Comparative Study on Liquefaction of Creosote and Chromated Copper Arsenate (CCA)-treated wood and Untreated Southern Pine Wood: Effects of Acid Catalyst Content, Liquefaction Time, Temperature, and Phenol to Wood Ratio

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Abstract

Creosote- and chromated copper arsenate (CCA)-treated wood waste and untreated southern pine wood were liquefied with phenol and sulfuric acid. The effects of sulfuric acid content, liquefaction time, liquefaction temperature, and phenol to wood ratio on liquefaction rate (i.e., wood residue content) were investigated and analyzed by analysis of variance (ANOVA). The results showed that both creosote- and CCA-treated could be liquefied at the same liquefaction conditions as untreated southern pine wood and they all exhibited similar trends on liquefaction rate. In general, Lower residue content could be obtained by higher sulfuric acid content, liquefaction temperature, phenol to wood ratio and longer liquefaction time. Despite the similarities in major effects, the interactions between variables varied among these three liquefaction materials, which could be due to the participation of the preservatives during liquefaction.

Introduction

Wood preservatives are well known to significantly prolong the service life of wood products and thereby extend the forest resource and enhance its sustainability (Shiraishi and Hse, 2000). Preservative-treated wood products are an important tool for homeowners to use to combat wood decay and insect attacks, particularly the Formosan subterranean termite (*Coptotermes formosanus*), which has been estimated to damage as much as $1 billion worth of wood per year in the US (McClain, 2001). Chromated copper arsenate (CCA) and creosote were the two most commonly used wood preservatives in the world for many years. About 28.8 million pounds of CCA (dry oxide concentrate basis) was consumed by the U.S. treating industry in 2004 (Vlosky, 2006). Creosote is derived from coal tar, a by-product of cooking coal in order to produce coke for the steel industry. Creosote production in 2005 was 91.1 million gallons (Pallet Enterprise, 2006).

Traditional treatments for decommissioned treated wood include land-filling and incineration. However, the environmental and human health impacts of preservative treated wood have received increasing attention because of the release of residue preservative into the environment with these two options. Hexavalent chromium (Cr(VI)) is known to be carcinogenic and mutagenic as well as the polycyclic aromatic hydrocarbons (PAHs) in creosote (Kartal, 2003; Catallo and Shupe, 2003). As such, environmentally friendly and economically feasible recycling options for decommissioned treated wood are of great importance. A recycling method for treated wood with wood liquefaction as a key technology has been proposed (Shiraishi and Hse, 2000; Lin and Hse, 2002). Wood liquefaction dissolves wood in an organic solvent at moderate temperature (120 to 250ºC) with or without acid catalysts. It has potential to convert treated wood waste into useful products or remove of residual preservatives from treated wood. The objective of this study was to investigate the effects of several liquefaction variables (i.e., time, temperature and phenol to wood ratio) on the liquefaction of two types of preservative-treated wood (i.e., CCA and creosote) as well as a comparison with untreated wood.

Experimental

Materials

Creosote treated wood sample was from recycled utility poles in a previous study (Roliadi et al., 1996). Recycled CCA treated wood was obtained from Arnold Forest Product Co. in Shreveport, LA. All three types of liquefaction wood materials were reduced to sawdust and passed through a 20 mesh sieve before use. All chemicals were of reagent grade and were used as received.

Wood liquefaction

All treated and untreated samples were southern pine. Each type of wood materials, phenol, and sulfuric acid (as a catalyst) were premixed with a designed ratio. The mixture was then transferred to a small glass tube with one open and one sealed end. The open end was then sealed before the tube was put into the heating chamber of a Parr (Moline, Illinois) reactor. After liquefaction reaction, the liquefied product was cooled to room temperature and taken out by methanol washing. Sufficient methanol was used to wash the liquefied product and followed by filtration. The residue was dried over night in an oven at 105 ºC. The percent of residue content was calculated by the following equation:

$$residue\,content\,(\%) = \frac{W_r}{W_o} \times 100$$

where *Wr* is the weight of oven dried residue and *Wo* is the starting weight of wood materials.

