EFFECT OF PRETREATMENT WITH ACETIC ACID AQUEOUS SOLUTION ON CARBONIZATION OF SUGI(*CRYPTOMERIA JAPONICA* D. Don) WOOD*

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Abstract: Sugi woods treated with acetic acid aqueous solution were found to become lighter in weight. Treated and untreated sugi woods were carbonized at 400 ℃ to afford wood-vinegar, wood-tar and charcoal. Yield of wood-vinegar from the pretreated wood was increased, but yields of wood-tar and charcoal were decreased. Yields of wood-vinegar and wood-tar were almost constant, though yield of charcoal was slightly decreased with the increase of acetic acid aqueous solution concentration. Components in wood-vinegar from the treated and untreated sugi woods were determined by capillary gas chromatography (capillary GC). Amounts of 2-furaldehyde and 5-hydroxymethyl-2-furaldehyde in wood-vinegar from the treated wood were increased, but amounts of carboxylic acids, phenols, pyrocatechol, guaiacols, and maltol were almost constant. Amount of 2-furaldehyde were increased with the increase of acetic acid aqueous solution concentration from 0 to 3%, and almost constant from 3% to 30%.

Key words: sugi(*Cryptomeria japonica* D. Don) wood; wood-vinegar; carbonization; capillary gas chromatography(capillary GC)

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醋酸水溶液预处理对柳杉木材炭化的影响

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摘 要: 杉木(日本柳杉)经醋酸水溶液处理后, 重量减少。将处理前后柳杉木材在 400 ℃ 下进行炭化, 得到了木醋液、木焦油和木炭。与未处理材相比, 处理材木醋液的收率增加, 而木焦油和木炭的收率减少。处理液的醋酸浓度增加后, 木醋液和木焦油的收率几乎不变, 但木炭的收率稍微减少了。用毛细管气相色谱法对木醋液的成分进行了定量分析。与未处理材相比, 处理材木醋液中糠醛(呋喃甲醛)及 5-羟甲基糠醛的收量增加, 而羧酸类、苯酚类、邻苯二酚、愈创木酚类及麦芽酚的收量几乎不变。当醋酸浓度从 0 至 3% 时, 糠醛的收量随着增加, 但是当醋酸浓度从 3% 增至 30% 时, 其收量却几乎不变。

关键词: 杉木(日本柳杉); 木醋液; 炭化; 毛细管气相色谱法

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Biography: 保旺 (1967-), 男, 河南南召人, 工程师, 日本崎大学大学院硕士研究生, 研究方向: 木材炭化及沸石催化剂。

Sugi wood was carbonized at 400 ℃ for 1 h under nitrogen gas, to give products such as wood-vinegar, wood-tar and charcoal. Carbonization of sugi wood was found to occur over 258 ℃. Carboxylic acids, furans and maltol in wood-vinegar were produced over 258 ℃ through thermal decomposition of hemi-cellulose and cellulose in sugi wood, and phenols, pyrocatechol and guaiacols over 300 ℃ through that of lignin[1]. Wood-vinegar is used widely as insect repellent and deodorant in agriculture. Today it has become more important in many fields.

We are studying carbonization of sugi wood and utilization of carbonization products. In this study, acetic acid aqueous solution was used for the treatment of sugi wood to investigate the effect of pretreatment with acetic acid aqueous solution on carbonization of sugi wood.

1 Experimental

1.1 Materials and pretreatment

Sugi sapwood samples used in this study were produced in Miyazaki prefecture of Japan. Wood samples were powdered in a mill, passing through 60 mesh and trapped in 115 mesh, and then dried at 100 ℃ for 24 h.

Acetic acid of CP grade was used. Wood samples were immersed in 0, 3%, 30% acetic acid aqueous solution respectively, for about 1 h at room temperature with a supersonic waves cleaning apparatus. Subsequently, they were filtered through a fused glass funnel, evaporated in a rotary evaporator, washed with distilled water, and then dried at 100 ℃ for 48 h in a drying apparatus. Moisture content of the treated samples is similar to the untreated sample, being about 0.9%.

1.2 Preparation of carbonization products

Treated and untreated sugi wood samples were carbonized separately in a carbonization apparatus as shown in Fig. 1. About 20 g of sugi wood sample in the carbonization apparatus was streamed with nitrogen gas for about 15 min at 100 mL/min, then heated at the rate of 200 ℃/h from room temperature to 400 ℃ under nitrogen gas at 20 mL/min, held at 400 ℃ for 1 h, then cooled to room temperature. Crude sugi wood-vinegar and charcoal were obtained and wood-tar was gathered with acetone. Crude sugi wood-vinegar was centrifuged to remove wood-tar. The gathered wood-tar was evaporated in a vacuum rotary evaporator to eliminate acetone. Wood-tar obtained from crude wood-vinegar and the gathered wood-tar were put together.

