Methanol Mediated Extraction of Phenolic Compounds from Wood Tar

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(Received January 22, 2002; CL-020076)

The methanol-mediated extraction was applied to wood carbonization tar. Phenolic compounds could be extracted from the wood tar. This shows the possibility of the selective extraction of phenolic compounds, although wood tar consists of many kinds of oxygen-containing compounds such as alcohols, phenols, ketones, esters, ethers, aldehydes, carboxylic acids, furans, and so on. The extraction is expected as a new method for the utilization of wood tar.

Biomass and biomass wastes are focused on as one of the alternative energy sources. Pyrolysis or carbonization is a promising method for conversion of biomass and wastes to energy, although it is a traditional method. In some countries, wood carbonization is still an important industry, ex. for steel production.[1] The carbonization is also considered as a waste treatment method.[2] Wood carbonization produces three main products: charcoal, liquids and gas. The liquids usually separate into an aqueous and oil phase, and the latter is also called wood tar. The wood tar is a complex and unstable mixture of many compounds, including phenols, which are valuable and useful chemicals. It has, however, been used as a low-value fuel or disposed without use. Many studies have been performed on solvent elution chromatography, liquid-liquid extraction and fractional distillation for the purposes of characterization and utilization of the wood tar, including separation of phenols.[1]

On the liquid-liquid extraction, acid-base extraction using water and organic solvent is usually performed, and a phenolic fraction is separated by aqueous alkaline extraction, followed by acidification of the aqueous phase.[1] We have researched and developed a methanol-mediated extraction for the recovery of phenols and their derivatives (phenolic compounds) from coal

