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Studies of the Hydrocracking of Lignin. I. The Hydrocracking of Desulfonated Sulfite Waste Lignin

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The raw material for the hydrocracking was prepared by treating alcohol fermented sulfite waste liquor with lime, desulfonating the thus-prepared slurry by heating, and deashing the precipitate with sulfur dioxide. The hydrocracking was run with a high-boiling fraction of lignin-hydrogenated oil as the solvent (pasting oil) and with Fe-promotor-sulfur as the catalyst. The yield of monophenols was 24% (based on klason lignin) with a 100% recovery of the pasting oil under reaction conditions of a temperature of 430°C, an initial hydrogen pressure of 130 kg./cm^2, and a catalyst dosage of 3% (based on the lignin). The higher reaction pressure resulted in a slight increase in the yield of monophenols. The formation of non-volatile pitch decreased with the increase in the initial pressure up to 130 kg./cm^2 but a further increase of the pressure exerted no effect. The higher reaction temperature gave more hydrogen absorption and a higher yield of monophenols, and less pitch formation and pasting oil recovery. However, it is essential to select reaction conditions where the highest yield of monophenols is obtained with a 100% recovery of the pasting oil.

Numerous studies of the hydrogenation of lignin have been reported since 1931.[1] Particularly from the end of the 1930's through the 1940's, Harris and Adkins,[2] Hachihama and Jodai,[3] and Lautsch[4] conducted energetic research, mainly for academic purposes. Although few studies were conducted with commercial applications in mind, the yield of phenols, the possible major commercial products, was low, and no particular consideration was paid to the recovery of the solvent, which was the most critical factor in considering the economic feasibility of the process.

Recently, Sakakibara et al.[5] hydrogenated wood-hydrolysis lignin (concentrated sulfuric acid process) with cyclohexanol as the solvent and with a CuCrO type catalyst, the yield of the acidic fraction was 38.9%.

Giesen[6] claimed in his patent that a 55% yield (lignin base) of the 150—325°C (6 mmHg) fraction could be obtained by hydrogenating wood-hydrolysis lignin (Scholler process) using xylenols as the solvent, of which a 100% recovery was claimed. The studies of lignin hydrogenation with phenol, cyclohexanol, tetralin, crude petroleum oil and other materials as the solvents have been reported by one of the present authors.[7] The solvent recovery was very low in the above work, and the low solvent recovery made the process economically unattractive.

In lignin hydrocarcking processes, it is usual to use a solvent in an amount from 1 to 3 times as great as that of lignin. Excellent solvents for the lignin hydrocracking process, such as phenols, sometimes react with lignin in the course of hydrocracking; this makes the analysis and evaluation of the process very complicated.

For the purpose of eliminating the above-mentioned complications and disadvantages, the present authors utilized as a solvent the high-boiling-point fraction of the lignin-hydrogenated product; a 100% recovery of the solvent was successfully achieved by the so-called pre-stabilization of the high-boiling-point fraction. The process proposed here is the one where monophenols are obtained from lignin. The effects of various reaction conditions were fully studied.

Although the present authors[8] have reported a fairly high liquefaction yield (yield of liquid material) and a high yield of monophenols, further detailed experimental work has proved that the

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[1] A. Lindbalt, *Ing. Vetenskaps Akad.*, No. 107, p. 7 (1931).

[2] E. E. Harris, J. D'Ianni and H. Adkins, *J. Am. Chem. Soc.*, **60**, 1467 (1938).

[3] Y. Hachihama and M. Jodai, *J. Soc. Chem. Ind. (Kōgyō Kwagaku Zassi)*, **43**, 280 (1940); ibid., **44**, 773 (1941).

[4] W. Lautsch and G. Piazolo, *Ber.*, **70**, 486 (1943).

[5] K. Takubo, A. Sakakibara and T. Araki, FAO Technical Panel on Wood Chemistry, Tokyo (Japan) 10—15, 10, (1960).

[6] G. Giesen, U. S. Pat. 2870133 (1959).

[7] K. Kashima and T. Osada, *J. Chem. Soc. Japan, Ind. Chem. Sect. (Kogyo Kagaku Zasshi)*, **64**, 916 (1961).

