ENCLOSURE (B) 16

STUDIES ON THE HYDROGENATION OF COAL.

THE MECHANISM OF COAL HYDROGENATION

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by

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LIST OF TABLES AND ILLUSTRATIONS

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SUMMARY

These experiments were made in a specially designed autoclave to study in more detail the chemical changes occuring during the hydrogenation of coal. On the basis of experimental results, conclusions are drawn as to the reaction mechanism.

I. DETAILED DESCRIPTION

A. Apparatus

The autoclave used for these experiments was an electrically-heated rotating type made of V 2 A-steel, with a capacity of 2.4 liters. Two thermocouples were used, one of which served to measure the inner temperature of the autoclave, and the other to measure the wall temperature of the autoclave as shown in Figure 1(B)16.

Both temperatures were measured on a recording pyrometer. Twenty steel balls, with a diameter of 20mm, were put in the autoclave to agitate the contents. The autoclave was rotated within an electric heater at the rate of 42 RPM.

B. Sample

Fushun Oyama coal, with the properties given below and in Table III(B)15 was used for these experiments. After crushing to below 60 mesh, it was stored in a constant humidifier (using $CaCl_2$ solution, 1.30 sp. gr.). 150 grams of coal were used in each experiment and 5% (by wt) of $ZnCl_2$ catalyst was added. The hydrogen was prepared by electrolysis.

Proximate Analysis of Coal (wt %)

Water	5.5	Ash	7.0
Volatile Matter	41.1	Calorific value (cal/g)	7,200
Fixed Carbon	46.4		

C. Test Procedure

After the sample and steel balls were put in the autoclave, air was displaced and hydrogen was added to the desired pressure. The temperatures were recorded every minute by the pyrometer and the pressure was measured every five minutes. The heating rate of the autoclave was controlled to 2.75°C/min. When the inner temperature reached the desired level, heating was stopped and the upper half of the electric heater was removed. The rotation of the autoclave was continued until the outer temperature had dropped to 100°C. Accordingly, the outer temperature showed a smooth curve, but the inner temperature showed the change due to reaction heat. After cooling, the gas was released and the reaction products were taken out. The small amount of products remaining in the autoclave were washed out with benzene. The greater part of the liquid and solid products was topped at 180°C and the water and oil distilled over were measured. After cooling the distillation residue was separated into two portions; benzene soluble and insoluble. The benzene soluble portion, after distilling off benzene, was fractionated in an Engler flask. The portion insoluble in benzene was vacuum dried for several hours, until benzene was removed completely, and was weighed. The gas was analyzed by Hempel's method.

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D. Experimental results

Each experiment was carried out using the same starting conditions and the same heating rate, but different maximum inner temperatures of 100°C, 200°C, 300°C, 325°C, 350°C, 360°C, 380°C, 425°C and 450°C. The experimental results are given in Table I(B)16 and Table II(B)16 and a typical temperature-pressure curve is shown by Figure 2(B)16.

Analyses of the solid matter remaining in the autoclave for experiments below 300°C are shown in Table III(B)16.

Results of analyses of the oil produced are given in Table IV(B)16.

A plot showing production of gas constituents is given by Figure 3(B)16.

C_nH_{2n+2} showed the greatest change, first appearing at 390°C and increasing rapidly. The waste gas at 450°C inner temperature was passed through active charcoal and the gaseous hydrocarbons absorbed were fractionated in a Podbielniak apparatus. The results are given below

Analysis of Light Hydrocarbons (vol %)
(450° Reaction Temperature)

C_1	58.9
C_2	18.0
C_3	15.1
C_4	8.0

The data in Tables III(B)16 and IV(B)16 were plotted in Figure 4(B)16.

As shown by Figure 4(B)16 if the main component of the sample coal is $C_nH_mO_x$, the substance having a composition of C=73.2, H=5.7, O=12.0 is changed by the hydrogenation and heat decomposition into unsaturated hydrocarbons having a composition C_nH_{2m-x}. Until about 340°C, the H/C in Figure 4(B)16 shows little change from the original coal, but between 340 and 390°C, the oil formation reactions began and continued to 450°C.