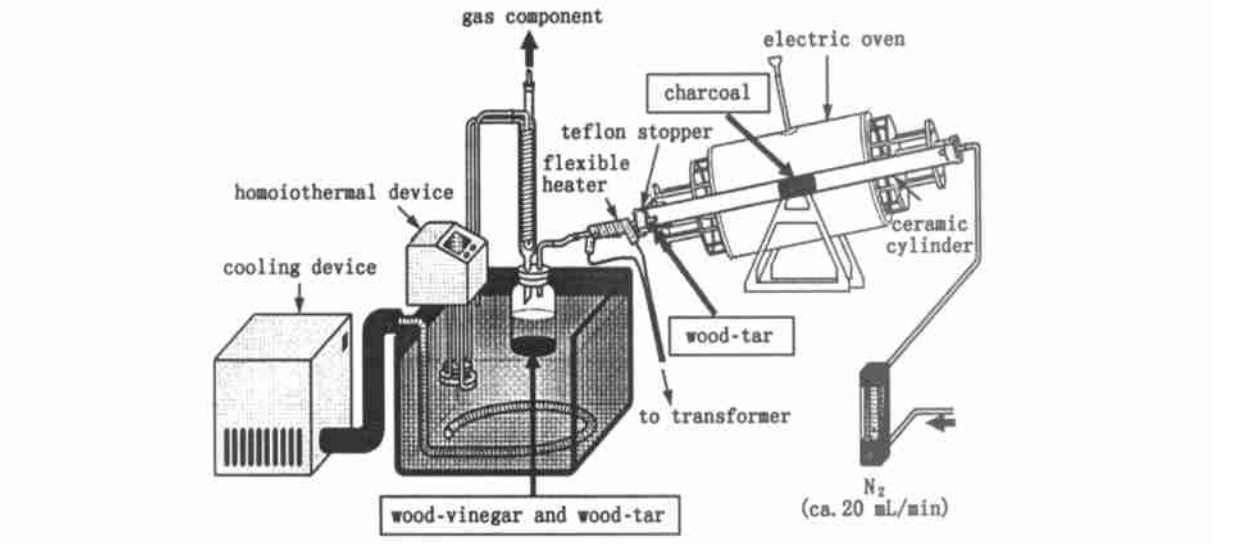

Fig. 1 Apparatus for carbonization of sugi wood

1.3 Analyses of components in sugi wood-vinegar by capillary GC

Capillary GC was carried out with a GC-14B model(Shimadzu, Japan) coupled with hydrogen flame ionization detector and data management apparatus(chromatopac C-4A), in a capillary column BP-21(0.25 mm I.D. 25 m, SGE Japan). The carrier gas was helium at 1.61 mL/min. The column temperature programming for methanol, acetic acid and propionic acid was 3 min at 45 ℃, 45– 109 ℃ at 4 ℃/min, injection temperature was 150 ℃ and detector temperature was 300 ℃. The column temperature programming for 2-furaldehyde, 5-hydroxymethyl-2-furaldehyde, maltol, phenol, *o*-cresol, pyrocatechol, guaiacol and 4-methylguaiacol was 3 min at 45 ℃, 45– 209 ℃ at 4 ℃/min, holding at 209 ℃ for 6 min. Injection and detector temperature were both 300 ℃.

Wood-vinegar was filtered with a 0.45 μm filter, then analyzed at 0.1 μL injection. Wood-vinegar had been found to contain 37 components[1] by capillary GC. Quantitative analyses were performed using additional method[2] with authentic samples. Here 11 components[3] in wood-vinegar of the treated sugi woods were selected for capillary GC. Chemical structures of 11 components in sugi wood-vinegar are shown in Fig. 2.

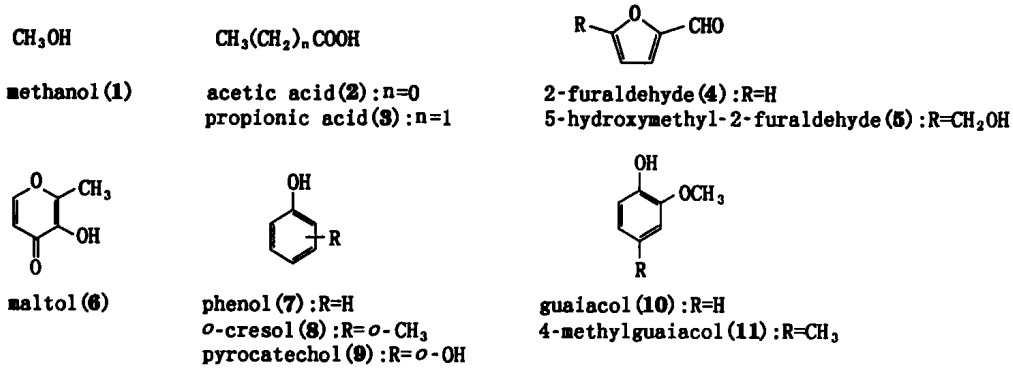

Fig. 2　Eleven components in wood-vinegar of sugi wood

2 Results and discussion

2.1 Change in weight of sugi wood treated with acetic acid aqueous solution

Change in weight of sugi wood treated with acetic acid aqueous solution is shown in Table 1, which was found to become lighter in weight and the change of sugi woods weight were increased with the increase of acetic acid aqueous solution concentration because of elution[4] of extractives and hydrolyzed non-crystalline cellulose and hemi-cellulose in sugi wood.

