

ENCLOSURE (B) 10

THE COAL HYDROGENATION REACTION

by

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SUMMARY

To obtain oil of good quality from the hydrogenation of coal, the reaction must be carried on at a favorable low temperature since thermal cracking and polymerization occur at higher temperatures. This can be achieved by using a catalyst to activate the reactant (coal).

I. INTRODUCTION

In Japan, KOMATSU and SUMIMOTO*, had studies the hydrogenation of coal components, namely, resinous coal substance and unchanged vegetable substance. The most important component in coal is "coal substance" and studies on the hydrogenation of it are of particular interest.

This investigation was centered on the hydrogenation of coal substance from Fushun Oyama coal and of pure humus derived from cane sugar, using nickel oxide and zinc chloride as catalysts.

II. DETAILED DESCRIPTIONA. Raw Materials

1. Coal substance was prepared from Fushun Oyama coal according to the method described by Francis and Wheeler**. The yield and properties of coal substance were as follows:

Yield (wt.% of Oyama coal).....	85.98%
Analysis (wt.% of coal substance)	
H ₂ O.....	4.50%
Organic substance.....	86.65%
Ash.....	9.85%
Elementary Analysis (wt.% of coal substance)	
C.....	62.81
H.....	4.49
N.....	4.89
S.....	0.55
O (difference).....	27.25
C/H ratio.....	12.0

2. Humus, prepared from pure cane sugar by steaming under pressure, was a black brownish powder and its yield and properties were as follows:***

Yield (wt. of cane sugar).....	12.20
Content of H ₂ O.....	6.75
Elementary Analysis (wt.% of humus)	
C.....	66.10
H.....	4.48
O (difference).....	29.42
C/H ratio.....	12.0

3. Catalyst: ZnCl₂ (commercial grade)
Ni₂O₃ (Prepared from nitrate by precipitation method)

* S. KOMATSU and H. SUMIMOTO: Bull. Chem. Soc. Japan 261 (1935).

** W. Francis and R. V. Wheeler: J. Chem. Soc. 2967 (1928).

*** C. TAMAKA and S. KOMATSU: Beragent of Prof. Y. OSAKA.

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4. Hydrogen: Prepared by electrolysis of water.

B. Test Apparatus and Procedures

A shaking type autoclave of 600cc capacity was used in these experiments. 50 grams of coal substance or humus and 2.5 grams (5 wt.%) of catalyst were used as charge in these experiments. Initial hydrogen pressure was 100 kg/cm² (standard conditions) and the period at reaction temperature was one hour.

After the reaction period was completed, shaking was continued until temperature dropped to 100°C. After cooling overnight, the gas was released, the liquid reaction product was divided into three parts, and the amounts of water, benzene soluble (Bitumen), and benzene insoluble substance were determined.

III. EXPERIMENTAL RESULTS

A. Coal Substance

1. The absorption of hydrogen by coal substance, as shown in Figure 1(B)10 was very slow at 200-300°C. At 300-350°C the absorption rate increased, but at 350-400°C it decreased and above 400°C it increased again.

From this experiment, it appeared that hydrogen absorption up to 300°C was mainly due to saturation of double bonds and carbonyl radicals and also, that the rapid hydrogen absorption period from 300-350°C was due to saturation of benzene nuclei in polycyclics. It appeared that the ZnCl₂ catalyst was less active in promoting these reactions than Ni₂O₃. The distribution of oxygen radicals in coal has been reported by W. Fuchs as shown in Table I(B)10.

2. The relation between yield of product and reaction temperature is given in Figure 2(B)10. The composition of reaction gases is given in Table II(B)10.

It will be noted that the cracking of oxygen compounds, indicated by high production of CO₂ and CO, reached a maximum at 350°C. Formation of light hydrocarbon gases began at 400°C, probably the result of cracking of aromatic hydrocarbons. This phenomenon was confirmed by study of the bitumen content, which began to be produced at 330°C, reached 50% at 430°C and then began to decrease (refer to Figure 3(B)10). Benzene insoluble substances began to decrease suddenly at 330°C and finally dropped to 13% at 430°C (refer to Table III(B)10 and Figure 2(B)10).