[8] K. Kashima, *Annual Report of the Noguchi Inst.*, **9**, 23 (1960); ibid., **11**, 327 (1962); M. Oshima and K. Kashima, FAO Technical Panel on Wood Chemistry, Tokyo (Japan) 10—15, 10 (1960). M. Oshima, Panel Discussion, Lignin Symposium held in Chicago in 1961.

previously-published data should be rechecked because of the complicated effect of the solvent and the poor analytical techniques previously utilized. The work reported on here is the reinvestigation of the previous work and, hence, the conclusion of our work.

Experimental

The Preparation of Lignin (Desulfonated SWL).—Alcohol-fermented softwood sulfite waste liquor (solid content, 12%) (15 kg.) and calcium hydroxide (0.25 kg.) were mixed and agitated for 30 min. at 70°C, the precipitate thus formed was collected by a centrifugal seperater, 0.05 kg. of calcium hydroxide was added to the filtrate, it was heated for 30 min. at 70°C, and the precipitate was collected. The combined filter cake weighed roughly 3 kg. (containing approx. 50% water). The alcohol-fermented sulfite waste liquor (1.5 kg.) was mixed with the filter cake and heated for 1 hr. at 195°C. The precipitated desulfonated lignin (with 20—30% ash) was filtered, suspended in water, and acidified with SO_2 gas. The deashed lignin was filtered, washed, and dried. The lignin thus prepared will hereafter be referred to as desufonated SWL for the sake of simplicity. The lignin was analyzed and found to be as follows: lingin (klason lignin), 92.2%; ash, 4.7%; total sulfur; 2.4%. The moisture content ranged from 3 to 6%. The lignin sample used in this study was manufactured by the above-mentioned authors' process and supplied by the Crown Zellerbach Corporation, U. S. A.

The Preparation of the Catalyst.9)—Reduced iron, copper powder, tin powder and sulfur (in an atomic ratio of Fe : Cu : Sn : S=10 : 1 : 1 : 12) were charged into a porcelain ball mill with three times as much water as the combined weight of the above ingredients and crushed and mixed for about one day. After the catalyst had settled, the water layer was discarded and the catalyst was stored wet. (The catalyst should always be wet in order to prevent the loss of its activity). The well-settled catalyst slurry contained approx. 50% water.

The catalyst will be referred to as the standard catalyst hereafter.

Pasting Oil (Solvent).—Pasting oil was the stabilized highboiling-point fraction (b. p.>247°C) of the hydrocracking product of lignin. The pasting-oil fraction was collected from several runs of a bench-scale pilot-plant unit. The authors named this fraction "green pasting oil."

When the green pasting oil was used as the solvent, an excessive degradation took place in it, thus a 100% recovery of the oil was very difficult, and the reproducibility of the data was very poor. The green pasting oil was pretreated as follows to make a so-called stabilized pasting oil. The green pasting oil was hydrogenated with the standard catalyst at a specified temperature. A fraction boiling above 247°C was recovered; this fraction, desulfonated SWL, and the standard catalyst were then mixed and hydrogenated again under same conditions. The fraction of the product boiling above 247°C was the pre-stabilized (or simply stabilized) pasting oil at the specified temperature. Unlike the green pasting oil, the stabilized pasting oil could be recycled with fairly reproducible results without excessive degradation.

Reaction Procedure.—Specified amounts of desulfonated SWL, stabilized pasting oil, a catalyst, and, for better agitation, a rod 13 mm. in diameter and 460 mm. long were charged into an autoclave (2.8 l.; externally-heated rotating type). Hydrogen was then charged in up to the specified pressure, the autoclave was rotated (23 r. p. m.) and heated to the specified temperature within 3 hr.,[*1] kept at that temperature for 2 hr., and then left to cool while the autoclave was rotated and the final pressure was recorded.

