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Volatile Organic Compounds of Black Locust Logs Heated at 250℃[1]

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ABSTRACT

Less used small diameter logs of black locust were heated at 250℃ for improving utilization. The volatile compounds emitted by the heated logs were analyzed. Their effect of formaldehyde absorption was evaluated with PB. Ester and acid compounds were dominant in content. Especially, methyl acetate and acetic acid showed the highest contents. The total content of aromatic compounds decreased as heating time increased. Amoung ketone compounds, The contents of 2-propanone, 2-pentanone, 3-petanone, 3-hexanone and cyclopentenone decreased with the increase of heating time, but the others did not. The contents of the chemicals, furfural and 3-pentanol, increased with heating time, while that of 2-methyl butanal decreased. It was hard to say that formaldehyde was absorbed by the heated black locust samples. Some decorative goods were designed with the heated logs.

Key words:Heat treatment, *Robinia pseudoacacia* L.. Volatile compound, Formaldehyde absorption.

1. INTRODUCTION

Heat treatment reduces the growing stress of wood, increases the crystallinity of cellulose, decreases equilibrium moisture content, and improves the dimensional stability (Tejada et al., 1997). It has been reported that the crystallinity of wood heat-treated at high moisture content was increased as twice as that at oven-dry condition (Bhuiyan et al., 2000).

Heat treatment decreases the hygroscopicity of wood, which, however, is recovered by steaming at 100℃. It proves that heat treatment does not increase the crystallinity of cellulose, but makes amorphous material changed chemically (Obataya et al., 2000).

The color of heat-treated softwoods turns into noble dark, so they can substitute expensive hardwoods. Furthermore they are highly stable in dimension and thus can be used in severe conditions, such as floor-heating room and sauna (Kang, 2008).

Hemicellulose is pyrolized at 150~230℃ to produce acid and furfural (Browne, 1958). These chemicals are major components of wood vinegar, which is antibacterial and disinfecting. Large amount of small logs produced by thinning and branching are not properly utilized except for fuel. Black locust *(Robinia pseudoacacia* L.) is one of fast-grown species and well-growing most area in this country. The density of black locust is as high as oak and extractives are full in its (Bae and

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Ham, 2000). Nontheless it has been less utilized especially for small diameter logs. It was proposed that a thermally modified black locust would produce various volatile compounds. These chemicals included in a log would evaporate steadly for a while.

In this study small diameter black locust logs were heated at 250℃for various treatment times and the volatile compounds were analyzed. Their effect of formaldehyde absorption was evaluated with PB. Some decorative goods were designed with the heated logs.

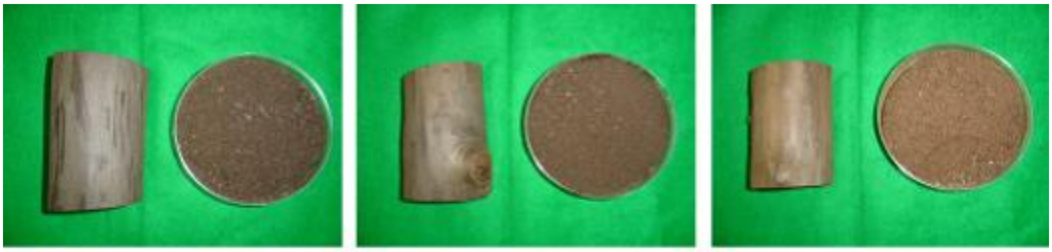
2. MATERIAL and METHODS

2-1 Heat treatment

Logs of 6-9cm diameter were cut from sprouts and large branches of black locust trees growing on Chungnam National University campus. The green logs were cut into one meter long and were heated 250℃ in the thermal modification chamber described in the previous paper (Kang, 2008b). It took 2 hours from room temperature to 250℃. Three levels of duration times, such as 6, 8 and 10 hours, were used for comparison. The heated logs were cooled down to room temperature in the chamber and cut into 20 cm long.

2-2 Analysis of volatile compounds

The heated logs were milled into sawdust and analysed with SPME((Solid Phase Microextraction) method. The volatile compounds were absorbed by Carboxane/ Polydimethylsiloxane fiber(75 ㎛ coating thickness) using Supelco^{TM} Solid Phase Microextraction Fiber Holde (Supelco, Inc., USA). The SPME fiber was activated at 250℃ for 30 minutes in GC injection port.