As shown on Figure 4(B)16 deoxygenation started at about 120°C, proceeded slowly until 340°C, become very rapid between 340 and 400°C, and then slowed down again. Figure 3(B)16 indicates that below 340°C the deoxygenation occurred by the elimination of CO_2. It is presumed that the CO_2 was produced when COOH groups in the resinous matter, and the uncharged vegetable matter in the coal were decomposed by heat. The formation of CO above 340°C indicated that deoxygenation next occured due to break down of ketones, aldehydes and cyclic bindings, and the molecular weight decreased rapidly due to collapse of the higher molecules. Further, the existence of the more stable oxygen bonds was indicated from the fact that the deoxygenation did not progress so rapidly at the higher temperature. It can be presumed, from the existence of the phenolic oil in the product, that the OH radical is most stable. The formation of CH_4 and slow increase of CO and CO_2 at higher temperature indicated the decomposition of the cyclic compounds, and the hydrogenation of CO and CO_2 to methane.

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II. CONCLUSIONS

1. From the preceding, it is concluded that the decomposition of COOH groups starts at about 120°C, as indicated by formation of CO_2. On the basis of water formation and the temperature gradients, it is known that the hydrogenation began at about 250°C. At this temperature, the coal powder began sticking to the wall of the autoclave, and indicating formation of a boundary oil film. deoxygenation become vigorous, a great deal of water was formed, and CO began to appear from 340-350°C due to the decomposition of ketones aldehydes and cyclic bound oxygen compounds.

At 390°C the H/C-ratio changed from that of coal to that of oil.

From the fact that the molecular weight decreased rapidly from above 2000 to about 500 at 390-400°C. it is concluded that the molecules collapsed due to deoxygenation of the polycyclic compounds. It is presumed that the sudden rise of temperature from about 375 to 390°C was the result of the violent evolution of heat due to the deoxygenation. Another rise from about 390 to 430°C was probably due to the heat of reaction from the cracking of hydroaromatic hydrocarbons.

Table I(B)16
EXPERIMENTAL RESULTS

Max. Temp (°C)		Pressure (atm)			Product			
Inner	Outer	Initial	Final	Decrease	Appearance	(Wt% or Coal)		
						Water Content	Solid Matter	Soluble in Benzene
100	120	100	100		Original form	5.9	94.1	
200	228	100	100		Original form	6.6	93.9	
300	340	100	99	1	Original form	8.0	92.0	
325	370	100	95	5	Pitch like	9.3	83.5	7.1
350	390	100	88	12	Pitch like	11.5	50.5	37.4
360	400	100	79.5	20.5	Pitch like	12.7	41.6	44.7
380	442	100	72.2	27.8	Low fluidity	13.2	19.9	56.6
425	450	100	70	30	High fluidity	12.6	17.3	61.4
450	450	100	68	32	Very high fluidity	12.3	17.3	60.3

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TABLE II(B)16
ANALYSIS OF GAS (VOL %)

Max. Inner Temp. (°C)	Gas Analysis					
	CO_2	C_nH_{2n}	CO	H_2	C_nH_{2n+2}	n
100	0.2	0	0	99.6	0	0
200	0.2	0	0	99.7	0	0
300	0.3	0	0.2	99.5	0	0
325	0.3	0.3	0.3	99.0	0	0
350	0.3	0.4	0.3	97.0	2.0	1.0
360	0.4	0.6	0.4	95.9	2.3	1.3
380	0.5	0.6	0.5	94.6	3.2	1.3
425	0.5	0.7	0.6	91.3	5.9	1.3
450	0.7	0.7	0.6	90.2	6.2	1.7

Table III(B)16
ULTIMATE ANALYSIS OF SOLID RESIDUE (%)

Max. Inner Temp(°C)	C	H	N	S	O	H/C
Original Coal	73.2	5.7	1.2	0.5	12.0	0.933
100°C	73.2	5.8	1.2	0.5	11.9	0.950
200°C	73.1	5.8	1.2	0.5	11.7	0.951
300°C	73.2	5.9	1.2	0.5	11.6	0.967