Experimental design

A factorial experimental design was carried out to evaluate the liquefaction rate (i.e., residue content) of untreated southern pine wood, CCA- and creosote-treated wood. The four variables selected during the liquefaction process were:

A. Sulfuric acid (SA) content at 4 levels: 1, 3, 5, 7%;
B. Liquefaction time (TIME) at 2 levels: 60 and 90 min.;
C. Liquefaction temperature (TEMP) at 2 levels: 120 and 150ºC;
D. Phenol to wood ratio (PWR) at 2 levels: 1.5/1 and 2/1.

Results and Discussion

Wood residue content was used as a measurement to evaluate the rate of the liquefaction reactions. The average residue contents of liquefied untreated wood, creosote- and CCA-treated wood are presented in Table 1. The effects of the four variables mentioned in the experimental design section were analyzed by analysis of variance (ANOVA) procedures. Since the ANOVA result indicated the existence of a significant interaction among all of the three investigated preservatives (i.e., untreated southern pine, creosote- and CCA-treated wood), it was deemed to perform a paired comparison procedure. Therefore, an additional Turkey's test was performed for each variable. Throughout the analysis, an overall significant level of 0.05 was chosen.

Table 1. Average residue content of liquefied untreated southern pine, creosote, and CCA treated wood at different liquefaction conditions.

Sulfuric acid content	Liquefaction time	Liquefaction time: 120ºC Phenol/wood ratio: 1.5/1 untreated	creosote	CCA	Phenol/wood ratio: 2/1 untreated	creosote	CCA
1%	60 min.	65.53	77.23	76.62	46.99	68.60	62.52
	90 min.	57.68	74.02	71.63	46.31	65.89	60.43
3%	60 min.	44.60	57.49	62.93	38.01	44.36	51.15
	90 min.	44.52	47.54	50.27	35.00	36.15	42.84
5%	60 min.	44.93	49.65	55.24	33.96	34.37	46.06
	90 min.	36.80	38.28	42.61	25.74	25.95	38.96
7%	60 min.	38.41	47.14	45.99	25.99	31.32	37.82
	90 min.	39.00	36.85	41.36	25.19	25.64	32.38
		Liquefaction time: 150ºC Phenol/wood ratio: 1.5/1			Phenol/wood ratio: 2/1		
1%	60 min.	38.79	66.65	45.99	27.24	43.24	38.06
	90 min.	34.14	61.57	34.51	26.47	44.62	33.75
3%	60 min.	26.92	26.81	33.94	9.58	15.86	17.16
	90 min.	16.30	26.63	21.98	4.94	14.74	9.72
5%	60 min.	12.56	13.64	26.67	0.86	1.14	7.37
	90 min.	9.20	12.10	20.08	0.29	1.17	2.26
7%	60 min.	12.03	12.35	18.40	0.02	3.10	0.93
	90 min.	2.55	11.40	3.22	0.02	0.10	0.46

Liquefaction of untreated southern pine wood

The ANOVA result of untreated southern pine wood liquefaction was presented in Table 2. All four variables have significant effects on the residue content of liquefied untreated southern pine wood. The Tukey test (data not shown) indicates lower residue content could be obtained by higher sulfuric acid content, liquefaction temperature, phenol to wood ratio, and longer liquefaction time as reported by many other researchers (Pu et. al., 1993; Alma *et. al*., 1998).

Table 2. Analysis of variance for untreated southern pine by GLM procedure

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Dependent variable: Residue Content					
SA[1]	3	8997.36	2999.12	462.92	0.0001**
TIME[2]	1	351.78	351.78	54.30	0.0001**
TEMP[3]	1	16993.36	16993.36	2622.28	0.0001**
PWR[4]	1	2982.05	2982.05	460.28	0.0001**
SA*TIME	3	29.80	9.93	1.53	0.2126
SA*TEMP	3	174.86	58.29	9.00	0.0001**
SA*PWR	3	12.17	4.06	0.63	0.6001
TIME*TEMP	1	2.25	2.25	0.35	0.5576
TIME*PWR	1	53.57	53.57	8.27	0.0052**
TEMP*PWR	1	9.80	9.80	1.51	0.2225

[1]sulfuric acid content [2]liquefaction time
[3]liquefaction temperature [4]phenol to wood ratio
**significance at alpha = 0.05.

