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# Studies of the Hydrocracking of Lignin. III. The Hydrocracking of Various Types of Lignin

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Three types of raw material for lignin hydrocracking were prepared and their reactivities were compared in relation to the refined lignin reported in the authors' previous paper (*Bull. Chem. Soc. Japan,* **39**, 2750 (1966)). The raw materials were prepared; 1) by autoclaving the alcohol-fermented sulfite waste liquor (heat-precipitated lignin); 2) by drying the liquor (dried SWL), and 3) by concentrating the liquor (concentrated SWL). Although these three types of lignin are less costly to prepare, they showed poor reactivities in the hydrocracking process. Heat-precipitated lignin gave a 16—20% monophenol yield [Analyzed by rectification and gas chromatography (no alkaline extraction was conducted).] at a 100% recovery level of pasting oil. No definite monophenol yield figures could be concluded in the runs with dried or concentrated SWL because of the scattered data. The poor reproducibility of data in the cases of these two types of lignin is discussed.

In the previous paper, the hydrocracking of the refined lignin (desulfonated SWL) was reported on in detail.1) Although the yield of monophenols was high, the cost of the lignin was too high for the commercial success of the process.

In the present paper, several types of lignin which are less costly to prepare were investigated. The lignins studied here are; a lignin solid prepared by simply autoclaving the fermented sulfite waste liquor—heat-precipitated lignin, a lignin solid prepared by drying the same waste liquor—dried SWL, and a thick lignin paste containing a 50% solid from the same origin—concentrated SWL.

## Experimental Procedures

**Heat-precipitated Lignin.** — Ten killograms of alcohol-fermented sulfite waste liquor (softwood) was heated to 210°C over a 3 hr. period, kept at that temperature for 1 hr., and then cooled overnight. The lignin solid precipitated was filtered, washed, and dried.

The analysis showed the solid contained lignin (Klason lignin) (83.5%) and inorganic ash (13.3%) (on a dry basis).

**Dried SWL.**—Alcohol-fermented sulfite waste liquor was concentrated to a 50% solid content and oven-dried at 110°C. This was prepared and supplied by the Crown Zellerbach Corporation, U. S. A. The content of the solid on the dry basis was; lignin (analyzed by the $\beta$-naphthylamine method) (56.8%) and inorganic ash (13.9%).

**Concentrated SWL.**—This was also supplied by the Crown Zellerbach Corporation, U. S. A. The content was: water (48.7%), lignin (analyzed by the $\beta$-naphthylamine method) (28.9%), and inorganic ash (7.2%).

**The Preparation of the Catalyst.**—The standard catalyst used in our previous paper1) was used here; it consisted of reduced iron, copper powder, tin powder, and sulfur in an atomic ratio of 10 : 1 : 1 : 12.

The reaction procedures, the separation and the analysis of the reaction products have been described in the previous paper1) and the terms have been defined there.

## Results and Discussions

Tables I, II and III show the results of the runs with heat-precipitated lignin, dried SWL, and con-concentrated SWL as the raw materials respectively.

**Monophenol Yield.**—In considering the commercial feasibility of the process, the yield of monophenols at a 100% recovery of pasting oil is very important, as has been described in the previous paper.1)

Figures 1 and 2 show the relations between the monophenol yield and the pasting-oil recovery in the runs with heat-precipitated lignin, dried SWL, and concentrated SWL respectively. The data points in Figs. 1 and 2 are distributed over a considerably wide range as compared with the case of refined lignin in the previous paper. The reason for the scattered data will be discussed later.

Table IV, correlation analysis, shows that, although the first-order regression may be concluded for the runs with heat-precipitated lignin with more than a 99% confidence level, no correlation can be assumed for the runs with dried SWL or concentrated SWL.

In the runs with heat-precipitated lignin as the raw material, the monophenol yield at 100% pasting

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

TABLE I. HEAT-PRECIPITATED LIGNIN
(Initial hydrogen pressure; 170 kg./cm$^2$)