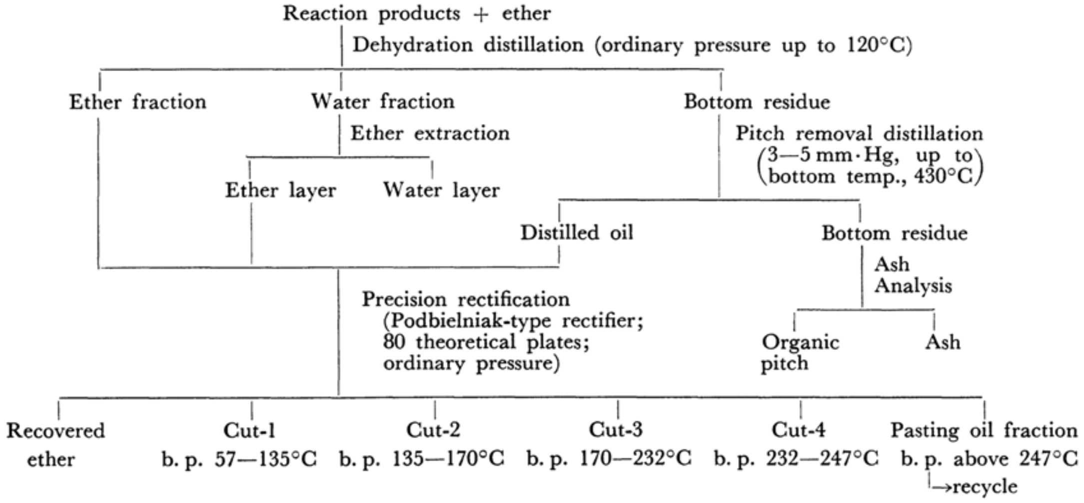

Fig. 1. The fractionation of the reaction products.

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9) M. Oshima, Y. Maeda and K. Kashima, Can. Pat. 700210; U. S. Pat. 3223698; M. Oshima and K. Kashima, Japanese Pat. 405634 (1963).

[*1] A faster heating-up time results in a poorer reproducibility of the results. Hence, no isothermal condition was obtained in the reaction. Therefore, the reaction temperatures and pressures are not exact in a strict sense.

After the gas had been purged, the autoclave was opened and the contents were washed out with ethyl ether.

The Fractionation and Analysis of the Reaction Products.—Cut-2 through cut-4 (Fig. 1) were analyzed by gas chromatography for the monophenol content. The apparent yield of monophenols was a little higher than the actual yield since some neutrals were contained in the phenol fractions of the gas chromatogram. For the sake of brevity, the monophenol yields in this paper are the figures calculated from the chromatogram without any alkaline extraction (see "Neutrals in Monophenols Fraction"). The weights of individual phenols were assumed to be proportional to the areas occupied on the chromatogram. This assumption had been verified in the authors' laboratory. For cut-2, containing large amounts of low-boiling materials, the inner standard method, with *p*-cresol as the standard, was used. The gas chromatograph was operated as follows: Stationary phase, dilaurylphthalate; column, 5 m. long, 0.6 cm. in diameter; temp., 170°C; carrier gas, H_2, 180 cc./min. An example of the gas chromatograms is shown in Fig. 2.

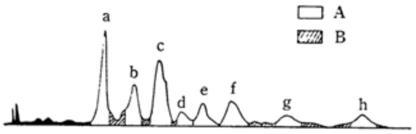

Fig. 2. Analysis of monophenols in the gas chromatogram of cut-3.
a phenol, b *o*-cresol, c *m*- and *p*-cresole
d 2-ethylphenol, e 2, 4-xylenol, f 3- and 4-ethylphenols g 2-(*n*-propyl)phenol, h 4-(*n*-propyl)phenol
A identified phenols, B unidentified phenols
Monophenols = A + B

The Analysis of Neutrals in the Monophenol Fraction.—The different fractions of cut-3 were combined, and then 50 g. of this mixture was treated as is shown in Fig. 3.

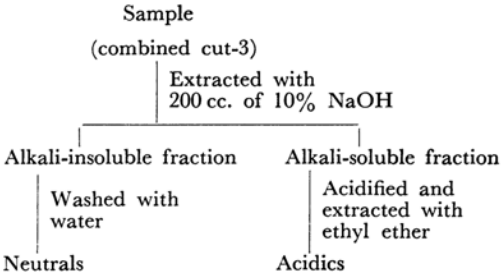

Fig. 3. The analysis of neutrals.