The interactions between sulfuric acid content and temperature, phenol to wood ratio and temperature were significant as well. Figs 1 and 2 are block charts illustrating the interaction effects of sulfuric acid content by temperature and phenol to wood ratio by temperature, respectively. The inconsistencies of sulfuric acid affecting the residue content at temperature 120 and 150ºC are exhibited in Fig. 1. Although, in general, the residue content decreased as the sulfuric acid content increased at both temperatures, it decreased dramatically at 150ºC compared to 120ºC. A similar interaction between phenol to wood ratio and temperature is shown in Fig. 2. Lower residue contents were obtained at a higher phenol to wood ratio; but this effect is more pronounced in the case of higher a liquefaction temperature.

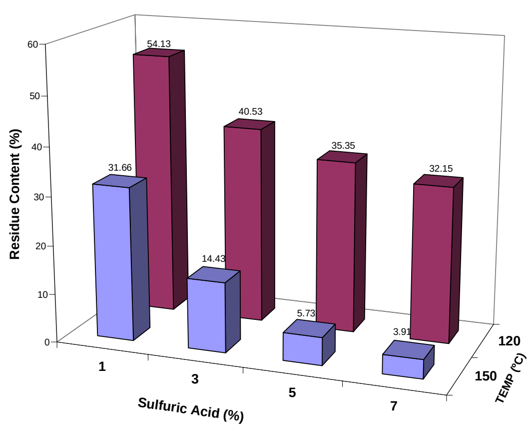

Fig. 1. Interaction plot between sulfuric acid content and temperature of untreated southern pine wood liquefaction.

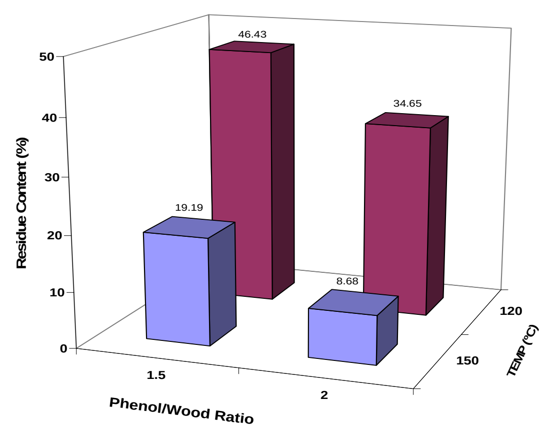

Fig. 2. Interaction plot between phenol to wood ratio and temperature of untreated southern pine wood liquefaction.

Liquefaction of creosote-treated wood

The effects of the 4 factors on the liquefaction of creosote-treated wood exhibit similar trends to those of untreated wood. In other words, the average residue content of liquefied creosote-treated wood decreased as liquefaction time, temperature, phenol to wood ratio, and sulfuric acid content increased (Table 3). However, the result of the Tukey test (Table 4) on sulfuric acid content showed that the difference between 5 and 7% sulfuric acid catalyst content was not statistically significant, which implied that increasing sulfuric acid content would not improve the liquefaction rate of creosote-treated wood when it reaches a certain amount (5% in this experiment).

The interactions between sulfuric acid content and liquefaction temperature, liquefaction time and temperature were highly significant (Table 3). Similar to liquefaction of untreated wood, the catalyst effect for sulfuric acid was more profound at the higher temperature than the lower temperature. As shown in Fig. 3, the residue content decreased from 21.01% to 7.01% and 6.74% when the sulfuric acid content increased from 3% to 5% and 7%, respectively, at a liquefaction temperature 150ºC. However, it only decreased from 46.39% to 37.06% and 35.26% at 120ºC. The interaction plot of liquefaction temperature and time is shown in Fig. 4. It can be seen that the decrease of residue content did not show a parallel trend at liquefaction temperatures 120ºC and 150ºC as the reaction time prolonged from 60 min. to 90 min. It dropped from 51.3% to 43.8% at 120ºC, but it did not show a substantial difference at 150ºC, which indicated that prolonged liquefaction times could not greatly affect the liquefaction rate as it did at the lower temperature.