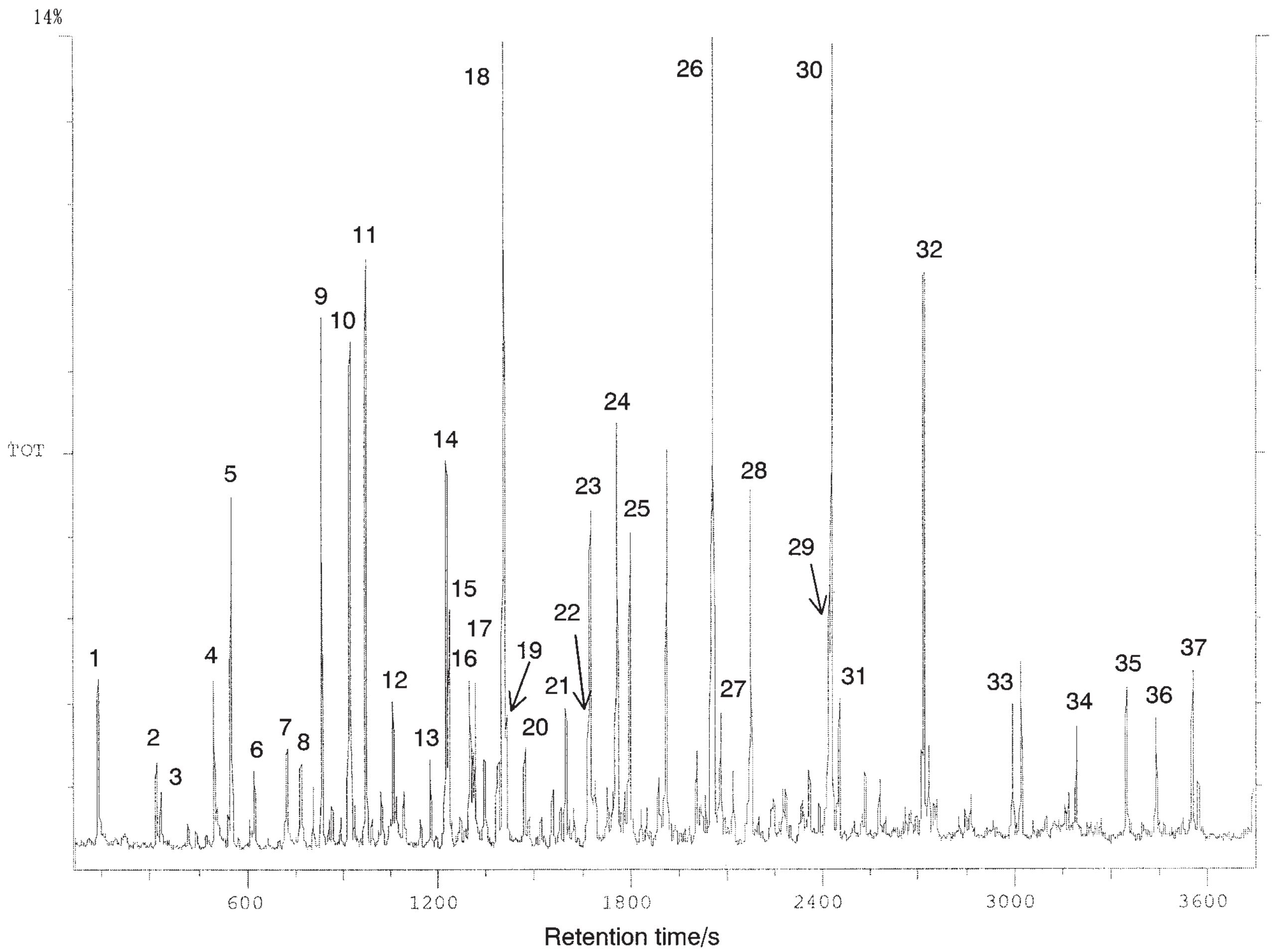

Figure 1. GC/MS chromatogram of extractive.

liquid and coal tar, and the process has been completed.[3–7] Since the extraction uses no acid or alkali, simple and clean process could be established. The purpose of this study is to apply the methanol-mediated extraction for wood tar, which consists of many kinds of oxygen-containing compounds; not only phenols but also alcohols, ketones, esters, ethers, aldehydes, carboxylic acids, furans, and so on.

The wood tar, the sediment in the pyrolysis liquid derived from wood (Dakekanba, *Betula ermanii* Cham.) by traditional carbonization, was used for the experiments. It was supplied from Kitami Institute of Technology. Its elemental composition was carbon, 70.2, hydrogen, 7.3, and oxygen, 22.5 wt%, respectively.

At first, the wood tar of 3 ml was charged into a test tube. Methanol, a special grade, of 3 ml was added, and shaken to mix. It formed a homogenous layer. Then 3 ml of water was added, and shaken to extract. The water layer became white muddy at once, and then it formed emulsion by shaking. Finally it was centrifuged for separation. A water-methanol layer was obtained on the wood tar layer. The water-methanol layer of 0.1 ml was diluted by ethanol of 1.5 ml, and then it was qualitatively analyzed by a gas chromatography-mass spectrometry (Finnigan mat); column, DB-5MS ($60\,m \times 0.25\,mm\phi$), temperature program, 50 to 300 °C by 2 °C/min, scan speed, 1 scan (50 to 350 mass weight)/s, Library, WILEY.

The chromatogram was shown in Figure 1. Thirty-seven peaks were identified, and they were shown in Table 1. Almost of them were phenolic compounds with methyl, ethyl and methoxy functions; e.g. phenol (peak 5), cresol (peaks 9, 10 and 11) and so on. Benzenediols (peaks 22, 23 and 25) and a diphenol (peak 37) were also detected. Thus, phenolic compounds could be extracted by the methanol-mediated extraction from wood tar. The extraction can be expected as a new method for the utilization of wood tar. A quantitative study with an optimum extraction conditions is planned.

Wood consists mainly of cellulose, hemicellulose and lignin. Since lignin has phenylpropane as a basic structure with phenolic OH, ketone, methoxy and so on,[8] phenol and phenolic compounds are considered as decomposed materials from lignin, and the compounds with the lignin basic structure, phenylpropane, were detected; propenyl phenols with methoxy (peaks 27 and 31) and with dimethoxy (peaks 33 and 35). On the other hand, furans or cyclic hydrocarbons were also detected as minor; a furfural (peak 4), furans (peaks 2 and 6) and cyclic hydrocarbons (peaks 3, 7, 8 and 18). Cellulose is a polymer of glucose residue, and hemicellulose is a polymer of monosaccharide residue. These are decomposed by pyrolysis to furfurals, furans and cyclic hydrocarbons through anhydrosugar.[9] Although many kinds of aromatic compounds could be formed from lignin and also from cellulose and hemicellulose, only two aromatic compounds, trimethoxy-benzenes (peaks 30 and 32), were detected. The methanol-mediated extraction can be also used as a characterization technique of phenolic compounds in wood tar and pyrolysis liquid.