From Table III(B)10 it is noted that hydrogen content increased gradually from 200°C to 350°C, and above 350°C began to decrease, whereas the carbon content varied inversely.

3. The most important problem in the hydrogenation of coal is to remove oxygen from the coal substance. Data on the conversion of oxygen into CO, CO and H₂O, obtained in this study and reported for the low-temperature carbonization of coal,*** are given in Table V(B)10. In the hydrogenation of coal substance, a maximum was reached at 350°C.

*** S. SUMIMOTO: The Report of the Naval Fuel Depot, 100(1945)

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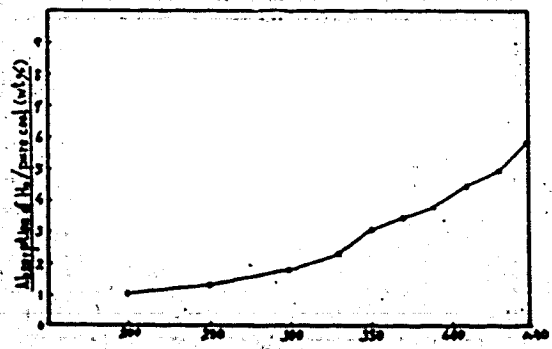
This phenomenon was quite different from the desoxidation reactions in low-temperature carbonization. The oxygen contents of bitumen and benzene insolubles produced from coal substance by catalytic hydrogenation are given in Table IV(B)10. The content is smaller in the case of $ZnCl_2$ than for Ni_2O_3 , and in this respect $ZnCl_2$ is better than Ni_2O_3 as a catalyst for hydrogenation of coal substance.

B. Humus

1. The oxygen in humus was mainly contained in carbonyl, hydroxyl and ether groups and accordingly, consumption of hydrogen was less than for coal substance, in which the oxygen was mainly in carbonyl form.

2. The desoxidation rate of coal substance was greater than that for humus up to $350^{\circ}C$, but at $390^{\circ}C$, was less (refer to Table V(B)10). This was due to high saturation of benzene nuclei in humus at $390^{\circ}C$ and over.

3. Analyses of bitumen and benzene insoluble substance are given in Table VI(B)10.



Reaction Temperature (°C)

Figure 1(B)10

H₂ ABSORPTION CURVE OF COAL SUBSTANCE (Ni₂O₃)

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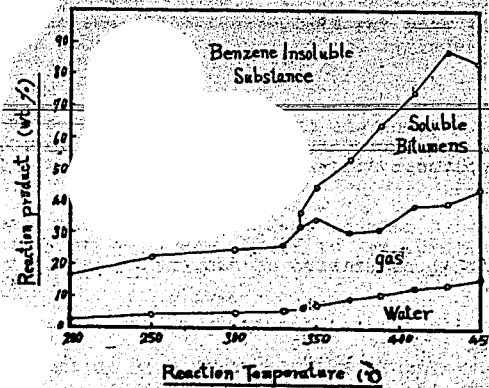


Figure 2(B)10

RELATION BETWEEN YIELD OF PRODUCTS AND TEMPERATURE (N₂O₃)

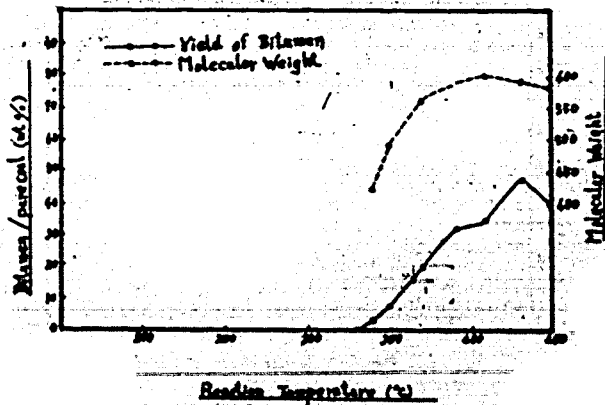


Figure 3(B)10

YIELD OF BITUMEN AND ITS MOLECULAR WEIGHT (COAL SUBSTANCE) (N₂O₃)

