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Studies of the Hydrocracking of Lignin. II. The Components of Lignin Hydrocracking Products

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The components of the hydrocracking products of alcohol-fermented softwood sulfite waste lignin were identified by rectification, gas chromatography, and IR spectrophotometry. In the acidic fraction (b. p. 170—232°C) phenol, *o*-cresol, 2,6-xylenol, *m*-cresol, *p*-cresol, 2-ethylphenol, 2, 4-xylenol, 2, 5-xylenol, 4-ethylphenol, 3-ethylphenol, 3, 5-xylenol, 2-(*n*-propyl)phenol, 3, 4-xylenol, 4-(*n*-propyl)phenol and 3-(*n*-propyl)phenol were identified. In the neutral fraction (b. p. 170—232°C) naphthalene, 2-methylnaphthalene, and tetralin were identified. In the fraction (b. p. 135—170°C) ethylbenzene, *m*-xylene, *p*-xylene, *o*-xylene, and *n*-propylbenzene were found. In the fraction boiling between 57 and 135°C toluene was identified.

The preceding paper reported on our study of the reaction conditions of the hydrocracking process. In the analysis of monophenols in that paper, the component contents were determined merely by the retention time and the percentages of the areas of peaks in the gas chromatogram.

In this paper, a detailed investigation of the components of the products of the runs conducted with the refined lignin (desulfonated SWL) as the raw material and pre-stabilized pasting oil as the solvent will be reported. Precise rectification, alkaline extraction, gas chromatography, and infrared spectrophotometry techniques resulted in the identification of eleven acidic components and four neutral components, besides the compounds previously reported by some of the present authors. *p*-Cresol, *o*-cresol, 4-ethylphenol and 4-(*n*-propyl)-phenol had been reported to be obtained from the products of lignin hydrocracking with phenol solvent,[1] and *m*-xylene, *p*-xylene, *o*-xylene and ethylbenzene were obtained from the runs with a tetralin solvent.[2]

Experimental Procedures

Cuts-1—4 of all the runs reported in the previous paper[3] were collected and combined. Cut-1, an alkali-unextracted portion of cut-2, and alkali-extracted and unextracted portions of cut-3 were gas chromatographed; the peaks to be identified were numbered for the sake of convenience.

Cut-2 and cut-3 were rectified and separated into fractions with narrow boiling-point ranges. From each fraction, after the contaminating component had been removed by alkali extraction if necessary, the component to be identified was collected from the effluent of the gas chromatograph. (No rectification of cut-1 was conducted. Cut-1 was directly gas chromatographed, and the components desired were collected.)

The components were identified from their boiling points, retention times in the gas chromatogram,

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[1] K. Kashima, H. Tabata and H. Watanabe, *J. Chem. Soc. Japan, Ind. Chem. Sect. (Kogyo Kagaku Zasshi)*, **64**, 919 (1961).

[2] K. Kashima and T. Osada, ibid., **64**, 916 (1961).

[3] M. Oshima, K. Kashima, T. Kubo, H. Tabata and H. Watanabe, This Bulletin, **39**, 2750 (1966).

TABLE I. OPERATING CONDITIONS OF THE GAS CHROMATOGRAPH

Procedure	1	2	3
Purpose	Identification	Identification	Collection of components
Stationary phase	DLP*	CE**	CE
Column; Inside dia.	6 mm.	10 mm.	10 mm.
Length	5 m.	5 m.	7.5 m.
Carrier gas	H_2	H_2	H_2
Flow rate of gas	180 cc./min.	300 cc./min.	300 cc./min.
Quantity of sample	0.01 cc.	0.01 cc.	0.5—1.0 cc.

* Dilaurylphthalate

** Celanese ester No. 9 manufactured by the Celanese Corporation.

and infrared spectra. The alkali-extraction procedure has been explained in a previous paper.[3)]

Analysis and Collection by Gas Chromatograph.—A model GC-1B gas chromatograph manufactured by Shimadzu Seisaku-sho was used under the operating conditions as shown in Table I.

Infrared Analysis.—When the authentic material was available, the infrared spectrum of the authentic material was compared with that of the sample obtained from lignin. Infrared charts (IRDC Card)*[1] were used instead of the standard spectrum when no standard sample was available.

Results and Discussions

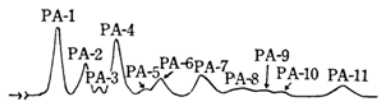
Combined Cut-3.—A precision rectification was made with a 1 kg. sample of the combined cuts-3+4 (cut-3; 750 g., cut-4; 250 g.) as prepared by the procedure mentioned before. The fractions collected are shown in Table II.

Acidic Fraction.—The acidic fraction of combined cut-3 was gas chromatographed as shown in Fig. 1.