Authors thank to Prof. Tsutomu Suzuki of Kitami Institute of Technology for his supply of wood tar and his valuable comments.

Table 1. Compounds extracted by methanol-mediated extraction from wood tar

No. (see Fig. 1)	Compounds	Molecular formula
1	Pyridinol or Pyridinone	C_5H_5NO
2	Dimethylfuran	C_6H_8O
3, 8	Dimethylcyclopentenones	$C_7H_{10}O$
4	Methylfurfural	$C_6H_6O_2$
5	Phenol	C_6H_6O
6	Benzofuran	C_8H_6O
7	Ethylcyclopentanone	$C_7H_{12}O$
9, 10, 11	Cresols	C_7H_8O
12, 14, 15, 17, 19	Dimethylphenols	$C_8H_{10}O$
13, 16	Ethylphenols	$C_8H_{10}O$
18	Methylethylencyclohexanone	$C_9H_{14}O$
20	Trimethylphenol	$C_9H_{12}O$
21, 24	Ethylmethylphenols	$C_9H_{12}O$
22	Methoxylbenzenediol	$C_7H_8O_3$
23, 25	Methylbenzenediols	$C_7H_8O_2$
26	Dimethoxyphenol	$C_8H_{10}O_3$
27, 31	Methoxypropenylphenols	$C_{10}H_{12}O_2$
28	Methylmethoxyphenol	$C_8H_{10}O_2$
29	Ethylmethoxyphenol	$C_9H_{12}O_2$
30	Trimethoxybenzene	$C_9H_{12}O_3$
32	Methyltrimethoxybenzene	$C_{10}H_{14}O_3$
33, 35	Dimethoxypropenylphenols	$C_{11}H_{14}O_3$
34	Dimethoxyformylphenol	$C_9H_{10}O_4$
36	Dimethoxyphenylethanone	$C_{10}H_{12}O_4$
37	(diphenyl compound)	$C_{14}H_{10}O_2$

References and Notes

1 C. A. Chen, H. Pakdel, and C. Roy, *Biomass Bioenergy*, **13**, 25 (1997).

2 K. Yasumura, et al., the 12th Annual Conference of The Japan Society of Waste Management Experts, Yokohama, November 2001, Abstr., No. B7-3; Y. Ryou, et al., the 12th ··· Abstr., No. B7-4; N. Senba, et al., the 12th ··· Abstr., B7-5; T. Harada, the 12th ··· Abstr., No. B7-5.

3 Y. Kodera, K. Ukegawa, A. Matsumura, and M. Xiaoliang, *Fuel*, **72**, 57 (1993).

4 S. Sato, A. Matsumura, Y. Kodera, I. Saito, K. Ukegawa, and M. Nagoya, *J. Japan Institute of Energy*, **76**, 1054 (1997).

5 A. Matsumura, S. Sato, Y. Kodera, I. Saito, and K. Ukegawa, *Fuel Process. Technol.*, **68**, 13 (2000).

6 A. Matsumura, S. Sato, I. Saito, and K. Ukegawa, *J. Japan Institute of Energy*, **79**, 236 (2000).

7 A. Matsumura, S. Sato, I. Saito, and K. Ukegawa, in ''Prospects for Coal Science in the 21th Century,'' ed. by B. Q. Li and Z. Y. Liu, Shanxi Science & Technology Press, Taiyuan (1999), p 855.

8 ''Wood Chemistry,'' translated by T. Kondo, Kodansha, Tokyo (1986).

9 ''Wood Combustion,'' ed. by D. A. Tillman, A. J. Rossi, and W. D. Kitto, Academic Press, New York (1981).