

STUDIES OF THE STRUCTURE OF COAL AND COAL HYDROGENATION PROCESS

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Abstract - From 1956 to the present the coal research group at the Hokkaido University has continued its scientific research of coal structure and the coal hydrogenation process. As the basic aims, attempts were made to compile data by systematic research with an eye on the relationship between coal structure (characteristics) and chemical reaction (behaviour). A series of representative coals from Hokkaido coal fields ranging in coal rank (C: 70 - 86% d.a.f. basis) from brown coal to subbituminous coal and to non-caking and caking bituminous coal were studied. And our efforts have been concentrated on the elucidation of the chemical structure of coal together with the coal hydrogenation reaction itself in a parallel manner. The present paper is a comprehensive report on the essential points of our experimental results over the past twenty years. Namely in the field of coal structure, we have studied functional oxygen containing groups, structural units of coal and coal extracts, and a means of determining the distribution of structural units. We have also attempted to develop a computer-aided method of structural analysis. Further, with regard to our experimental results of basic research on the coal hydrogenation process, we have studied the reaction rate and the reaction mechanism. We have also conducted a detailed examination of the various components of hydrogenated oils, and we have developed a high pressure differential thermal analytical apparatus (DTA) and have applied this DTA method to the coal hydrogenation reaction.

INTRODUCTION

Liquefaction of coal by hydrogenation and utilization of the products as raw materials and also as a clean energy source is or will be a problem common to industrial countries of the world. It is a problem of growing importance and rapid advances are hoped for. We have continued scientific research of coal structure and coal hydrogenation process at the Hokkaido University since 1956. And as our basic aims we have attempted to compile data from systematic research with an eye on the relationship between coal structure (characteristics) and chemical reaction (behaviour) (Ref. 1 & 2). Namely, using a series of Japanese coals with differing ranks (C: 60-86% d.a.f.), we have concentrated our efforts on the elucidation of the chemical structure of coal together with the coal hydrogenation reaction itself in a parallel manner. The results thus obtained may be rationally selected and utilized for development of new technics for the utilization of coal. Our research history course on structural analysis and research subjects on coal hydrogenation process are shown in Table 1 and Table 2. It may be added that the coal utilization processes would be greatly affected by the nature or characteristics of various raw coals used for a given purpose.

TABLE 1. Research history course on structural analyses at Hokkaido University

PERIOD	METHODS	SAMPLES
1957 - 1962	(1) Krevelen's densimetric method	15 Japanese coals
1963 -	(2) Brown-Ladner's ^1H -NMR method	Pyridine extracts of 12 Japanese coals
1963 - 1973	(3) Combination of IR and ^1H -NMR method	12 Japanese coals
1971 -	(4) Computer method	Coal tar pitch and heavy oil ends from petroleum cracking
1974 -	(5) ^{13}C -NMR method	Oils from coal hydrogenation
1975 -	(6) Mass spectrometric method	n-Hexane soluble portion of coal tar pitch

TABLE 2. Research subjects on coal hydrogenation process at Hokkaido University

PERIOD	SUBJECTS
1956 -	(1) Coal Hydrogenation Reaction 1. Hydrogenolytic characteristics of 15 Japanese coals 2. Reaction rate and mechanism
1965 -	(2) Mild and Stepwise Hydrogenation of Coal 1. Initial stage of coal hydrogenation reaction 2. Chemical structure of coal related to the initial stage of coal hydrogenation 3. Structural analysis of all coal hydrogenation products
1956 - 1963	(3) Coal Hydrogenation by a Small Scale Continuous Apparatus (5Kg/hr. 450°C, 200 atm.)
1955 -	(4) Development of Differential Thermal Analysis Apparatus Under Pressure and Its Application (Type I-IV; 500-800°C, 200 atm.) (4)-1 Development of 4 types of high pressure DTA apparatuses (4)-2 Application 1. Hydrogenation of aromatic compounds 2. Hydrogenation of coal 3. Comparison of catalyst activity 4. Calculating method of kinetic data 5. Hydrodesulfurization of heavy oil 6. Coal liquefaction with carbon monoxide and water

STUDIES ON THE STRUCTURE OF COAL, COAL EXTRACTS AND COAL DERIVED HEAVY OILS

For the purpose of selecting appropriate conditions for the hydrogenation reaction and effective utilization of liquefied products the chemical structure of coal and coal derived heavy oils were investigated.

Structure of coal and coal extracts

Coal may be presumed to consist of structural units, which are aromatic clusters partially substituted by oxygen containing and aliphatic and/or alicyclic groups. The size of the average structural unit varies with the degree of coalification, and therefore coal is considered to be an organic macro-molecular material in which various structural units are polymerized by bridging of the ether or aliphatic bonds etc. (Ref. 1).

To study the chemical structure of coal, therefore, it would be necessary to elucidate the following items; 1) Size of the average structural unit 2) Distribution of the structural units 3) Linkage between the structural units 4) Molecular structure of the polymerized units.

At the beginning in 1957 to start off the research on the elucidation of the chemical structure of coal itself, an analysis of the coal characteristics was made on 15 Japanese coals using the classic van Krevelen's densimetric method (Ref. 3), and aromaticity f_a and the total number of rings R were evaluated in accordance with their ranks by Nagai (Ref. 4). According to Nagai Figure 1 shows, as an example of the results thus obtained, the change of aromaticity f_a against the values O/C of the 15 Japanese coals.