Table 3. Analysis of variance for creosote-treated wood by GLM procedure

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Dependent variable: Residue Content					
SA[1]	3	27278.11	9.92.70	1085.46	0.0001**
TIME[2]	1	465.83	465.83	55.61	0.0001**
TEMP[3]	1	15435.87	15435.87	1842.68	0.0001**
PWR[4]	1	3860.17	3860.17	460.81	0.0001**
SA*TIME	3	30.42	10.14	1.21	0.3117
SA*TEMP	3	564.16	188.05	22.45	0.0001**
SA*PWR	3	21.65	7.22	0.86	0.4649
TIME*TEMP	1	230.18	230.18	27.48	0.0001**
TIME*PWR	1	19.56	19.56	2.33	0.1306
TEMP*PWR	1	12.32	12.32	1.47	0.2289

[1]sulfuric acid content [2]liquefaction time
[3]liquefaction temperature [4]phenol to wood ratio **significance at alpha = 0.05.

Table 4. Tukey's test result for sulfuric acid content effect on residue content of liquefaction of creosote-treated wood.

Tukey Grouping	Mean	N	Sulfuric acid content (%)
A	62.7658	24	1
B	33.6983	24	3
C	22.0371	24	5
C	21.0008	24	7

Note: dependent variable is residue content. alpha= 0.05. Means with the same letter are not significantly different.

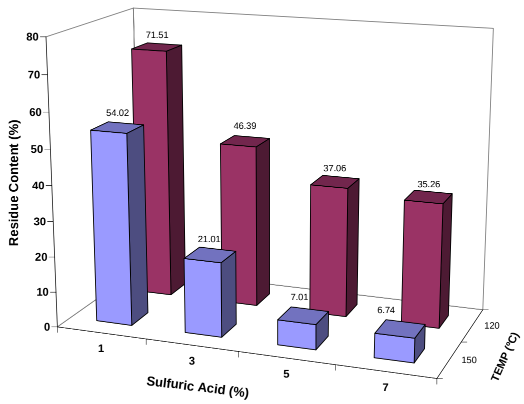

Fig. 3. Interaction plot between sulfuric acid content and temperature of creosote-treated wood liquefaction.

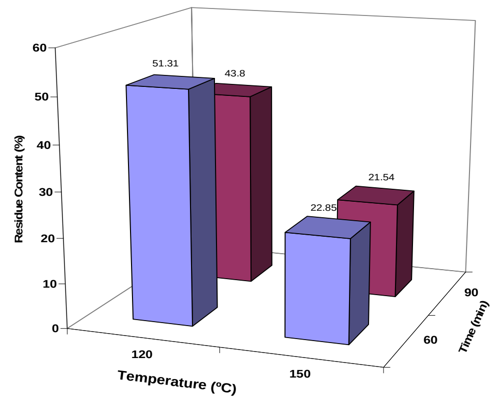

Fig. 4. Interaction plot between temperature and time of creosote-treated wood liquefaction.

Liquefaction of CCA-treated wood

The effects of all 4 main factors on the liquefaction of CCA-treated wood were very similar to those on the liquefaction of untreated wood and creosote treated wood (Table 5). The differences between each level of all 4 variables were statistically significant (data not shown). Increasing sulfuric acid content, liquefaction time, temperature, and phenol to wood ratio could significantly lower the residue content of liquefied CCA-treated wood.

Fig. 5 illustrates the interaction between phenol to wood ratio and liquefaction time. The residue content of liquefied CCA treated wood decreased as the phenol to wood ratio increased from 1.5/1 to 2/1 regardless of liquefaction time. However, the decreasing rate of residue content at a liquefaction time of 60 min. was greater than that at 90 min., indicating that increasing the phenol to wood ratio had a greater effect on improving the liquefaction of CCA-treated wood at the shorter reaction time. The interaction plot between phenol to wood ratio and liquefaction temperature is shown in Fig. 6. It is interesting to note that the residue content decreased dramatically as the temperature increased from 120ºC to 150ºC. Similar to the interaction between phenol to wood ratio and liquefaction time, the residue content decreased at both liquefaction temperatures as the phenol to wood ratio increased. Nevertheless, the decreasing rate at the higher liquefaction temperature was greater than that at the lower temperature. The combination of higher phenol to wood ratio and liquefaction temperature resulted in the lowest residue content (Figs 4-6).