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Table I(B)10
WT. % OF SUBSTANCE

Type of Oxygen Radical	In Humic Acid	In Brown Coal
Carboxyl group	4	1 - 10
Hydroxyl group	6	2 - 8
Methoxyl group	2	1 - 5
Carbonyl group	5	3 - 4

Table II(B)10
GAS YIELD FROM COAL SUBSTANCE*

Gas Component	Temperature (°C)									
	200	250	300	330	350	370	390	410	430	450
CO ₂	2.76	4.83	5.41	5.76	8.67	5.55	4.84	5.77	4.70	3.61
C ₂ H ₂	0.34	0.40	0.53	0.51	0.18	0.22	0.21	0.25	0.24	0.22
CO	-	0.13	0.26	0.33	1.07	1.32	1.48	1.58	1.78	1.89
H ₂	6.51	4.38	4.19	3.95	3.62	3.45	3.32	3.00	2.81	2.34
C ₂ H ₄	-	-	-	-	-	-	-	1.47	2.29	4.73
H ₂	2.49	2.47	2.44	2.42	2.13	1.98	1.96	1.93	1.73	1.50
H	-	-	-	-	-	-	-	1.5	1.8	1.6
Total	10.10	12.21	12.83	12.97	15.67	12.52	11.81	14.00	13.55	14.29

* Grams of N₂O₃

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Table III(B)10
ANALYSIS OF BENZENE INSOLUBLE SUBSTANCE*

Reaction Temp. (°C)	Yield (wt.%)	Carbon (wt.%)	Hydrogen (wt.%)	Oxygen (wt.%)
200	84	68	3.2	22.6
330	74	77	4.9	11.7
350	56	80	5.4	11.8
390	37	80	5.2	9.7
430	13	88	5.1	7.6
450	18	90	4.6	6.2

* Ni₂O₃

Table IV(B)10
OXYGEN CONTENT IN HYDROGENATED COAL SUBSTANCE
WT.% OF MATERIAL

Catalyst	Ni ₂ O ₃		ZnCl ₂	
	Bitumen	B. Insob. Sub.	Bitumen	B. Insob. Sub.
Material React. Temp (°C)				
300	-	20.2	-	18.4
350	10.8	11.8	8.9	8.2
390	9.9	9.7	12.2	9.9
450	14.3	6.2	11.4	5.6

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Table VI(B)10
 CONVERSION OF TOTAL OXYGEN INTO CO₂, CO and H₂O
 (WT.%)

R. Temp. (°C)	(Ni ₂ O ₃ Catalyst) Hydrogen of Humus				(Ni ₂ O ₃ Catalyst) Hydrogen of C. Subst.				Low Temp. Carb.		
	CO ₂	CO	H ₂ O	Sum	CO ₂	CO	H ₂ O	Sum	CO ₂	CO	Sum
200	9.2	2.3	4.3	15.9	17.1	-	9.3	26.6	-	-	-
250	10.4	2.3	9.1	21.8	26.9	0.7	13.3	40.8	-	-	-
300	18.5	2.1	14.5	35.0	33.5	1.3	15.2	50.0	2.1	0.7	2.8
350	29.7	2.4	34.1	66.2	53.7	5.2	22.8	81.7	4.7	2.3	7.0
390	38.3	7.3	44.4	90.0	30.0	7.1	36.1	73.3	6.1	3.8	9.9
450	31.4	5.9	60.7	98.0	22.4	9.2	52.0	83.6	7.0	6.9	13.9

Table VI(B)10
 YIELD AND ANALYSIS OF BITUMEN AND BENZENE INSOLUBLE SUBSTANCE
 (WT. % Ni₂O₃)

Reaction Temp. (°C)	Bitumen			Benzene Insol. Sub.		
	Yield	C	H	Yield	C	H
200	0	-	-	91.4	68	4.0
250	0	-	-	89.4	69	4.5
300	0	0	-	84.7	72	4.5
350	4.8	82	7.3	68.9	74	4.6
390	20.1	86	7.8	36.6	86	5.1
450	16.5	89	7.6	29.4	97	3.9