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Studies of the Hydrocracking of Lignin. IV. The Evaluation of the Catalysts

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In order to find a more active catalyst than the standard catalyst (*Bull. Chem. Soc. Japan,* **39**, 2750) (1966)), some seventeen materials were tested in the hydrocracking reaction of lignin. Although no catalyst was found that would alter the economic picture of the process, several interesting pieces of information were obtained. Selenium and zinc iodide gave a very high hydrogen absorption, indicating their activities as the catalyst. The reaction mechanism with these catalysts, seemed, however, very different from that with the standard catalyst. They resulted in high neutral yields and poor phenol yields. Cobalt octacarbonl, cobalt sulfide, ammonium molybdate, Raney iron, iron pentacarbonyl, nickel oxalate, and Ni-S showed fair activities. A closer evaluation of some of the above catalysts revealed that the standard catalyst was, at least at present, the most preferable catalyst.

The standard catalyst discussed in previous papers,[1-3] consisted of iron, copper, tin and sulfur in an atomic ratio of 10 : 1 : 1 : 12. The catalyst was discovered by improving the Fe-S*-type catalyst, which was originally employed in the study of coal hydrogenation.[4]

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* The expression, for example, Ni-S, shows that the catalyst was produced by the wet-ball milling of Ni and S powders.

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

[2] M. Oshima, K. Kashima, T. Kubo, H. Tabata and H. Watanabe, ibid., **39**, 2756 (1966).

[3] M. Oshima, K. Kashima, H. Watanabe, H. Tabata and T. Kubo, ibid., **39**, 2760 (1966).

[4] E. Munekata, Japanese Pat. 152898 (1942).

Sulfur has been known to show a slight activity in the hydrocracking reaction. In this study, selenium and tellurium, belonging to the same group as sulfur in the periodical table, were examined as catalysts of the reaction.

Halogenated metals, such as ferric chloride, or stannous iodide, had been used in the hydrogenation of coal. This type of compound was suspected to be also active in the lignin hydrogenation. Zinc iodide was tested as an example of this type of catalyst.

Compounds of nickel, cobalt, or molybdenum have long been known as catalysts for various types of hydrogenation reactions. Studied in this paper were: nickel compounds such as Ni–S* and nickel oxalate, cobalt compounds such as cobalt sulfide and cobalt octacarbonyl, a molybdenum compound (ammonium molybdate), iron compounds such as iron pentacarbonyl, and Raney iron.

Experimental Procedures

Raw Material Lignin. — Three types of lignin, refined lignin (desulfonated SWL), heat-precipitated lignin, and dried SWL, were used in the present study. For a detailed explanation of the preparative procedures and an analysis see our previous papers.1,3)

The Preparation of Catalysts. — Selenium and tellurium were commercial reagent of the metallic grade. Ammonium molybdate ($(NH_4)_6Mo_7O_{24}\cdot 4\,H_2O$), zinc iodide, nickel oxalate, zinc oxide, and cobalt sulfide were also commercial reagents (Extra Pure grade). Ni-S was prepared by milling a mixture of nickel and sulfur in an 1 : 1 atomic ratio in aqueous media using a porcelain ball mill. Iron aluminum alloy (Fe 44.36%, Al 50.2%) was treated with a caustic solution by the usual procedure to prepare Raney iron. The catalyst was stored in dry ethanol.

Cobalt octacarbonyl ($Co_2(CO)_8$) was prepared as follows. Cobaltous carbonate ($CoCO_3$) (13.7 g.) and petroleum ether (150 ml.) were charged into a stainless steel autoclave, pressurized to 250 kg./cm^2 with 1 : 1 mixture of hydrogen and carbon monoxide gas, and heated for 3 hr. at 150—160°C. The product was then filtered, and the filtrate cooled. The crystallized cobalt octacarbonyl was filtered and dried under a dry carbon monoxide atomosphere.

In order to prepare iron pentacarbonyl, pyrite cynder was reduced in a hydrogen stream for 5—6 hr. at 630—730°C; 80 g. of it was then charged in a 500 ml. stainless steel autoclave and pressurized to 170 kg./cm^2 with carbon monoxide gas and kept at 190—200°C for 3 hr. The autoclave was cooled, the remaining gas was purged, and the autoclave was pressurized again to 170 kg./cm^2 with fresh carbon monoxide gas and heated at 190—200°C for 3 hr. The iron pentacarbonyl ($Fe(CO)_5$) thus formed was separated from unreacted iron powder by filtration.