Individual peaks on the gas chromatogram were named PA-1 through PA-11; their relative retention times (RRT), like that of phenol as the standard, are listed in Table III.

The relative retention times of the standard phenolic reagents are shown in Table IV.

The fractions shown in Table II were extracted with alkali if necessary and gas chromatographed. From the effluent of the chromatograph, portions corresponding to the peaks to be identified were collected by cold trapping and were subjected to infrared analysis. Although some peaks were easily identified by simply comparing the infrared spectra of the components with those of the standards, while others were mixtures; some more comments will be given below.



Retention time

Fig. 1. Gas chromatogram of acidic fraction of cut-3.
Column, CE; Column temp., 170°C

TABLE II. RECTIFICATION OF CUT-3+4*

Fraction No.	B. p., °C	Amount, g.
1	175—177.4	23.1
2	179.5	26.3
3	181.5	47.0
4	186.0	11.5
5	190.0	10.8
6	191.6	29.0
7	195.5	7.0
8	199.0	31.5
9	200.0	44.0
10	201.0	90.7
11	201.6	25.7
12	204.8	10.9
13	207.6	5.6
14	212.0	55.9
15	213.8	4.5
16	216.0	38.8
17	217.2	43.0
18	220.0	40.1
19	221.4	8.8
20	223.0	10.3
21	224.0	9.3
22	224.8	12.0
23	225.8	16.8
24	226.2	7.3
25	227.8	11.3
26	228.2	5.4
27	229.4	6.8
28	231.0	13.2
29	232.2	35.6
30	233.4	47.8
31	235.0	30.0
Still residue		193.0

* Podbilniak type rectifier with 80 theoretical plates was used at a reflux ratio of 30 : 1—40 : 1.

PA-4.—From the acidic fraction of fr-10, a portion corresponding to PA-4 was gas chromatographically collected. Figure 2(a) is the infrared spectrum of PA-4.

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*[1] Published by the Infrared Data Committee of Japan.

TABLE III. RELATIVE RETENTION TIMES OF INDIVIDUAL PEAKS

Stationary phase	CE	DLP
PA—1	1.0	1.0
2	1.3	1.3
3	1.4	—
4	1.6	1.6
5	1.9	1.9
6	2.0	2.0
7	2.4	2.4
8	2.8—2.9	2.8, 2.9
9	3.0	3.0
10	3.2	3.2
11	3.8	3.8

TABLE IV. RELATIVE RETENTION TIMES OF SOME STANDARD MATERIALS

Stationary phase	CE	DLP
Phenol	1.00	1.00
o-Cresol	1.3	1.3
2, 6-Xylenol	1.4	1.5
p-Cresol	1.6	1.6
m-Cresol	1.6	1.7
2-Ethylphenol	1.9	1.9
2, 4-Xylenol	2.0	2.0
2, 5-Xylenol	2.0	2.0
4-Ethylphenol	2.4	2.4
3-Ethylphenol	2.4	2.4
3, 5-Xylenol	2.4	2.8
2-(*n*-Propyl)phenol	2.7	2.8
3, 4-Xylenol	2.8	2.9
4-(*n*-Propyl)phenol	3.8	3.8

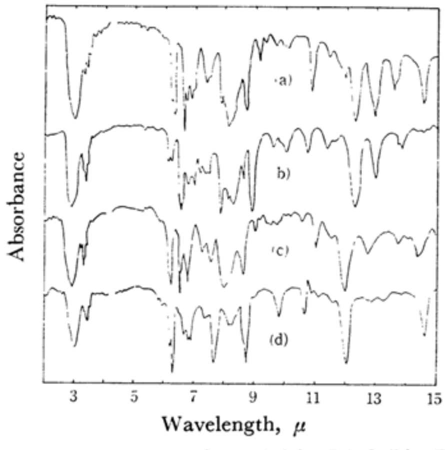

Fig. 2. IR spectra of PA-4 (a), PA-6 (b), PA-7 collected from fr-18 (c) and PA-7 collected from fr-19 (d). (Liquid film method)

The absorptions of PA-4 at 10.8 μ, 11.4 μ and 14.5 μ belong to *m*-cresol, and those at 11.9 μ and 12.3 μ, to *p*-cresol.

