated wood is effective in reducing Cr^{6+}, Cu^{2+}, and As^{6+} or liberating the heavy metals from their corresponding organic chelates. A combination of chemical reduction *in situ* and post-precipitation treatment leads to effective removal of CCA. A recycling system based on wood liquefaction technology accomplishes detoxification and recycling of CCA-treated wood simultaneously.

References

American Wood Preservers' Association. (1995a) Standard for wet ashing procedures for preparing wood for chemical analysis. A7-93. AWPA Book of Standards. AWPA, Woodstock, MD.

American Wood Preservers' Association. (1995b) Standard method for the analysis of wood and wood treating solutions by inductively coupled plasma emission spectrometry. A21-00. AWPA Book of Standards. AWPA, Woodstock, MD.

Clausen, C.A. (1997) Enhanced removal of CCA from treated wood by *Bacillus licheniformis* in continuous culture. Document IRG/WP 97-50083. International Research Group on Wood Preservation, Stockholm, Sweden.

Clausen, C.A., Smith, R.L. (1998) Removal of CCA from treated wood by oxalic acid extraction, steam explosion, and bacterial fermentation. J. Ind. Microbiol. Biotechnol. 20(3/4):251–257.

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

Cooper, P.A., Ung, Y.T. (1992) Leaching of CCA-C from jack pine sapwood in compost. Forest Prod. J. 42(9):57–59.

Dobbs, A., Grant, C. (1978) The volatilization of arsenic on burning copper-chrome-arsenic (CCA) treated wood. Holzforschung 32:32–35.

Eisler, P. (2002) Deal will phase out popular lumber. USA Today, February 2. Washington.

Falk, B. (1997) Wood recycling: opportunities for the wood waste resource. For. Prod. J. 47(6):17–22.

Helsen, L., Van den Bulck, E. (2000) Metal behavior during the low-temperature pyrolysis of chromated copper arsenate-treated wood waste. Environ. Sci. Technol. 34(14): 2931–2938.

Hingston, J.A., Collins, C.D., Murphy, R.J., Lester, J.N. (2001) Leaching of chromated copper arsenate wood preservatives: a review. Environ. Pollut. 111:53–66.

Precipitation of metals during liquefaction and in the presence of Fe^{2+} ions:

Complexes of metals in solid state	Liquefaction: $PEG+H_2SO_4+$ glycerin	Metals in liquid (organic chelates = org. ch)	$+Fe^{2+}$	Metals in liquid phase
$CrAsO_4$-lignin	→	$CrAsO_4$-org. ch. $+CrAsO_4\downarrow$	→	Fe^{2+}-org. ch. $+CrAsO_4\downarrow$
$CuCrO_4$-lignin	→	$CuCrO_4$-org. ch. $+CuCrO_4\downarrow$	→	$Cu(III)+Fe^{2+}$-org. chel. $+Cu^{2+}+Fe^{3+}$
Cu^{2+}-lignin and cellulose	→	Cu^{2+}-org. ch. $+Cu^{2+}$	→	Fe^{2+}-org. chel. $+Cu^{2+}$
		Cu^{2+}	→	Cu^0+Fe^{3+}

Precipitation of metals in the presence of phosphoric acid:

	$+H_3PO_4$	
Cu^{2+}-org. ch.	→	$Cu_3(PO_4)_2\downarrow$ + org. matters
Cr(III)	→	$CrPO_4\downarrow+H_2O$
As(V)	→	$As_3(PO_4)_5\downarrow$

Precipitation of metals in the presence of calcium hydroxide:

	$+OH^-$	
Cr(III)	→	$Cr(OH)_3\downarrow$
Cu^{2+}	→	$Cu(OH)_2\downarrow$
Fe^{3+}	→	$Fe(OH)_3\downarrow$

Hirata, T., Inoue, M., Fukui, Y. (1993) Pyrolysis and combustion of wood treated with CCA. Wood Sci. Technol. 27(1):35–47.

Honda, A., Kanjo, Y., Kimoto, A., Koshii, K., Kashiwazaki, S. (1991) Recovery of copper, chromium, and arsenic compounds from waste preservative-treated wood. Document IRG/WP/3651. International Research Group on Wood Preservation, Stockholm, Sweden.

Legay, S., Labat, G. (1997) Biosorption of metals for wood waste effluent clean up. Document IRG/WP 97-50090. International Research Group on Wood Preservation, Stockholm, Sweden.

Leithoff, H., Peek, R.-D. (1997) Experience with an industrial scale-up for the biological purification of CCA-treated wood waste. Document IRG/WP 97-50095. International Research Group on Wood Preservation, Stockholm, Sweden.

McMahon, C., Bush, P., Woolson, E. (1986) How much arsenic is released when CCA-treated wood is burned? For. Prod. J. 36(11/12), 45–50.

Mengeloglu, F., Gardner, D.J. (2000) Recycled CCA-treated lumber in flakeboards: evaluation of adhesives and flakes. For. Prod. J. 50(2):41–45.

Munson, J.M., Kamdem, D.P. (1998) Reconstituted particleboards from CCA-treated red pine utility poles. For. Prod. J. 48(3):55–62.

Pu, S., Shiraishi, N. (1993) Liquefaction of wood without catalyst. II. Weight loss by gasification during wood liquefaction and effects of temperature and water. Mokuzai Gakkaishi 39(4):453–458.

Stephan, I., Peek, R.-D. (1992) Biological detoxification of wood treated with salt preservatives. Document IRG/WP 92-3717. International Research Group on Wood Preservation, Stockholm, Sweden.

Vick, C.B., Geimer, R.L., Wood Jr, J.E. (1996) Flakeboards from recycled CCA-treated southern pine lumber. For. Prod. J. 46(11/12):89–91.

Warner, J., Solomon, K. (1990) Acidity as a factor in leaching of copper, chromium and arsenic from CCA-treated dimension lumber. Environ. Toxicol. Chem. 9(11):1331–1337.

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