The standard catalyst was a ball-milled mixture of iron, copper, tin and sulfur with an atomic ratio of 10 : 1 : 1 : 12. The details of the preparative procedures have been given in a previous paper.1)

Reaction Conditions.—The reaction conditions are tabulated in Table I.

Conditions A, C and D, where a xylenol mixture was used as the solvent, were for the preliminary evaluation of the catalyst, while B and E were the regular reaction procedures. The types of lignin used were the ones which were of particular interest at the time when the study was made, hence, there is no special meaning in the selection of lignin.

The activity of the catalysts were tested and compared with the standard catalyst under these conditions. First catalysts were evaluated preliminarily under the conditions A, C and D, only those with promising activities were subjected to full evaluation under the B and E conditions.

The reaction condition B is identical with the one used in Part III.3) A lower reaction temperature was used in D and E in order to observed the activity at a lower temperature.

A commerially-available industrial-grade xylenol-mixture was distilled to remove a low-boiling fraction (b. p. below 205°C); the residue was then used as the solvent.

The stabilized pasting oil was prepared by a usual procedure fully described in a previous paper.1)

The Separation and Analysis of the Product.—For A, C and D, the procedure described in Fig. 1 was used.

With the runs under B and E reaction conditions the analytical procedures were the same as in the previous paper.1)

Definitions of Terms.—The terms used in this paper are as have been described in the previous paper1) except for the following. In the preliminary runs;

Table I. A list of the reaction conditions

Reaction conditions	A	B	C	D	E
Autoclave	300 ml. Shaking	3 l. Rotating	3 l. Rotating	3 l. Rotating and agitating	3 l. Agitating
Solvent	Xylenols	Stabilized pasting oil	Xylenols	Xylenols	Stabilized pasting oil
Raw material	Refined lignin	Heat-precipitated lignin	Refined lignin	Dried SWL	Dried SWL
Reaction temp., °C	400	400	400	360	360
Reaction time, hr.	2	2	2	2	2
Initial pressure, kg./cm^2	130	170	130	130	130
Raw-material charged, g.	17	230	170	250	250
Solvent charged, g.	30	400	300	350	350

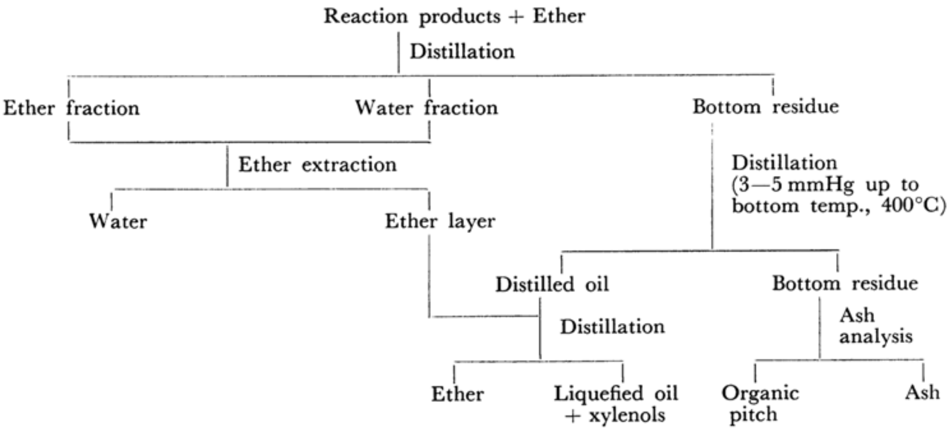

Fig. 1. The separation and analysis of the products of preliminary runs (Conditions A, C and D).

Liquefaction yield (L. Y.) = (distillable oil recovered-xylenol charged)/(lignin charged) × 100%. In all the runs; Pressure difference (ΔP) = (Initial hydrogen pressure at room temp.—Final pressure at room temp.) (kg./cm^2)

TABLE II. PRELIMINARY RUNS (Condition A)

Run No.	Catalyst	A. C.[*1]	L. Y.	P. Y.[*2]	Δp
2—18	Standard	10.4	41.0	19.5	21
2—22	Standard	11.1	27.2	30.1	18
2—30	Se	20.8	35.1	22.8	40
2—32	Se	2.08	22.2	41.2	41
2—37	Se	6.95	10.4	22.9	17

[*1] Amount of catalyst
[*2] Pitch yield

Results and Discussion

Selenium,5) Tellurium and Zinc Iodide.—Table II shows the results of the preliminary runs with selenium metal as the catalyst under the condition A. A high hydrogen absorption of 21% (lignin charged) was observed when selenium was used. This cannot be explained by the consumption of hydrogen by selenium to form hydrogen selenide. As compared with the runs with a 10% standard catalyst, the run with 2% selenium gave more organic pitch, but the runs with selenium more than 7% the quantity of lignin gave an almost comparable pitch yield.

