

ENCLOSURE (B) 9

STUDIES ON THE HYDROGENATION  
OF LOW-TEMPERATURE TAR

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by

CHEM. ENG. T. OGAWA

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SUMMARY

This investigation was made to determine properties of products, and the effect of different catalysts on the hydrogenation of low-temperature tar from FUSHUN coal. The low temperature tar was hydrogenated with and without catalysts, and the following significant results were obtained:

(1) When no catalyst was used, optimum conditions were established as follows:

Temperature	450°C
Pressure	2.50 atm.
Time	2 hr

In this case, many acidic, basic, and asphaltic substances included in the raw tar were not removed by hydrogenation.

(2) In the case of catalytic hydrogenation, several different catalysts were investigated and molybdenum sulphide was found to be the most effective. Asphaltene, and acidic and basic substances were catalytically reduced to neutral hydrocarbon oils by using  $\text{MoO}_3$  or  $\text{MoS}_2$ .

I. INTRODUCTION

Low temperature carbonization oil cannot be used directly for motor fuel owing to the high content of acidic, basic and asphaltic substances.

These experiments were started in 1936, and continued until March 1937, to investigate the hydrogenation of low-temperature tar as a process for making satisfactory motor fuel.

II. DETAILED DESCRIPTIONA. Test Apparatus and Procedure

A rotating type autoclave of 2.4 liters capacity was used in these experiments.

300 grams of low-temperature tar were charged and, after displacing air by hydrogen, the pressure was increased to 100 kg/cm<sup>2</sup>. About 2 hours was allowed for heating and the autoclave was held at the reaction temperature for 1 hour. After cooling, the products were removed and analyzed.

The gaseous product was analyzed by Hempel's method.

A part of the liquid product, including solid substances such as coke, ash and catalyst, was filtered, and the properties of the filtered oil were determined.

Benzene was added to the other portion of the liquid product, (including solid matter), and moisture and benzene-insoluble substances were determined.

B. Experimental Results

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1. The properties of the low-temperature tar used as feed stock are given below:

d <sub>40</sub> .....	1.019
Benzene-insoluble (wt %) .....	2.3
Asphaltenes (wt %) .....	27.3
Distillation (wt %)	
-180°C .....	0.6
180-230°C .....	2.2
230-280°C .....	16.2
280-360°C .....	37.3
Above 360°C .....	43.2
Loss .....	0.5

2. Tests without a catalyst.

The effects of temperature and time on hydrogenation, in the absence of a catalyst, were investigated and the results are tabulated in Tables I(B)9 and II(B)9.

The hydrogen consumed and content of unsaturated hydrocarbons in the gas increased with increasing temperature, but the yield of liquid product decreased. The content of acidic substances remained practically constant above 425°C.

It was concluded that the optimum reaction conditions were as follows:

Temperature: .....450°C  
 Pressure: .....250 kg/cm<sup>2</sup> at reaction temperature  
 Time: ..... 2 hours

3. Tests with catalysts.

The following catalysts were used and the experimental results are given in Tables III(B)9 and IV(B)9.

Catalysts:	(1) Fe <sub>2</sub> O <sub>3</sub>	Commercial grade
	(2) NiO	Nickel nitrate was ignited at 300°C
	(3) Al <sub>2</sub> O <sub>3</sub>	Freshly precipitated aluminum hydroxide was dried at 150°C.
	(4) MoO <sub>3</sub>	Ammonium molybdate was ignited at 350°C.
	(5) MoS <sub>3</sub>	The precipitate from the neutralization of ammonium-thio-molybdate solution with dil. H <sub>2</sub> SO <sub>4</sub> was washed and dried at 150°C.
	(6) CoS	Freshly precipitated by H <sub>2</sub> S and washed and dried at 115°C.
	(7) AlCl <sub>3</sub>	Commercial grade
	(8) ZnCl <sub>2</sub>	Commercial grade

In all cases, yield of the reaction product was almost constant. It was difficult to conclude that the amount of water formed was dependent on the acidic substances in the raw tar, since water might be produced by the reduction of the catalyst in some cases.

The properties of the liquid product were affected by the type of catalyst used. Acidic and basic substances were converted into neutral oils by using MoO<sub>3</sub> as a catalyst. The yield of light oil was better using MoS<sub>3</sub> than with NiO, CoS, AlCl<sub>3</sub> and ZnCl<sub>2</sub>.

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## III. CONCLUSIONS

1. When no catalyst was used, the optimum conditions for motor fuel production by hydrogenation of low-temperature tar were determined as: reaction temperature, 450°C; pressure, 250 kg/cm<sup>2</sup>; and time, 2 hours.

Asphaltene content was lowered to 3-4%, but the content of acidic substances was not reduced in those experiments.

2. When a catalyst was used, the yield of liquid product was almost constant in all cases, but the properties of the liquid were affected by the catalyst used. MoO<sub>3</sub> or MoS<sub>3</sub> catalyst appeared to be the most suitable for production of high yields of light oil, in which all acidic, basic, and asphaltic compounds had been reduced to neutral oil.