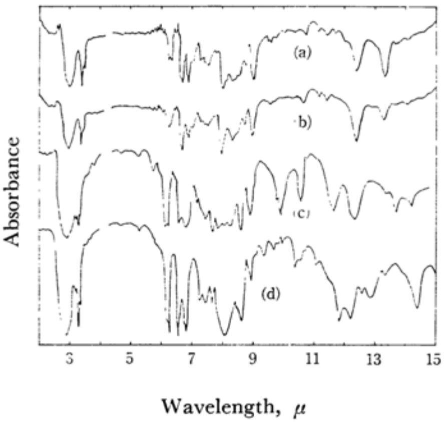

Fig. 3. IR spectra of PA-8 collected from fr-18 (a), from fr-19 (b) and from fr-23 (c), and PA-11 (d). (Liquid film method)

PA-6.—The infrared spectrum of PA-6, collected as before from the acidic fraction of fr-10, is shown in Fig. 2(b). Figure 2(b) shows that PA-6 was composed mainly of 2, 4-xylenol (7.9 μ and 13.0 μ). Weak absorptions of 2, 5-xylenol (10.0 μ, 10.7 μ and 13.8 μ) were also detected.

PA-7.—The infrared spectra of two PA-7 fractions collected from acidic fractions of fr-18, and fr-19 respectively, are shown in Figs. 2(c) and 2(d).

In the spectrum of PA-7 collected from fr-18, absorptions of 4-ethylphenol (12.1 μ) and those of 3-ethylphenol (11.0 μ, 12.8 μ and 14.4 μ) are observed. The PA-7 collected from fr-19 gave an infrared spectrum almost identical to that of 3, 5-xylenol.

PA-8.—Three PA-8 fractions were collected from fr-18, fr-19 and fr-23 separately.

As is shown in Figs. 3(a) and 3(b), the infrared

TABLE V. IDENTIFIED COMPONENTS IN ACIDIC FRACTION OF COMBINED CUT-3

Gas chromatographic Peak No.	Identified component
PA-1	Phenol
PA-2	*o*-Cresol
PA-3	2, 6-Xylenol*
PA-4	*m*- and *p*-Cresols
PA-5	2-Ethylphenol
PA-6	2, 4- and 2, 5-Xylenols
PA-7	3-, and 4-Ethylphenols, 3, 5-xylenol
PA-8	2-(*n*-Propyl)phenol, 3, 4-xylenol and at least one unidentified compound
PA-9	Unidentified
PA-10	Unidentified
PA-11	4-(*n*-Propyl)phenol, 3-(*n*-propyl)phenol

* No IR spectrum was obtained because gas chromatographic collection of the peak was difficult.
The component was identified from RRT and boiling point.

spectra of two PA-8 fractions resemble that of 2-(*n*-propyl)phenol very closely (12.3 μ, 13.3 μ and others), except that the absorption at 12.3 μ is stronger than that of the standard sample, indicating the presence of some unknown meterials in PA-8. The infrared spectrum of PA-8 (Fig. 3(c)) collected from fr-23 is identical with that of 3, 4-xylenol.

PA-11.—Figure 3(d) shows the infrared spectrum of PA-11, collected from the acidic fraction of fr-29.

Absorption of 4-(*n*-propyl)phenol (12.2 μ and 12.6 μ) and those of 3-(*n*-propyl)phenol (11.1 μ, 11.8 μ, 12.9 μ and 14.4 μ) are observed in the spectrum of PA-11.

The above results are summarized in Table V.

Neutral Fraction.—Figure 4 is a gas chromatogram of the alkali-insoluble portion of the combined cut-3. The major peaks in Fig. 4 were named PN-1 through PN-5.

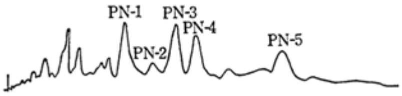

Fig. 4. Gas chromatoram of neutral fraction of cut-3. Column, CE; Column temp., 170°C

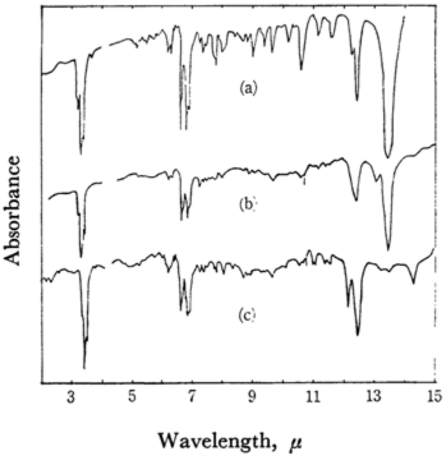

Fig. 5. IR spectra of PN-1 (a), PN-2 (b) and PN-5. (Liquid film method)

PN-1.—The infrared spectrum of PN-1 collected from the neutral fraction of fr-10 is shown in Fig. 5(a) and is identical with that of tetralin.

PN-2.—The infrared spectrum of PN-2 collected from the neutral fraction of fr-10 is shown in Fig. 5(b); it indicates that PN-2 is 1, 2-dialkylbenzene. From its boiling point (approx. 200°C), PN-2 was estimated to be 2-methylbutylbenzene.