Selenium, suspected to be a peculiar catalyst in the preliminary runs, was fully evaluated under the B reaction condition, which is identical with that of Table I of Part III of a previous report.3) As is shown in Table III, a remarkably high hydrogen absorption was observed, as had been expected. The neutral materials in the cut-3 fraction comprized, however, as much as 73% of the total. The gasification was almost twice as much as the run with the standard catalysts and amounts of neutral materials and low boilers were high. Thus, the reaction mechanism seemed to be different from that with the standard catalyst. From a commercial point of view, the selenium catalyst was concluded to be less desirable than the standard catalyst. Tellurium was examined under the C reaction condition (Table IV). Tellurium showed a hydrogen absorption almost comparable to that of the standard catalyst, but the amount of organic pitch residue was exceptionally large. Tellurium was thus rejected.

Zinc iodide also gave a very high final-initial pressure difference. The product oil, however, was dark brown, tarry material and gave much non-distillable pitch (Table IV). The reaction mechanism seems to be different from the standard catalyst. A combination of zinc iodide and sulfur gave less pressure difference and a higher pitch yield than did zinc iodide without sulfur.

Other Miscellaneous Catalysts.—Although a vertical, mechanically-agitated autoclave and a horizontal, rotating autoclave were used (Table

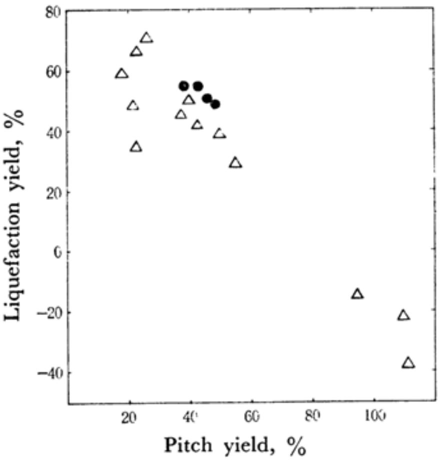

Fig. 2. Liquefaction yield against pitch yield.
● Standard catalyst

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5) M. Oshima, K. Kashima, H. Tabata, T. Kubo and H. Watanabe, Japanese Pat, 460177 (1965).

Table III. Evaluation of selenium catalyst (Condition B)

Run No.	Catalyst	A. C.	P. O. R.*1	M. P. Y.*2	L. Y.	P. Y.	G & L*3
37—115	Se	21.6	96.8	5.79	32.6	16.1	52.1

*1 Pasting oil recovery *2 Monophenols yield *3 Gasification and loss

Table IV. Preliminary runs (Condition C)

Run No.	Catalyst	A. C.	ΔP	L. Y.	P. Y.
2—44	Standard	10.9	32	59.2	18.7
2—47	Standard	10.7	29	44.7	18.1
2—51	Te	18.1	31	44.2	29.7
2—52	ZnI_2	10.1	42	—	35.3
2—54	ZnI_2+S	14.6	27	19.7	50.1

Table V. Preliminary runs (Conditions D)

Run No.	Catalyst	A. C.	L. Y.	P. Y.	ΔP	Autoclave*
3— 50	Standard	30W	51.1	45.6	37	R
3— 51	Standard	30W	49.3	48.4	39	R
3— 63	Standard	30W	55.3	38.5	42	A
3— 65	Standard	30W	55.0	43.4	38	A
3— 52	None	None	−21.6	110.0	3	R
3— 59	S	15	−15.1	94.8	9	R
3— 69	ZnO	30	38.8	50.0	30	R
3— 76	ZnO	30	29.1	43.9	30	A
3— 67	Ni-S	30W	45.3	37.5	42	A
3— 68	$NiC_2O_4 \cdot 2H_2O$	20	50.3	40.3	37	A
3— 74	Zn-S	30W	−38.1	111.3	1	A
3— 88	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	30	34.8	22.4	61	A
3—100	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	30	48.7	21.9	60	A
3— 7	$Co_2(CO)_8$	30	59.0	18.0	50	A
3— 21	CoS	30W	66.0	22.8	51	A
3— 75	Raney Fe	20W	41.8	42.5	29	A
4— 10	$Fe(CO)_5$	20	70.6	26.2	38	A