Table 5. Analysis of variance for CCA treated wood by GLM procedure

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Dependent variable: Residue Content					
SA[1]	3	12073.66	4024.56	423.54	0.0001**
TIME[2]	1	1359.23	1359.23	143.04	0.0001**
TEMP[3]	1	23846.39	23846.39	2509.56	0.0001**
PWR[4]	1	2696.30	2696.30	283.76	0.0001**
SA*TIME	3	67.16	22.39	2.36	0.0784
SA*TEMP	3	47.27	15.76	1.66	0.1830
SA*PWR	3	70.15	23.38	2.46	0.0689
TIME*TEMP	1	2.07	2.07	0.22	0.6417
TIME*PWR	1	148.88	148.88	15.67	0.0002**
TEMP*PWR	1	39.79	39.79	4.19	0.0441**

[1]sulfuric acid content [2]liquefaction time
[3]liquefaction temperature [4]phenol to wood ratio **significance at alpha = 0.05.

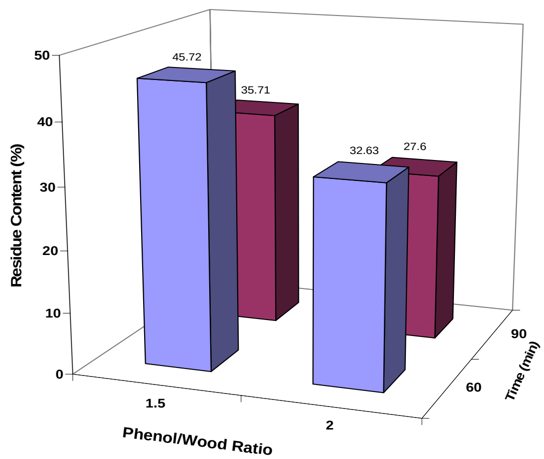

Fig. 5. Interaction plot between phenol to wood ratio and time of CCA-treated wood liquefaction.

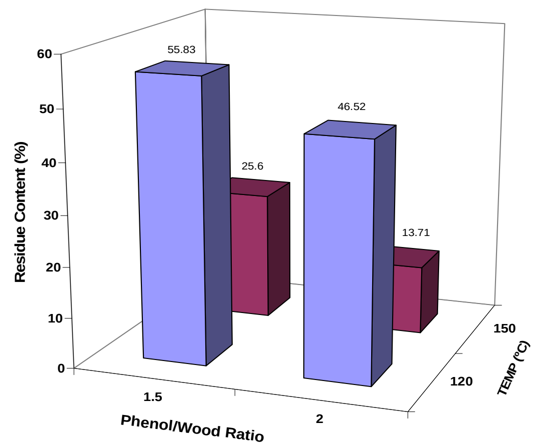

Fig. 6. Interaction plot between phenol to wood ratio and temperature of CCA-treated wood liquefaction.

Comparison of liquefaction of untreated wood, creosote- and CCA-treated wood

The effects of selected variables on the liquefaction of untreated wood, creosote and CCA-treated wood were very similar. This similarity implied that treated wood could undergo a similar liquefaction mechanism to that of untreated wood. However, with the participation of the preservatives (i.e., creosote and CCA), the interactions between variables varied.

As shown in Table 1, the average residue contents of creosote- and CCA-treated wood were generally higher than untreated wood. It is interesting to note (Table 1) that in general, as the liquefaction conditions became harsher, the difference between residue content of treated and untreated wood became greater. For example, the residue contents of liquefied creosote treated wood were higher than untreated wood from 4% (sulfuric acid content 5%, time 90 min.) to 22% (sulfuric acid content 3%, time 60 min.) at a phenol to wood ratio of 1.5/1, and liquefaction temperature 120ºC. Similarly, the differences between CCA treated wood and untreated wood varied from 6% (sulfuric acid content 7%, time 90 min.) to 29% (sulfuric content 3%, time 60 min.) at the same phenol to wood ratio and temperature. However, as the liquefaction temperature and phenol to wood ratio increased to 150ºC and 2/1, respectively, the differences in residue content between treated and untreated wood increased to 99% (creosote, sulfuric acid content 7%, time 60 min.) and 98% (CCA, sulfuric content 7%, time 60 min).

Conclusions

Creosote- and CCA-treated could be liquefied at the same liquefaction conditions as untreated southern pine wood and they all exhibited similar trends on liquefaction rate. In general, Lower residue content could be obtained by higher sulfuric acid content, liquefaction temperature, phenol to wood ratio and longer liquefaction time. Despite the similarities in major effects, the interactions between variables varied among these three liquefaction materials, which could be due to the participation of the preservatives during liquefaction.

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