The neutral fraction thus obtained was gas chromatographed, and the relative areas on the chromatogram were subtracted from the areas of monophenols on the chromatogram (Fig. 2.) Thus the true amounts of the individual monophenols were obtained.

Definition of Terms.—Intitial pressure (I. press.): Gauge pressure of hydrogen gas charged into the autoclave at room temperature (kg./cm^2). Maximum pressure (Max. press.): Maximum gauge pressure (kg./cm^2) (it does not necessarily appear at the reaction temperature). Amount of catalyst (A. C.): (catalyst charged (dry basis))/(klason lignin charged) × 100(%). Pasting oil recovery (P. O. R.): (fraction boiling above 247°C recovered)/(oil boiling above 247°C charged) × 100(%).

Monophenols yield (M. P. Y.): (amount of monophenols analyzed by chromatogram)*[2]/(klason lignin charged) × 100(%). Liquefaction yield (L. Y.): (Total oil boiling above 57°C recovered-Pasting oil charged)/(klason lignin charged) × 100(%). Pitch yield (P. Y.): (organic pitch)/(klason lignin charged) × 100(%). Hydrogen absorption index (H. A. I.): this is not an accurate measure of the hydrogen absorption. See "Effect of Hydrogen Pressure." (Initial pressure − final pressure)/(klason lignin charged) × 100(%) (kg./cm^2/100 g. room temp.).

Results and Discussions

The experimental results are tabulated in Table I.

The Effect of the Amount of Catalyst.—Figure 4 shows that a catalyst amount of 3% based on lignin is sufficient for the reaction.

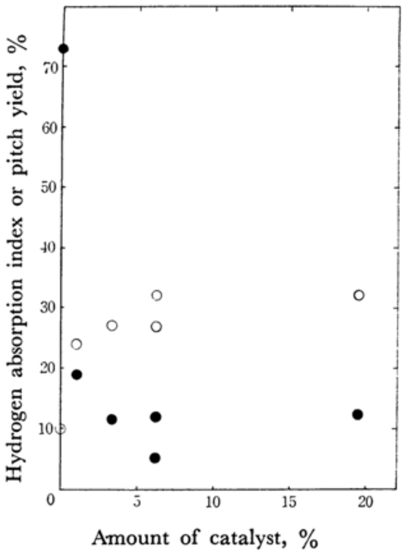

Fig. 4. Effects of amount of catalyst on hydrogen absorption index (○) and pitch yield (●).

The Monophenol Yield.—From the commercial point of view, the most valuable products from the lignin hydrocracking are monophenols; a 100% recovery of pasing oil should also be secured. Under too mild conditions, the pasing oil recovery exceeds 100%. By running with more severe reaction conditions, one can make the recovery of pasting oil lower and the yield of monophenols higher. As the reaction conditions giving a 100%

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*[2] For the details, see "Fractionation and Analysis of the Reaction Products" and "Neutrals in the Monophenols Fraction".