* R: Rotating autoclave, A: Agitating autoclave, W: Weight of catalyst in a wet state

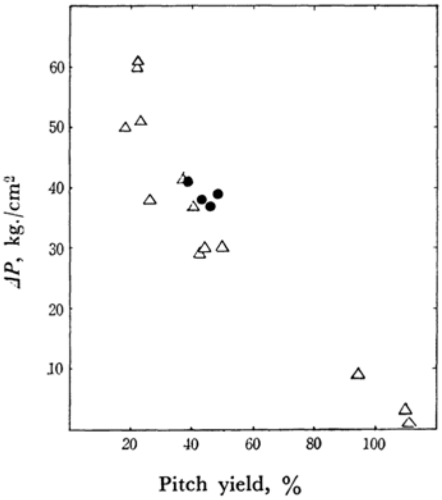

Fig. 3. Pressure difference between final-initial pressure against pitch yield.
● Standard catalyst

V), no difference was observed. These data gave the relation between the pitch yield and the liquefaction yield, and that between the pitch yield and the final-initial pressure difference, shown in Figs. 2 and 3 respectively.

Ni-S and nickel oxalate behaved almost identically as the standard catalyst. Raney iron was almost comparable to the above three. Cobalt sulfide and cobalt octacarbonyl showed a large final-initial pressure difference and a very low pitch yield. The two catalysts seemed to be better than the standard catalyst as far as the preliminary examination was concerned. Ammonium molybdate and iron pentacarbonyl showed a pressure difference comparable to that of the standard catalyst. They also showed a low pitch yield and a high liquefaction yield.

Zinc oxide unexpectedly showed a fair activity, though it was a little inferior to the standard catalyst. On the other hand, Zn-S showed no activity. Elemental sulfur showed very little activity.

TABLE VI. EVALUATION OF AMMONIUM MOLYBDATE AND IRON PENTACARBONYL (Condition E)

Run No.	Catalyst	A. C.	L. Y.	P. Y.	ΔP	M. P. Y.	P. O. R.
3—99	Standard	30	34.8	46.1	36	11.2	100.9
3—11	Standard	30	34.8	48.3	31	11.8	101.1
3—19	Standard	30	39.7	52.6	35	7.9	103.8
3—16	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	30	47.4	32.3	57	9.9	106.5
3—17	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	30	47.2	36.8	57	14.6	102.8
3—18	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	30	51.2	37.2	54	8.6	108.2
3—20	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	30	64.9	27.5	62	17.8	103.2
3—22	$Fe(CO)_5$	20	47.8	44.6	29	10.9	104.4
3—23	$Fe(CO)_5$	15	43.9	38.8	39	10.3	106.8
3—24	$Fe(CO)_5$	20	35.9	46.2	38	9.3	102.9
3—25	$Fe(CO)_5$	15	15.6	51.7	25	7.0	97.4

Ammonium Molybdate and Iron Pentacarbonyl. — In the preliminary examination described in the previous section, cobalt sulfide, cobalt octacarbonyl, ammonium molybdate, and iron pentacarbonyl seemed to be a little more active than the standard catalyst. The former two are expensive and so are not attractive for the commercial process. The latter two, ammonium molybdate and iron pentacarbonyl, were studied in detail under the E reaction condition (Table VI).

Statistical analysis showed that no difference in pitch yield, pressure difference, and monophenol yield could be deduced between the standard catalyst and the iron pentacarbonyl catalyst. In the case of ammonium molybdate, a higher pressure difference and a lower pitch yield than in the case of the above two catalysts can be concluded with more than a 99% confidence level. However, as far as the monophenol yield and the pasting oil recovery are concerned, no clear differences could be concluded to exist among the three catalysts studied.

From the commercial point of view, the monophenol yield at a 100% recovery of pasting oil is a critical factor. From this point of view, three catalysts showed almost identical activities. Considering the cost of preparation, the standard catalyst is, at least at present, the most desirable catalyst for the hydrocracking of lignin.

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