(A) 6hr at 250℃ (B) 8hr at 250℃ (C) 10hr at 250℃

Fig.1. Samples of the heated black locust logs and sawdust.

The sawdust sample of 3.0g with a standard material was sealed with aluminum crimp seal(Supelco, Inc., USA) in the 100 mL headspace glass vial(Supelco, Inc., USA). A SPME needle was inserted into the vial and it was placed in a water bath at 40℃ for 30 minutes. Three replications were conducted for each sample.

Table 1. Results of measuring the amount of water absorption for five species soaked in pure water, liquor with 30% alcohol content and ethanol with 95% alcohol content.

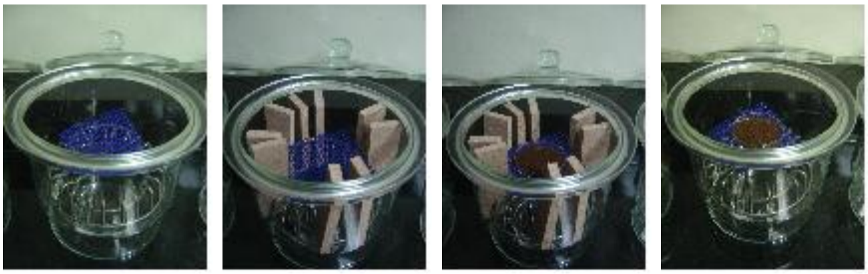
Fig.2. Apparatus for VOC absorption experiment and GC/MSD analysis.

GC/MS-QP2010(Shimadzu, Japan) was used for analysing volatile compounds with VB-1 capillary column (60 ㎜ length × 0.32 ㎜ i.d. × 1.00 ㎛ film thickness, Valco Instruments. Co., USA) and Splitless mode. The temperature of the Injection port was 250℃ and the linear speed of helium gas, a carrier, was set as 1.0 ㎖/min. The oven temperature was set 40℃ for 5 minutes, raised to 250℃ at 3℃/min, and 250℃for 5 minutes. The total time was 80 minutes. For MSD analysis the temperatures of capillary direct interface and ion source were, respectively, 250℃ and 200℃, while ionization energy and mass range were, respectively, 70eV and 35~350 amu.

The volatile compounds revealed from GC/MSD analysis were compared and evaluated with the mass spectra and RI(Retention indices) in Wiley library. The quantitative analysis of the volatile compounds was conducted with standard materials and the content of each chemical was computed per a gram of sample sawdust. The averages and sample standard deviations of the chemical contents were calculated.

2-3 Absorption of formaldehyde

KS M 1998-4 was slightly modified for the formaldehyde absorption test. A particle board of E_2 grade was cut into nine 150×50×15㎜ samples. Thus the total area of the samples were 1890㎠. The sawdust sample of 5g on a petri dish and a water vessel were placed in a desiccator with the PB samples and a lid was covered (Fig. 3). After 24 hours the water in the vessel was analyzed for formaldehyde absorption by an acetyl-aceton light absorption method. For comparison a desiccator contained only the PB samples without sawdust sample (Fig. 3).



Blank PB(Control) PB+Sample Sample

Fig.3. Photos of formaldehyde absorption tests.

3. RESULTS and DISCUSSION

3-1 Volatile compounds of heated black locust logs

The SPME analysis revealed that the black locust logs heated at 250℃ contained 69 volatile compounds, such as 17 aromatic, 11 terpene, 10 ketone, 10 ester, 7 acid, 7 alkane, 4 aldehyde, and 4 alcohol. Ester and acid compounds were dominant in content. Especially, methyl acetate(2848.91ng/g, 1503.86ng/g, 691.15ng/g), acetic acid(2841.52ng/g, 2285.13ng/g, 6292.10ng/g) showed the highest contents.

It was found that the total content of aromatic compounds decreased as heating time increased. But peculiarly 2-acetylfuran, phenol and 2-propionylfuran increased with heating time.