Table I. Experimental results

Run No.	Reaction temp. °C	I. press. kg./cm²	Max. press. kg./cm²	A. C. %	P.O.R.	M.P.Y. %	L.Y. %	P.Y. %	H.A.I.	Amount of charge*
37—45	365	98	200	6.2	114	13.9	45.8	26.1	19	B
37—38	400	100	220	6.2	114	17.6	45.8	10.2	25	B
36—55	405	94	226	5.9	101.5	24.7	37.9	14.7	26	A
37—51	405	132	280	6.9	109	20.9	48.6	9.1	28	B′
37—18	405	161	341	6.2	112	19.6	51.6	9.5	29	B
36—52	415	92	219	5.9	102	24.8	41.2	11.2	31	A
36—35	420	87	221	6.0	103.5	24.6	43.2	10.3	19	A
36—44	420	95	232	5.9	103	23.2	39.6	14.3	29	A
37—15	420	95	192	6.2	106	21.8	40.5	13.0	25	B
37—14	420	132	280	6.2	108.5	21.3	46.8	11.6	27	B
37—17	420	160	338	6.2	107	20.2	51.5	8.8	29	B
36—48	425	89	234	5.9	99	23.2	33.2	22.0	24	A
36—38	425	90	215	6.0	98.5	27.7	32.1	12.2	33	A
36—53	425	92	218	5.9	99	27.7	39.3	9.8	32	A
36—54	425	92	213	5.9	100	26.5	36.2	14.1	33	A
36—56	425	95	229	5.9	101.5	23.6	36.8	10.9	28	A
37—46	430	50	140	6.2	78	22.0	−8.6	47.0	12	B
36—41	430	89	216	6.0	104	22.4	39.6	17.9	25	B
37—49	430	100	220	6.2	103.5	23.0	34.5	11.0	34	B
37—20	430	133	280	6.2	104.5	26.1	46.5	8.6	34	B
37—23	430	160	357	6.2	103.5	—	45.4	6.1	40	B′
37—28	435	100	251	6.2	107	21.6	44.2	16.6	25	B
37—34	435	100	221	6.2	97	28.9	35.2	11.0	26	B
37—30	435	101	240	6.9	106.5	24.6	46.5	11.7	30	B′
37—40	435	120	333	0	62	—	−41	73	9.7	B
37—44	435	125	270	19.5	105	26.3	48.8	12.4	32	B
37—47	435	128	290	1.0	97.5	24.4	29.4	19.0	24	B
37—19	435	130	280	6.2	105	21.6	47.2	12.2	27	B
37—25	440	130	286	3.3	102	26.4	41.0	11.5	27	B
37—29	440	130	287	6.2	100	29.2	41.4	5.2	32	B′
37—21	440	165	345	6.2	93.5	38.9	41.2	5.6	35	B
37—22	440	165	351	6.2	107	—	48.4	8.6	32	B
37—26	440	180	400	6.2	98	29.8	48.3	6.2	29	B
37—35	445	160	360	6.2	94	33.7	35.8	5.0	32	B
37—41	445	160	355	6.2	105.5	26.7	50.7	7.0	32	B

* The followings were charged into the autoclave.

Symbol	Desulfonated SWL g.	Stabilized pasting oil g.
A	190	450
B	240	370
B′	170	262

recovery of pasting oil must be used commercially, the yield of monophenols under those conditions is very important in considering the commercialization of the process.

Monophenol yields from several runs under identical reaction conditions, such as the reaction temperature and pressures, were compared, but no definite conclusion could be drawn because of the scattered data. However, very remarkable correlations between the monophenol yield and the pasting oil recovery were observed when the initial pressures were nearly equal. This is illustrated by Fig. 5, where monophenol yield are plotted for all the runs with catalyst amounts of between 3 and 7%, and at various temperatures. From the figure we can see that the monophenol yield at initial pressures from 90 to 100 kg./cm² is 26—27%, while at more than 130 kg./cm² it is 29—30%, when pasting oil is fully recovered. No effect of the blending ratio of lignin to pasting oil on the monophenol yield was observed.

The Effect of the Hydrogen Pressure.—As is shown in Fig. 6, generally speaking, the hydrogen absorption index tends to increase and the

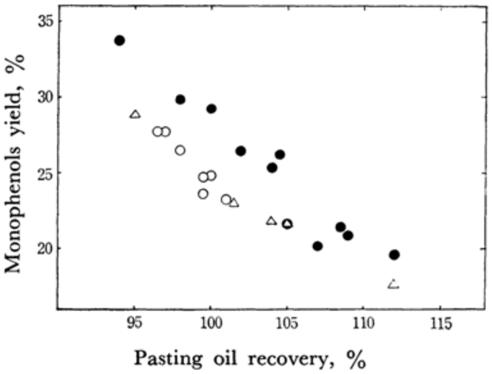

Fig. 5. Relation between pasting oil recovery and monophenols yield at initial pressures: of 90—100 kg./cm² (○, △), or above 130 kg./cm² (●),
○: 190 g. desulfonated SWL & 450 g. pasting oil were charged
●, △: 240 g. desulfonated SWL & 370 g. pasting oil were charged

pitch yield, to decrease with an increase in the initial hydrogen pressure up to approximately 130 kg./cm², but any further increase exerts no effect on the pitch yield.

Monophenol yields at 100% recovery of pasting oil tend to increase with the hydrogen initial pressure (Fig. 5).

