ENCLOSURE (B) 18

STUDIES ON CATALYSTS FOR COAL HYDROGENATION

by

CHEM. LIEUT. COMDR. K. MITSUI

CHEM. ENGINEER B. OKADA

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LIST OF TABLES AND ILLUSTRATIONS

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SUMMARY

The catalyst used in the Bergius process, as applied to the hydrogenation of Japanese brown coals, was investigated and a mixed catalyst of the composition Fe_2O_3 : S : $Sn(OH)_2$ (100 : 17 : 1) was found to be the most suitable for the purpose.

I. INTRODUCTION

The catalyst employed in the Bergius process at the Naval Fuel Depot was $ZnCl_2.H_2O$, but owing to difficulties in supply, this investigation for finding a suitable catalyst composed of cheaper substitute materials was undertaken. This project was started in 1940 and completed in 1943.

II. DETAILED DESCRIPTION

A. Materials Used

1. Coal Brown coal from the Agochi district, Korea, was ground to powder of 60 mesh, and showed the following composition:

Water	15.5%	C	68.23%
Ash	8.2%	H	7.35%
V.m.	43.6%	S	0.73%
F.c.	32.7%	N	1.56%
		Ash	9.49%

2. Tar The tar, used to make the paste, was that fraction of dephenolated low temperature tar boiling from 270° to 320°. The dephenolated tar was prepared by washing with 10% caustic soda solution.

d^{30}_{4}	1.037
Benzene Insol.	1.7%

Composition

C	86.75%
H	8.55%
N	0.85%
S	0.17%
Ash	0.1%

Distillation Test

I.B.P.(90°)	
90-270°	4.3%
270-300°	11.1%

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300-350° 31.0%

350- 52.2%

3. Hydrogen Hydrogen, of 99% purity was obtained by electrolysis of water.

4. Catalyst The following catalysts were tested.

a $ZnCl_2.3H_2O$,

b. MoO_3, Na_2MoO_3, MoO_3 with C, $H_2[MoO_3(C_2O_4)(H_2O)]H_2O$,

c. $Sn(C_2O_4)_2.3H_2O$, $Sn(C_2O_4)_4.3H_2O$, $Sn(C_2H_2O_2)_2.2H_2O$,

d. $Sn(C_2H_2O_2)_4.2H_2O$, $SnCl_2.2H_2O$, $SnCl_4$, $Sn(OH)_2$, $Sn(OH)_4$,

e. $Sn(C_{17}H_{35}CO_2)_4$,

f. $Na_2MoO_4/SnCl_4(4 : 1)$, $MoO_3/SnCl_2(4 : 1)$

g. Fe_2O_3, $Fe(C_2O_4)_2.2H_2O$, $Fe_2(C_2O_4)_3.2H_2O$,

h. $Fe_2(C_2O_4)_3.2H_2O/NH_4Cl(10 : 1)$, $Fe(C_2O_4)_2.2H_2O/NH_4Cl(10:1)$,

i. $Fe(SO_4)$, $Fe_2(SO_4)_3$, FeS,

j. $Fe_2O_3/S(4 : 1)$, $Fe_2O_3/S(10 : 1)$, $Fe_2O_3/Sn(OH)_2(100 : 1)$,

k. Fe Stearate Soap/$Sn(OH)_2$ (100 : 1), $Fe_2O_3/S/Sn(OH)_2$(100: 17:1),

l. $Zn(C_2O_4)_2.3H_2O$, $Zn(C_2H_3O_2)_2.3H_2O$, $Zn(C_2H_3O_3)_2.3H_2O/NH_4Cl$ (10:1),

m. $Pb(C_2H_3O_2)_2.3H\ O$, $Pb(C_2H_3O_2)_2,3H_2O/NH_4Cl(10 : 1)$.

The catalysts were prepared from the metallic chloride or nitrate by precipitation and mixing of the components. They were dried at 110°C and powdered.

B. Apparatus

A cast iron cylindrical autoclave of 2.4 litres capacity was used. It was equipped with a thermometer and manometer, and was heated externally by electric resistance, and mounted to rotate horizontally.

C. Procedures

A paste was made by mixing oil and coal in the weight ratio of 1 : 1.

In each experiment, 150gms of the paste and 4.5gms of the catalyst to be tested were put into the autoclave, and hydrogen was introduced, from a cylinder, to produce 100 atmospheres of pressure at 0°C. The autoclave was heated at a rate of 2°C/min, to the required temperature and kept at this temperature for one hour. The changes in pressure during the reaction were observed at intervals of five minutes. When the reaction was finished, the volume and the density of the gas in the apparatus were measured and the chemical compositions of the gas, liquid and, solid reaction products were determined by the usual methods.