Table IV(B)16
ANALYSIS OF TOTAL OIL PRODUCED

Max Inner Temp. (°C)	Ultimate Analysis (wt %)						Calorific Value (Cal/gm)	Sp. Gr. (20/4 °C)	Molecular Weight Using	
									Diphenyl	Benzene
	C	H	O	N	S	H/C				
350	86.1	8.5	4.3	0.9	0.2	1.21	9178	1.1088	320	443
360	85.8	8.6	4.6	0.9	0.1	1.20	9253	1.0952	467	388
380	86.7	8.7	3.7	0.8	0.1	1.20	9412	1.0934	314	370
425	87.5	8.9	2.8	0.7	0.1	1.22	9634	1.0136	252	222
450	87.8	8.9	2.6	0.6	0.1	1.22	9643	0.9770	223	189

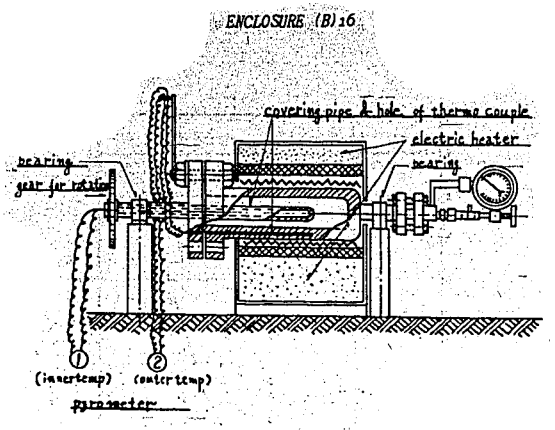

Figure 1(B)16
DIAGRAM OF AUTOCLAVE

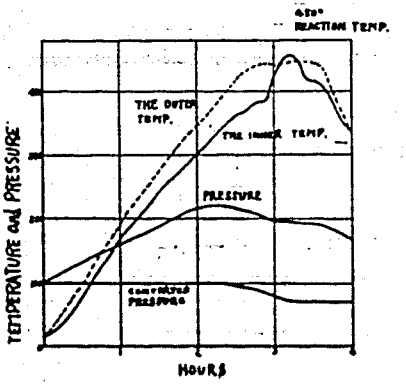

Figure 2(B)16
TEMPERATURE-PRESSURE-TIME CURVES

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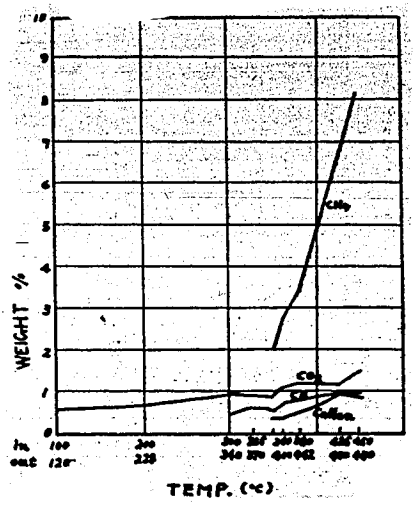

Figure 3(B)16
PRODUCTION OF GAS CONSTITUENTS

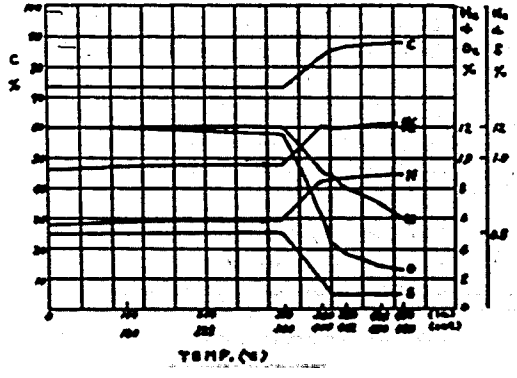

Figure 4(B)16
RESULTS OF ELEMENTAL ANALYSIS