| Run No. | A. C.*1 % | Reaction temp., °C | P. O. R.*2 % | M. P. Y.*3 % | P. Y.*4 % | Lignin/P. O.† |
|---|---|---|---|---|---|---|
| 68 | 10 | 370 | 113 | 8.7 | 25.8 | 0.4 |
| 75 | 8 | 370 | 103 | 5.7 | 26.9 | 0.5 |
| 56 | 5 | 400 | 105 | 11.6 | 14.6 | 0.7 |
| 60 | 5 | 400 | 106 | 14.3 | 21.1 | 0.5 |
| 69 | 7 | 440 | 104 | 15.5 | 12.2 | 0.7 |
| 96 | 6 | 440 | 100 | 17.7 | 16.9 | 0.6 |
| 97 | 6 | 440 | 98.8 | 17.9 | 11.5 | 0.6 |
| 101 | 5 | 440 | 103 | 18.3 | 14.2 | 0.6 |
| 102 | 5 | 440 | 103 | 17.0 | 12.0 | 0.6 |
| 109 | 6 | 440 | 97.8 | 16.1 | 27.3 | 0.6 |
| 112 | 6 | 440 | 92.3 | 28.4 | 9.7 | 0.6 |
| 113 | 6 | 440 | 102 | 22.1 | 13.0 | 0.6 |
| 116 | 6 | 440 | 97.4 | 18.5 | 14.8 | 0.6 |
| 120 | 5.5 | 440 | 103 | 18.2 | 11.0 | 0.6 |
| 127 | 5.5 | 440 | 95.0 | 26.2 | 12.1 | 0.6 |
| 128 | 5.5 | 440 | 95.5 | 20.0 | 16.6 | 0.6 |
| 130 | 5.5 | 440 | 103 | 16.4 | 15.5 | 0.6 |
| 137 | 5.6 | 440 | 99.8 | 19.2 | 11.0 | 0.6 |
| 146 | 5.6 | 440 | 102 | 15.8 | 20.0 | 0.6 |
| 149 | 5.6 | 440 | 100 | 16.1 | 9.5 | 0.6 |
| 131 | 6 | 470 | 82.3 | 33.0 | 6.2 | 0.6 |
| 138 | 6 | 470 | 82.7 | 26.0 | 9.6 | 0.6 |

*1 Amount of catalyst on the basis of klason lignin
*2 Pasting oil recovery
*3 Monophenols yield
*4 Pitch yield
† Klason lignin/pasting oil

TABLE II. DRIED SWL

| Run No. | A. C.* % | Reaction temp., °C | P. O. R. % | M. P. Y. % | P. Y. % | Lignin/P. O. |
|---|---|---|---|---|---|---|
| 55 | 7 | 370 | 93.4 | 10.8 | 60.4 | 0.36 |
| 59 | 8 | 370 | 88.7 | 11.7 | 70.9 | 0.36 |
| 63 | 7 | 370 | 95.0 | 13.1 | 47.6 | 0.40 |
| 54 | 7 | 400 | 89.6 | 21.0 | 50.8 | 0.38 |
| 58 | 7 | 400 | 94.3 | 14.5 | 54.7 | 0.43 |
| 62 | 7 | 400 | 95.5 | 11.0 | 51.4 | 0.46 |
| 124 | 6 | 400 | 90.3 | 16.7 | 42.7 | 0.42 |
| 148 | 6 | 400 | 98.7 | 19.1 | 43.7 | 0.42 |
| 57 | 7 | 440 | 85.5 | 29.2 | 31.0 | 0.38 |
| 61 | 7 | 440 | 91.1 | 28.8 | 26.7 | 0.38 |

* On the basis of lignin as determined by $\beta$-naphthylamine method.

TABLE III. CONCENTRATED SWL

| Run No. | A. C.* % | Reaction temp., °C | P. O. R. % | M. P. Y. % | P. Y. % | Lignin/P. O. |
|---|---|---|---|---|---|---|
| 143 | 6.9 | 370 | 125 | 9.4 | 42.2 | 0.96 |
| 121 | 6.9 | 400 | 127 | 12.4 | 27.1 | 0.96 |
| 126 | 6.9 | 400 | 115 | 16.7 | 14.4 | 0.96 |
| 132 | 6.9 | 400 | 105 | 11.7 | 38.6 | 0.96 |
| 139 | 6.9 | 400 | 119 | 14.1 | 18.3 | 0.96 |
| 141 | 6.9 | 400 | 114 | 10.1 | 28.8 | 0.96 |
| 145 | 6.8 | 400 | 119 | 11.9 | 34.2 | 0.96 |
| 133 | 6.9 | 440 | 113 | 15.4 | 16.6 | 0.96 |
| 136 | 6.9 | 440 | 103 | 15.3 | 27.6 | 0.96 |

* On the basis of lignin as determined by $\beta$-naphthylamine method.

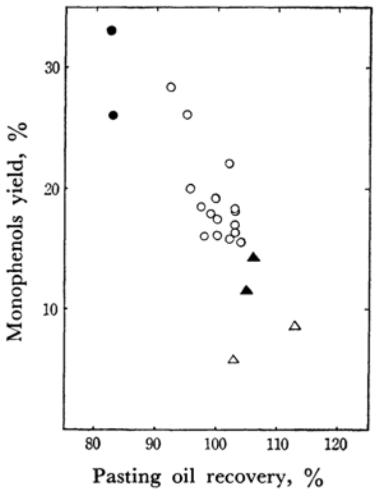

Fig. 1. Relation between monophenols yield and pasting oil recovery.
Reaction temperature: △ 370°C, ▲ 400°C
○ 440°C, ● 470°C

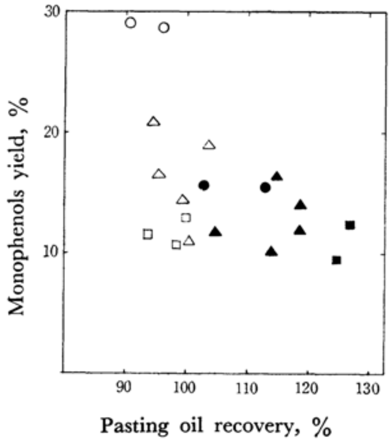

Fig. 2. Relation between monophenols yield and pasting oil recovery.