Among ketone compounds, the contents of 2-propanone, 2-pentanone, 3-petanone, 3-hexanone and cyclopentenone decreased with the increase of heating time, but the others did not. Among ester compounds the contents of methyl acetate, methyl butyrate and butyl acetate decreased with the increase of heating time, while that of methyl 2-furoate increased. Thus the total content of ester compounds did not show a certain pattern.

The total contents of terpene compounds slightly increased with heating time while those of acid, alkane, aldehyde and alcohol compounds did not show a certain pattern.

The contents of the chemicals, furfural and 3-pentanol, increased with heating time, while that of 2-methyl butanal decreased. It is known that furfural is antibacterial and of disinfection. Thus it could be carefully concluded that the heated black locust logs are preservative material. Further study is necessary for confirming it.

3-2 Absorption of formaldehyde

It was found that all heated black locust specimens emitted very little formaldehyde by 0.03mg/L (Table 2). The formaldehyde emission of PB and Sample 1 was slightly lower than that of PB only, but it was hard to say that formaldehyde was absorbed by Sample 1. For the tests of Sample 2 and 3 the emitted formaldehyde were more than the PB control. It confirm that the heated black locust emitted aldehyde compounds.

Table 1. Results of formaldehyde absorption tests for black locust logs heated at 250℃

	Sample 1 (6 hrs)	Sample 2 (8 hrs)	Sample 3 (10 hrs)	PB (Control)	PB+Sample 1	PB+Sample 2	PB+Sample 3
Formaldehyde emission (mg/L)	0.03	0.03	0.03	1.60±0.12	1.41±0.04	1.63±0.21	1.63±0.15

3-3 Decorative goods made of the heated black locust logs

This study revealed that the heated black locust logs contains acetic acid and furfural chemicals, which are good antibacterial and of disinfection. The outer barks of the heated black locust logs were destroyed with beautiful figures. Thus they can be used as decorative goods for disinfection purpose