The Effect of the Reaction Temperature.—The hydrogen absorption index, the pitch yield, the monophenol yield, and the pasting oil recovery as plotted against the reaction temperatures give a series of fairly scattered points on the graphs. As an example, relations between the reaction temperatures and the monophenol yield are shown in Fig. 7.

The statistical analysis of the data gave the results tabulated in Table II.

Table II shows that there are definite correlations between the temperature and the four variables with a 99% confidence level. That is to say, higher reaction temperatures give a higher hydrogen absorption index and monophenol yield and a lower pitch yield and pasting oil recovery.

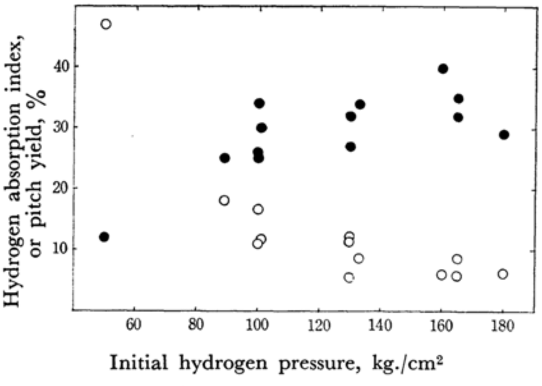

Fig. 6. Plots of initial hydrogen pressure versus hydrogen absorption index (●) and pitch yield (○).
Reaction temp.: 430—440°C

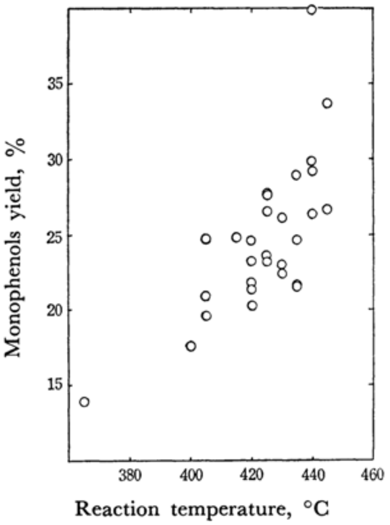

Fig. 7. Relation between reaction temperature and monophenols yield.

TABLE II. RELATIONS BETWEEN REACTION TEMPERATURES AND VARIOUS YIELDS

(Reaction conditions: initial pressure, above 87 kg./cm², catalyst, 3—8% lignin)

	H.A.I.	P.Y.	P.O.R.	M.P.Y.
Number of runs	31	31	31	29
First-order regression	162	210	226	342
Residual	448	443	531	317
Variance ratio	10.4**	13.7**	12.3**	29.2**

$F^1_{29}(0.01)=7.60$ $F^1_{27}(0.01)=7.63$

TABLE III. THE NEUTRALS CONTENT IN THE INDIVIDUAL MONOPHENOLS

	A	B
Phenol	11.4	3.3
o-Cresol	7.9	32.6
m, p-Cresols	19.8	6.8
2-Ethylphenol	2.2	19.0
2, 4-Xylenol	7.7	26.8
3 and 4-Ethylphenols	15.0	10.5
2-(*n*-Propyl)phenol	2.0	19.0
4-(*n*-Propyl)phenol	7.9	1.8
Unidentified phenols	16.2	41.4
Total monophenols	90.1	18.2
Unidentified compounds	9.9	94.0
Grand total	100.0	25.6

A: Analysis by the procedure described in "Fractionation and Analysis of the Reaction Products" (% based on cut-3).
B: Neutrals in individual peaks of the gas chromatogram (% of the individual peaks).

Neutrals in the Monophenol Fraction.—Neutrals in the monophenol fraction as defined in "Fractionation and Analysis of the Reaction Products" were quantitatively analyzed according to the procedures described in "Analysis of Neutrals in the Monophenol Fraction."

The neutrals content in the individual peaks of Fig. 2 are found to be as in Table III.

Table III shows that in the so-called monophenol, the yields shown in the figures and tables contain about 18% neutrals on the average. No complete analysis of the neutrals in monophenols fractions of individual runs has yet been made, however, and so the monophenol yield as defined by "Fractionation and Analysis of the Reaction Products" was used throughout this paper.

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