PN-3.—The alkaline extraction of fr-14 gave a white crystalline precipitate as an alkali-insoluble fraction. The melting point of the crystals was 79.5°C. Its gas chromatographic retention time, infrared spectrum, and mixed melting point showed that the compound was naphthalene.

PN-5.—PN-5 was collected from the neutral fraction of fr-29; it was found, from Fig. 5(c), to be composed mainly of 2-methylnaphthalene.

Table VI. Identified components in the neutral fraction of combined cut-3

Gas chromatographic peak No.	Identified component
PN-1	Tetralin
PN-2	2-Methylbuthylbenzene
PN-3	Naphthalene
PN-5	2-Methylnaphthalene

The results are summarized in Table VI.

Combined Cut-2.—Table VII shows the results of the rectification of the combined cut-2. The gas chromatogram of the neutral fraction of the combined cut-2, with the peak numbers of p-1 through p-19, is shown in Fig. 6.

From the neutral portions*² of several fractions,

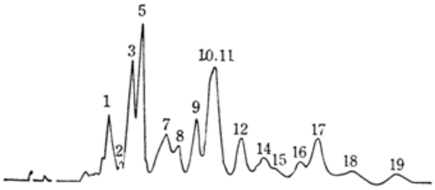

Fig. 6. Gas chromatogram of neutral fraction of cut-2.
Column, CE; Column temp., 130°C

Table VII. Rectification of combined cut-2

Fraction No.	B.p., °C	Amount, g.
1	108.4—124.6	15.0
2	128.6	8.8
3	131.6	12.5
4	133.3	5.6
5	134.3	12.0
6	139.8	10.7
7	144.0	14.7
8	148.4	10.1
9	153.0	13.5
10	155.0	10.8
11	159.0	12.4
12	161.2	8.2
13	162.6	18.1
14	167.4	18.1
15	169.6	12.0
16	173.2	11.1
17	175.0	7.6

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*² A small amount of phenol was present in the fractions because of the incomplete rectification.

TABLE VIII. IDENTIFIED COMPONENTS IN THE COMBINED CUT-2

Gas chromatographic peak No.	Identified component
p-3	Toluene
p-9	Ethylbenzene
p-10	*m*-, and *p*-Xylenes
p-12	*o*-Xylene
p-16	*n*-Propylbenzene

the main components were gas chromatographically-collected*3 and the infrared spectra of the components were measured. The infrared spectra thus obtained were compared with those of standard samples, and the compounds listed in Table VIII were identified.

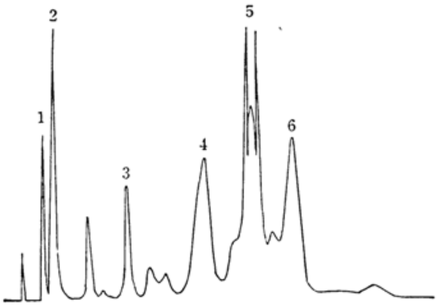
Further, the types of components were estimated by infrared analysis to be as follows; peak Nos. 5, 6, 7, 8, 11 and 18 were aliphatic hydrocarbons, while peak Nos. 14, 17 and 19 were aromatic hydrocarbons.

The combined cut-2 was thus found to be mainly composed of hydrocarbons.

Combined Cut-1.—A gas chromatogram of the combined cut-1, with the peak numbers p-1 through p-6, is shown in Fig. 7. The retention times (RT) of the peaks, and those of standard samples which were suspected to be components of cut-1, are shown in Tables IX and X respectively.

TABLE IX. RETENTION TIMES OF COMPONENTS OF COMBINED CUT-1

Peak No.	RT, min.
1	3.2
2	3.5
3	8.0
4	13.0
5	16.0
6	18.6



Retention time

Fig. 7. Gas chromatogram of cut-1. Column, DLP; Column temp., 100°C

TABLE X. RETENTION TIMES OF SOME STANDARD

Sample	RT, min.
Acetone	3.2
n-Heptane	6.5
Cyclohexane	6.0
Methanol	2.3
Ethanol	2.9
n-Butanol	9.9
Methyl ethyl ketone	5.5
Toluene	16
Benzene	7.7

Among the peaks of cut-1, only p-1 and p-5 have identical retention times with those of the standard samples, i. e., acetone and toluene respectively. Acetone is used as a solvent in the treatment of lignin reaction products; hence, no conclusion can be drawn as to whether a part of the acetone originates from lignin or not.

Although many gas chromatographic peaks in the combined cuts-1 remain unidentified, it was concluded that substantial amounts of *n*-heptane, cyclohexane, ethanol, *n*-butanol, methyl ethyl ketone and benzene were not present in cut-1.

The authors would like to express their appreciation to the Noguchi Institute for the permission to publish this study.

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[3] The gas chromatograph column temperature was changed from 100°C to 150°C depending on the vapor pressures of the fraction to be collected.