Table 2. Volatile organic compounds of the heated black locust logs

No.	RI	T_R	Compounds	Concentration (ng/g)			Method of Identification
				S1*	S2	S3	
			Aromatic compounds	**368.95**	**305.93**	**236.60**	
1	735	15.46	Pyridine	8.90 ± 2.45	25.47 ± 1.71	6.51 ± 1.32	MS
2	759	16.94	Toluene	43.50 ± 7.10	34.81 ± 0.86	13.67 ± 2.13	MS, RI, ST
3	806	19.77	2-Methylpyrazine	-	10.18 ± 1.35	-	MS, RI, ST
4	854	22.74	Ethylbenzene	23.48 ± 7.49	20.19 ± 1.10	7.91 ± 0.73	MS, RI, ST
5	862	23.22	m-Xylene	37.84 ±	30.99 ± 1.04	12.76 ± 2.76	MS, RI, ST
6	882	24.40	Styrene	122.30 ± 16.62	45.66 ± 3.60	26.01 ± 4.68	MS, RI, ST
7	890	24.93	2-Acetylfuran	27.32 ± 1.66	28.35 ± 1.14	56.77 ± 5.32	MS, RI
8	949	28.40	n-Propylbenzene	2.68 ± 0.80	4.23 ± 0.13	1.35 ± 0.60	MS
9	963	29.18	1,2,4-Trimethylbenzene	3.15 ± 0.26	-	-	MS, RI, ST
10	973	29.74	Phenol	3.22 ± 0.40	4.05 ± 0.07	4.31 ± 1.00	MS, RI
11	975	29.90	1,3,5-Trimethylbenzene	4.05 ± 0.78	-	-	MS, RI, ST
12	990	30.77	2-Propionylfuran	-	-	17.60 ± 2.53	MS, RI
13	1045	33.81	ñ-Cresol	4.12 ± 0.69	3.99 ± 1.16	5.15 ± 0.57	MS, RI
14	1076	35.47	Guaiacol	83.97 ± 9.59	91.33 ± 0.24	82.38 ± 4.62	MS, RI
15	1149	39.29	Benzoic acid	-	0.29 ± 0.11	-	MS
16	1271	45.22	4-Ethylguaiacol	2.46 ± 0.50	2.45 ± 0.19	0.54 ± 0.09	MS, RI
17	1334	48.12	2,6-Dimethoxy phenol	1.97 ± 0.50	3.93 ± 0.62	1.65 ± 0.26	MS, RI
			Terpenes	**46.00**	**53.46**	**68.39**	
1	941	27.90	á-Pinene	32.38 ± 2.81	34.02 ± 4.34	50.91 ± 13.89	MS, RI, ST
2	983	30.32	â-Pinene	4.08 ± 0.51	7.30 ± 0.60	10.14 ± 2.97	MS, RI, ST
3	1031	33.05	dl-Limonene	2.76 ± 0.31	3.88 ± 0.26	2.75 ± 0.87	MS, RI, ST
4	1117	37.66	D-Fenchyl alcohol	-	- -	1.66 ± 0.02	MS, RI
5	1142	38.90	Camphor	1.19 ± 0.26	- -	-	MS, RI
6	1405	51.26	Longicyclene	-	1.00 ± 0.02	-	MS, RI
7	1441	52.76	Junipene	5.37 ± 0.69	5.96 ± 0.37	2.93 ± 0.33	MS, RI
8	1496	55.08	ã-Muurolene	-	0.30 ± 0.01	-	MS, RI
9	1519	56.01	á-Muurolene	0.21 ± 0.08	0.48 ± 0.05	-	MS, RI
10	1534	56.59	ã-Cadinene	-	0.28 ± 0.05	-	MS, RI
11	1540	56.81	ä-Cadinene	-	0.22 ± 0.05	-	MS, RI
			Ketones	**448.35**	**340.27**	**218.74**	
1	<600	5.66	2-Propanone	124.79 ± 23.49	73.20 ± 6.50	35.61 ± 4.61	MS
2	678	11.95	2-Pentanone	57.26 ± 14.42	39.38 ± 1.97	21.32 ± 5.50	MS, RI
3	684	12.37	3-Pentanone	43.83 ± 3.17	29.26 ± 2.99	12.89 ± 1.21	MS, RI
4	768	17.46	3-Hexanone	69.85 ± 15.13	53.45 ± 6.00	30.66 ± 3.66	MS, RI
5	805	19.72	Cyclopentenone	20.88 ± 2.73	7.30 ± 1.28	6.62 ± 0.72	MS, RI
6	869	23.60	ã-Butyrolactone	121.63 ± 4.96	132.16 ± 5.19	74.97 ± 9.12	MS, RI
7	907	25.90	2-Cyclohexenone	-	-	1.39 ± 0.22	MS, RI
8	914	26.31	Dihydro-5-methyl-2(3H)-Furanone	1.78 ± 0.54	1.88 ± 0.06	1.39 ± 0.29	MS, RI
9	935	27.57	1-Acetoxy-2-butanone	-	3.63 ± 0.74	33.90 ± 2.59	MS
10	977	29.99	2,3-Dimethyl-2-cyclopenten-1-one	8.33 ± 1.15	-	-	MS, RI
			Esters	**3133.06**	**1825.96**	**810.83**	
1	<600	6.47	Methyl acetate	2848.91 ± 449.42	1503.86 ± 66.82	691.15 ± 121.41	MS
2	688	12.60	Methyl hydroxyacetate	20.05 ± 1.59	50.34 ± 6.48	17.79 ± 20.86	MS
3	714	14.19	Methyl butyrate	151.04 ± 28.17	123.81 ± 4.83	-	MS
4	728	15.03	Methyl lactate	66.73 ± 12.05	74.83 ± 4.38	37.63 ± 5.62	MS
5	748	16.26	Methyl trans-crotonate	10.23 ± 5.13	14.89 ± 1.91	14.20 ± 2.71	MS, RI
6	801	19.50	n-Butyl acetate	5.36 ± 1.65	4.44 ± 0.61	2.61 ± 0.25	MS, RI
7	957	28.81	Methyl 2-furoate	8.68 ± 1.33	13.35 ± 0.75	43.52 ± 1.97	MS, RI
8	958	28.90	Methyl 4-oxo-pentanoate	21.53 ± 2.99	34.54 ± 0.37	-	MS

9	975	29.86	Furfuryl acetate	-	5.16 ± 0.13	3.95 ± 0.73	MS, RI
10	1290	46.16	Isobornyl acetate	0.54 ± 0.06	0.72 ± 0.02	-	MS, RI