Table I(B)9  
EXPERIMENTAL CONDITIONS AND YIELD OF PRODUCTS. (NO CATALYST)

Run No.	Initial Press. (kg/cm <sup>2</sup> )	Temp. (°C)	Time (hr)	Press. Drop (kg/cm <sup>2</sup> )	H <sub>2</sub> Compound (gm)	Sat. H <sub>2</sub> S in gas (gm)	Oil Yield (wt %)	Water (wt %)	Cokes (wt %)	Asphaltene (wt %)
1	100	400	2	7.0	1.1	4.3	89.9	7.2	0.4	17.4
2	100	425	2	10.0	1.8	5.9	89.6	8.1	0.5	14.8
3	100	450	1	9.0	2.0	8.4	83.5	6.1	1.5	18.4
4	100	450	2	15.0	2.1	10.9	83.2	6.1	1.0	3.4
5	90	450	2	4.0	2.1	13.5	63.5	5.7	37.0	14.2
6	100	475	1	20.0	4.2	22.7	60.7	7.3	5.8	3.4
7	100	500	I	22.0	4.4	23.7	58.2	7.1	4.0	4.2

Table II(B)9  
PROPERTIES OF OIL PRODUCT. (NO CATALYST)

Run No.	Sp. Gr. (20/4)	Composition				Distillation (vol. %)				
		acidic (vol. %)	basic (vol. %)	neutral (vol. %)	I. D.	below 180°C	180°C-230°C	230°C-280°C	280°C-340°C	above 340°C
1	0.8008	29	1	67	62	5.0	7.0	17.0	31.0	39.9
2	0.8036	22	2	76	61	6.4	11.3	22.7	17.7	33.9
3	0.8036	26	3	71	68	15.3	18.1	23.6	25.1	37.0
4	0.8444	23	3	74	52	16.7	18.3	23.9	25.1	31.5
5	0.8034	23	4	71	50	20.8	26.4	22.7	20.1	30.9
6	0.8719	24	5	71	50	26.1	26.7	20.0	17.7	26.3
7	0.8772	25	6	69	38	28.8	23.7	20.1	16.8	13.2

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Table III(B)9  
EXPERIMENTAL CONDITIONS AND YIELD OF PRODUCT

Run No.	Initial Press. (kg/cm <sup>2</sup> )	Temp. (°C)	Time (hr)	Press. Drop (kg/cm <sup>2</sup> )	Catalyst	H <sub>2</sub> consumed (gm)	Sat. H <sub>2</sub> 's in gas(gm)	Oil yield (wt. %)	Water (wt. %)	Gases (wt. %)	Asphaltenes (wt. %)
4	100	450	2	15	none	2.1	10.9	83.2	6.1	1.0	3.4
8	100	450	2	19	Fe <sub>2</sub> O <sub>3</sub>	2.9	9.4	82.8	6.6	5.3	0.5
9	100	450	2	29	K <sub>2</sub> O	3.2	6.5	84.5	9.0	4.5	trace
10	100	450	2	15	Al <sub>2</sub> O <sub>3</sub>	2.6	11.0	79.2	6.0	6.2	0.9
11	100	450	2	38	MoO <sub>3</sub>	4.9	9.7	81.8	9.2	4.9	0.0
12	100	450	2	38	MoO <sub>3</sub>	4.6	7.5	80.0	11.4	4.2	0.0
13	100	450	2	27	CoS	3.4	7.9	84.1	9.2	4.2	0.7
14	100	450	2	26	AlCl <sub>3</sub>	3.2	9.3	82.2	4.2	11.9	0.4
15	100	450	2	22	ZnCl <sub>2</sub>	2.8	7.9	83.4	5.4	7.5	0.2

Table IV(B)9  
PROPERTIES OF OIL PRODUCT

Ex. No.	Sp. Gr. (25/4)	Constituent (vol. %)			Distillation Property (vol. %)					
		acidic	basic	neutral	I. D.	below 180°C	180°C-230°C	230°C-280°C	280°C-360°C	360°C-
4	0.9468	23	3	76	52	13.0	17.1	23.4	25.3	20.6
8	0.9466	24	5	71	58	12.2	17.4	25.4	25.4	19.0
9	0.9944	16	2	82	38	16.6	29.5	23.1	26.9	12.5
10	0.9393	20	4	76	48	13.4	21.1	22.9	25.2	16.5
11	0.8547	0	0	100	43	29.5	18.0	21.9	22.8	6.7
12	0.8567	0	0	100	66	31.4	20.8	23.1	20.7	4.5
13	0.9174	18	3	79	58	13.3	19.8	23.3	27.4	12.8
14	0.9266	18	1	81	49	16.4	29.5	24.5	25.5	14.0
15	0.9223	18	3	79	47	15.0	18.3	20.8	27.8	16.8