Table 1　Change in weight of sugi-wood treated with acetic acid aqueous solution

run No.	untreated sugi-wood		treatment	treated sugi-wood		loss/%
	weight/g	moisture content/%		weight/g	moisture content/%	
1	30.01	0.9	H_2O 1)	29.70	0.9	1.03
2	30.07	0.9	3% AcOH	29.71	0.8	1.20
3	30.07	0.9	30% AcOH	29.47	0.8	2.00

1) distilled water

2.2 Comparison of yields of carbonization products

Yields of carbonization products are shown in Table 2. Yield of wood-vinegar was increased, but yields of the wood-tar and the charcoal were decreased with the pretreatment by the acetic acid aqueous solution. Yields of the wood-vinegar and the wood-tar were almost constant, though yield of the charcoal was slightly decreased with the increase of the acetic acid aqueous solution concentration. It was suggested that extractives in sugi wood were extracted, and gasification became easy[5] because hydrolyses of cellulose and hemi-cellulose in sugi wood occurred after pretreatment.

2.3 Comparison of components in sugi wood-vinegar

Amounts of 11 components in wood-vinegar of the treated sugi woods are shown in Table 3. Amounts of 2-furaldehyde and 5-hydroxymethyl-2-furaldehyde in wood-vinegar were increased with the pretreatment of acetic acid aqueous solution, but amounts of 5-hydromethyl-2-furaldehyde, carboxylic acids, maltol, phenols, pyrocatechol and guaiacols were almost constant in spite of different acetic acid aqueous solution concentrations. On the other hand, amount of 2-furaldehyde was increased with the increase of the acetic acid aqueous solution concentration from 0 to 3%, and almost constant from 3% to 30%. These results suggest that hydrolysis of lignin in sugi wood could not be occurred, and the degree of polymerization of cellulose and hemi-cellulose in sugi wood were decreased through hydrolyses after pretreatment, which increased yields of 5-hydroxymethyl-2-furaldehyde and 2-furaldehyde in wood-vinegar. Hydrolysis of hemi-cellulose have not further proceeded though acetic acid solution concentration was increased from 3% to 30%, and hydrolysis of cellulose could occurred only by distilled water.

Table 2 Material balance of products on carbonization of sugi wood

treatment	carbonization conditions		yields/%			total/%
	temp./℃	time/h	wood-vinegar	wood-tar	charcoal	
none	400	1	35	13	35	83
H_2O[1)]	400	1	43	8	33	84
3% AcOH	400	1	43	9	31	83
30% AcOH	400	1	44	9	31	84

1) distilled water

Table 3 Amounts of 11 components in wood-vinegar of sugi wood

treatment	amounts based on 1 kg sugi wood/g[2)]									
	1	2	3	4	5	6	7+8	9	10	11
None	8.09	12.86	1.07	1.05	1.02	0.35	0.35	1.16	1.50	1.44
H_2O[1)]	8.17	12.85	1.15	4.21	6.13	0.40	0.37	1.31	1.44	1.43
3% AcOH	7.90	12.57	1.06	10.32	6.09	0.35	0.30	1.02	1.49	1.51
30% AcOH	8.09	12.56	1.02	10.35	6.12	0.40	0.36	1.18	1.50	1.49

1) Distilled water; 2) 1. methanol, 2. acetic acid, 3. propionic acid, 4. 2-furaldehyde, 5. 5-hydroxymethyl-2-furaldehyde, 6. maltol, 7. phenol, 8. *o*-cresol, 9. pyrocatechol, 10. guaiacol, 11. 4-methylguaiacol.

3 Conclusions

3.1 Treated sugi woods were found to become lighter in weight, while yield of wood-vinegar was increased, and those of wood-tar and charcoal were decreased with the pretreatment. Yields of wood-vinegar and wood-tar were almost constant, while yield of the charcoal was slightly decreased with the increase of the acetic acid aqueous solution concentration.

3.2 Amounts of 2-furaldehyde and 5-hydroxymethyl-2-furaldehyde in wood-vinegar were increased with the pretreatment. Amount of 2-furaldehyde was increased with increase of the acetic acid aqueous solution concentration from 0 to 3%, and almost constant from 3% to 30%.

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