D. Experimental Results

Experimental results are summarized in Table I(B)18. The data are presented only for the most promising of the catalysts.

III. CONCLUSIONS

The simple catalysts which gave the best results were, $ZnCl_2 2H_2O$, MoO_3, $Sn(OH)_2$, and $Sn(OH)_4$.

The mixed catalyst which may be recommended in any respect was Fe_2O_3 : S : $Sn(OH)_2$(100 : 17 : 1). This catalyst was suitable for commercial usage and was better than $ZnCl_2.2H_2O$, previously used commercially due to a higher yield of tar and no corrosion difficulties. The cost of this mixed catalyst is slightly higher than $ZnCl_2.2H_2O$ due to tin content. It was prepared by mixing commercial grade ferric oxide (prepared by precipitation of $Fe(OH)_3$ and subsequent calcining), commercial grade sulphur and $Sn(OH)_2$ in the weight ratio of 100 : 17 : 1. The $Sn(OH)_2$ was prepared by precipitation from a 1 N solution of $SnCl_2$ with 10% NaOH, and drying in an oven at 110°C. This catalyst was used at the Fushun S.M.R. coal hydrogenation plant on the basis of these experiments and satisfactory results were obtained.

Table I(B)18
CATALYSTS FOR COAL HYDROGENATION

		Catalyst											
		$ZnCl_2.2H_2O$		MoO_3		$Sn(CrO_4)_4.3H_2O$		$Sn(OH)_2$		Fe_2O_3	$Fe_2O_3.S.Sn(OH)_2$		$Sn(OH)_4$
Exp.No.		1	2	3	4	5	6	7	8	9	10	11	12
React. Temp. (°C)		400	420	420	450	375	400	385	400	400	410	420	400
Press. (max), kg/cm^2		260	277	287	298	270	270	275	278	282	260	260	292
Press. Drop, kg/cm^2		29	30	28	30	27.0	36.0	32	37	24.5	16.0	19.5	26
Yield (liquid and Solids) (gm)		131	127	85.7	129.6	96.8	130.4	117.7	125.5	104.0	-	-	113.5
Yield (by wt% of paste)		87	85	57	86	64	86.9	78.7	83.6	69.3	-	-	75.6
Water (wt% of tot. liquid)		24.5	25.7	27.5	28.9	25.0	26.3	25.3	25.3	23.7	13.0	13.0	24.3
Tar (<180°C)		10.5	11.3	3.0	6.8	2.6	8.2	7.1	11.1	4.9	4.2	5.6	5.9
Tar (180 - 320°C)		12.2	13.6	10.4	12.2	10.5	15.5	11.8	11.1	9.3	16.3	18.1	10.3
Tar (>320°C)		26.6	24.3	35.6	29.8	36.1	30.9	32.7	29.3	39.8	57.9	54.6	20.7
Residue		14.5	13.9	12.6	11.5	16.5	9.7	11.2	11.3	16.1	7.4	6.0	12.9
Gas Analysis	CO_2	1.8	1.8	1.7	0.9	2.2	1.8	2.2	2.0	2.4	0.6	0.6	2.1
	CO	0.7	0.6	0.8	1.0	0.4	0.8	0.6	1.0	1.1	0.8	1.0	1.0
	C_nH_{2n}	0.7	0.8	0.6	0.4	0.4	0.8	0.6	1.2	1.0	0.8	0.6	0.7
	H_2	87.5	86.9	89.8	89.8	90.6	86.1	91.2	89.1	90.2	90.0	89.0	90.6
	C_nH_{2n+2}	4.9	6.1	1.6	3.9	1.5	4.7	2.9	2.9	2.2	4.9	5.8	2.6
	N	1.2	1.2	1.0	1.2	2.0	2.0	2.0	2.0	1.5	2.7	2.0	1.5
Hydrogen consumed (gm)		7.7	8.0	7.5	7.7	7.0	9.3	7.6	9.1	6.6	4.9	5.7	6.8
Hydrogen (H_2/total, wt%)		37.3	38.8	36.4	37.3	33.9	45.1	36.9	44.2	32.0	24.2	28.4	33.0
Hydrogen (H_2/pure carbon in paste, wt%)		6.7	6.9	6.5	6.7	6.1	8.1	6.6	7.9	5.8	8.3	9.6	5.9
Yield of Tar (Total liquid product / paste charged)		65.0	64.6	61.0	64.2	64.4	70.8	67.9	70.6	56.5	84.9	83.9	61.9