No.	RI	T_R	Compounds	Concentration (ng/g)			Method of Identification
				S1*	S2	S3	
			Acids	**3356.33**	**2672.44**	**6889.32**	
1	638	9.55	Acetic acid	2841.52 ± 152.02	2285.13 ± 250.98	6292.10 ± 898.99	MS, RI
2	707	13.75	Propanoic acid	398.63 ± 58.47	286.74 ± 44.57	522.00 ± 64.32	MS, RI
3	752	16.47	2-Methylpropanoic acid	32.08 ± 10.04	36.70 ± 2.39	14.22 ± 2.82	MS, RI
4	779	18.13	Butyric acid	74.36 ± 2.60	53.13 ± 1.36	57.10 ± 5.62	MS, RI
5	832	21.36	Isovaleric acid	7.25 ± 1.32	8.75 ± 0.29	3.91 ± 1.37	MS, RI
6	851	22.55	Methyl 2-pentenoic acid	1.82 ± 0.55	1.14 ± 0.12	-	MS
7	912	26.20	Methyl hexanoic acid	0.66 ± 0.10	0.86 ± 0.08	-	MS, RI
			Alkanes	**22.78**	**36.36**	**20.69**	
1	901	25.58	Nonane	2.56 ± 0.36	7.02 ± 0.63	1.00 ± 0.11	MS, RI, ST
2	1001	31.37	Decane	11.95 ± 1.21	16.76 ± 1.04	12.61 ± 0.51	MS, RI, ST
3	1101	36.82	Undecane	4.15 ± 1.46	5.60 ± 1.26	2.99 ± 0.37	MS, RI, ST
4	1201	41.90	Dodecane	1.32 ± 0.08	2.15 ± 0.04	1.28 ± 0.04	MS, RI, ST
5	1301	46.64	Tridecane	1.09 ± 0.08	2.23 ± 0.13	1.14 ± 0.15	MS, RI, ST
6	1401	51.09	Tetradecane	1.44 ± 0.26	2.22 ± 0.05	1.32 ± 0.27	MS, RI, ST
7	1501	55.27	Pentadecane	0.27 ± 0.05	0.38 ± 0.01	0.35 ± 0.03	MS, RI, ST
			Aldehydes	**283.33**	**247.96**	**929.73**	
1	658	10.79	2-Methylbutanal	65.77 ± 4.73	57.98 ± 2.32	37.24 ± 9.16	MS, RI
2	782	18.33	Hexanal	19.41 ± 3.75	14.30 ± 0.55	23.21 ± 2.53	MS, RI
3	810	20.03	Furfural	193.43 ± 22.11	168.61 ± 15.05	864.32 ± 99.27	MS, RI
4	1088	36.11	Nonanal	4.73 ± 0.84	7.06 ± 0.46	4.96 ± 0.50	MS, RI
			Alcohols	**264.24**	**334.27**	**197.39**	
1	820	20.64	3-Pentanol	66.11 ± 9.38	95.30 ± 3.82	135.86 ± 17.97	MS
2	841	21.88	2-Furanmethanol	-	-	36.24 ± 7.25	MS, RI
3	985	30.49	Tetrahydrofurfuryl alcohol	198.13 ± 28.79	238.97 ± 6.05	25.29 ± 2.69S	MS

* Mean±S.D. (=3)

Fig.4. Decorative goods with small diameter logs of black locust heated at 250℃

4. SUMMARY

Small diameter black locust logs were heated at 250℃ for 6, 8 and 10 hours and the volatile compounds emitted from the heated logs were analyzed. Followings are the conclusions obtained from this study.

1) Ester and acid compounds were dominant in content. Especially, methyl acetate and acetic acid showed the highest contents.
2) The total content of aromatic compounds decreased as heating time increased.
3) Amoung ketone compounds, the contents of 2-propanone, 2-pentanone, 3-petanone, 3-hexanone and cyclopentenone decreased with the increase of heating time, but the others did not.
4) The contents of the chemicals, furfural and 3-pentanol, increased with heating time, while that of 2-methyl butanal decreased.
5) The heated black locust samples could not be used for formaldehyde absorption.

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