| Reaction temp. | Raw material: Concentrated SWL | Raw material: Dried SWL |
|---|---|---|
| 370°C | ■ | □ |
| 400°C | ▲ | △ |
| 440°C | ● | ○ |

TABLE IV. CORRELATION ANALYSIS:
Pasting oil recovery and monophenol yield

| | Heat-precipitated lignin | Dried SWL | Concentrated SWL |
|---|---|---|---|
| No. of runs | 22 | 10 | 9 |
| First-order regression | 635.4 | 99 | 6.8 |
| Residual | 306.6 | 420.3 | 43.8 |
| *F* | 41.5** | 1.88 | 1.11 |

oil revovery level was 16—20%. In the case of dried SWL or concentrated SWL, no definite conclusions have been drawn as to the monophenol yield.

**The Effect of the Reaction Temperature.**—From Fig. 1, a general trend may be observed for higher reaction temperatures to result in higher monophenol yields and lower pasting oil recoveries in the case of heat-precipitated lignin. The same trend, though not so clear, may also be observed in the cases of dried and concentrated SWL. These results show that an excessive degradation of both lignin and pasting oil, even though stabilized, takes place at higher temperatures.

The relations between the pitch yield and the reaction temperature are analyzed in Table V.

TABLE V. CORRELATION ANALYSIS:
Pitch yield and reaction temperature

| | Heat-precipitated lignin | Dried SWL | Concentrated SWL |
|---|---|---|---|
| No. of runs | 22 | 10 | 9 |
| First-order regression | 365.2 | 1023 | 246.4 |
| Residual | 353 | 515.6 | 514.2 |
| F | 20.6** | 15.9** | 3.36 |

Higher reaction temperatures give lower pitch yields in the cases of heat-precipitated lignin and dried SWL. No clear correlation was obtained in the case of concentrated SWL because of highly-scattered data.

**The Reactivities of Various Types of Lignin.**—The monophenol yields from the runs of the refined lignin are much higher than those from the runs of the three types of lignin in this study.

A very marked difference in pasting-oil recovery was observed between the runs with dried SWL and concentrated SWL. In the case of dried SWL, it was extremely difficult to get a pasting-oil recovery of more than 100%. On the contrary, in the case of concentrated SWL, it was hard to obtain a pasting-oil recovery of less than 100%.

Such a difference between concentrated SWL and dried SWL was unexpected since these two types of lignin are very close in their structures and impurities. As reasons for the difference, the following three can be postulated: (1) In the drying operation, the condensation of the lignin structure took place. (2) Excess water in concentrated SWL exerted some unknown effects on the reaction. (3) In the runs with concentrated SWL, the ratio of pasting oil to lignin was kept low because of the limitation of reaction pressure. With dried SWL, the ratio was more than 2, but in the case of concentrated SWL, it was around 1. The solvent-lignin ratio might have had some effects. The true reason is yet to be determined.

Pitch yields in the runs with the three types of lignin were much higher than the 5—10% pitch yields in the runs with the refined lignin reported previously.

The effect of the reaction temperature is very significant in the cases of heat-precipitated lignin and dried SWL, but it was less in the runs with concentrated SWL. This may clearly be seen from Figs. 1 and 2 and Table V.

**The Effects of Other Reaction Conditions.**—No significant effects of the hydrogen initial pressure (30—170 kg./cm$^2$), the amount of catalyst (3—30% of the lignin), and the rate of revolution of the autoclave (23—80 r.p.m.) were observed. In order to improve the dispersion of the catalyst, attempts were made to prepare catalysts by ball-milling the ingredients in acetone or pasting oil instead of water, but no significant effect was observed.

**The Reproducibility of the Data.**—A poor reproducibility of data was encountered in the study of the three types of lignin in this paper as compared with the case of the refined lignin. This made the interpretation of data quite difficult. Various efforts to eliminate the poor reproducibility were all fruitless. Impurities present in the three types of lignin might have exerted some serious effects.

Especially in cases of dried SWL and concentrated SWL, the problem was critical. By closely observing the course of the reaction conducted in a vertical mechnaically-agitated autoclave, we found the following evidence to show that the mixture of lignin and pasting oil first changed to a soft pitch-like solid mass before it was degraded by hydrocracking:

(1) When the temperature of the autoclave reached 200°C, a rubbing sound was heard from the autoclave. (2) An exothermic reaction was observed around 200°C. (3) If the autoclave was opened as soon as the reaction temperature reached 200°C, it was found that the autoclave contained a soft pitchy solid.

In the cases of heat-precipitated lignin and refined lignin, both of which had been prepared by heat precipitation processes, the above phenomena were not observed. In the cases of dried and concentrated SWL, the possible poor dispersion of the solid and the non-uniformity of the temperature in the reaction mass might have resulted in the poor reproducibility of the data and the low yield.

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