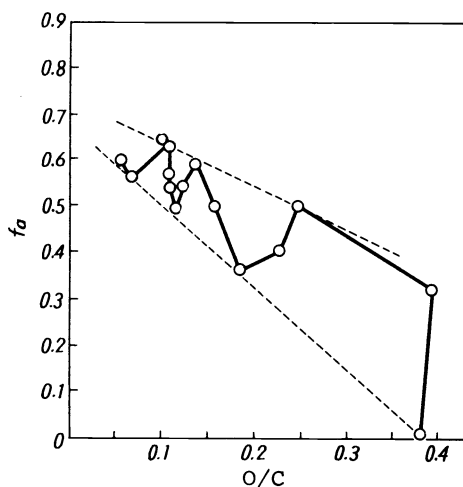


Fig. 1 Aromaticity f_a of 15 coals versus coal rank

It was clearly shown that the aromaticity f_a of 15 sample coals increases in a zigzagging manner with coal rank. Next, the mean structural units of pyridine extract were investigated. Table 3 shows the elementary analyses of sample coals and their pyridine extracts.

TABLE 3 Analyses of coal and its pyridine extract

Sample coals	Ultimate analyses									
	Coals(d.a.f.)					Pyridine extracts (d.a.f.)				
C	H	N	S	O (diff.)	C	H	N	O (direct)		
Ishikari peat	60.9	6.0	1.8	0.4	30.9	68.7	7.9	2.5	21.8	11.5
Tokachi lignite	61.5	5.7	1.0	0.0	31.8	69.9	7.9	1.5	19.3	13.8
Sohya coal	70.3	5.3	1.2	0.4	22.8	77.4	6.7	2.6	13.3*	16.6
Haboro coal	74.6	6.3	0.9	0.0	18.2	-	-	-	-	-
Sumiyoshi coal	75.5	6.2	1.2	-	17.1	78.4	6.8	1.6	13.2*	15.8
Taiheiyō coal	76.7	6.4	0.7	-	16.2	80.6	7.4	1.3	10.7*	16.7
Shakubetsu coal	77.6	5.8	1.9	0.6	14.1	76.2	6.3	2.9	13.6	12.8
Showa coal	79.6	6.2	1.8	0.2	12.2	79.6	6.7	2.5	11.7	16.8
Horonai coal	79.7	6.2	1.2	0.1	12.8	-	-	-	-	-
Shinhoronai coal	80.1	6.5	1.6	0.1	11.2	80.3	6.8	2.4	11.4	-
Bibai coal	80.7	6.0	1.7	0.1	11.4	80.0	6.1	2.5	11.2	-
Ohwada coal	81.4	6.2	1.1	0.1	11.2	81.6	6.5	1.8	9.8	14.1
Yubari coal	84.0	6.4	0.8	-	8.8	83.7	6.5	2.0	7.8*	18.5
Ohyubari coal	85.6	6.6	1.5	0.2	6.0	84.5	6.4	2.0	6.7	20.0

* Indicates that the oxygen estimation was done by subtracting S,H and N from the total 100.

As a first step for structural analysis, the functional oxygen containing groups (OH, =CO -COOH or -OCH₃ groups) in the pyridine extracts and in the 12 parent coals were measured by chemical methods (Ref. 5, 6, 7). These groups are a part of the main peripheral constituents of the aromatic cluster in the structural units. The results were as shown in Fig. 2.

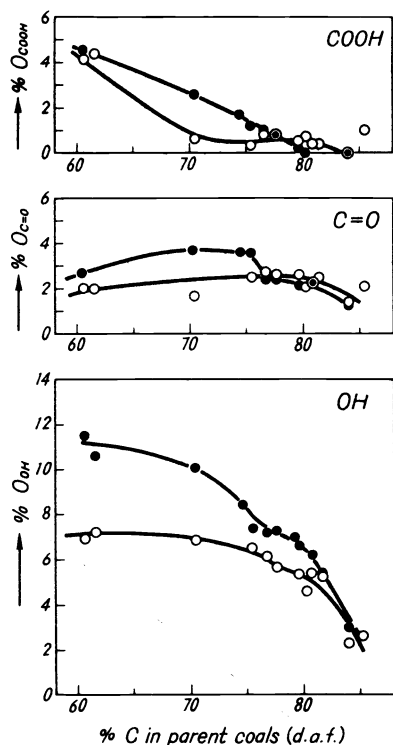


Fig. 2 Changes of functional oxygen containing groups in coals and in their pyridine extracts against the carbon content of parent coals. ● : Original coals, O : Pyridine extracts.

Next, to clarify the skeletal hydrocarbon structure of the structural unit, a technique after the Brown-Ladner's method based on proton NMR (Ref. 8) was applied to the pyridine extract.

From the contents of hydrogen atoms of different types estimated from NMR analysis and elementary analysis, the following structural parameters (fa, Hau/Ca, σ and Ho/H α) were calculated for the pyridine extract.

Parameters:

- | | |
|--------------------|---|
| fa | Carbon aromaticity, the ratio of the aromatic carbon to the total |
| Hau/Ca | The aromatic hydrogen-to-carbon ratio of the hypothetical unsubstituted aromatic material |
| σ | The degree of substitution of the aromatic systems |
| (Ho/H α)+1 | The number of carbon atoms of aliphatic side chains |

Plots of the calculated values of the 4 parameters obtained by the above are shown in Fig. 3 (Ref. 9). The chemical structure of pyridine extracts showed that with the increase in coal rank (C %), both fa and the number of condensed aromatic rings increased (i.e. the value of Hau/Ca decreased) and it was also clarified that both the substitution of the aromatic rings and the length of the aliphatic side chains decreased (Fig. 3).

For example, the mean structural unit of the pyridine extract of Tokachi lignite consists of 1 or 2 aromatic rings and structural units of pyridine extracts of bituminous coals consists of 4 or 5 rings of aromatic systems. The average number of carbon atoms of the aliphatic side chains on the aromatic systems is 7 or 8 for the extract of Tokachi lignite and 3 or 4 for

the extracts from bituminous coals with a carbon content ranging from 80 to 86%.

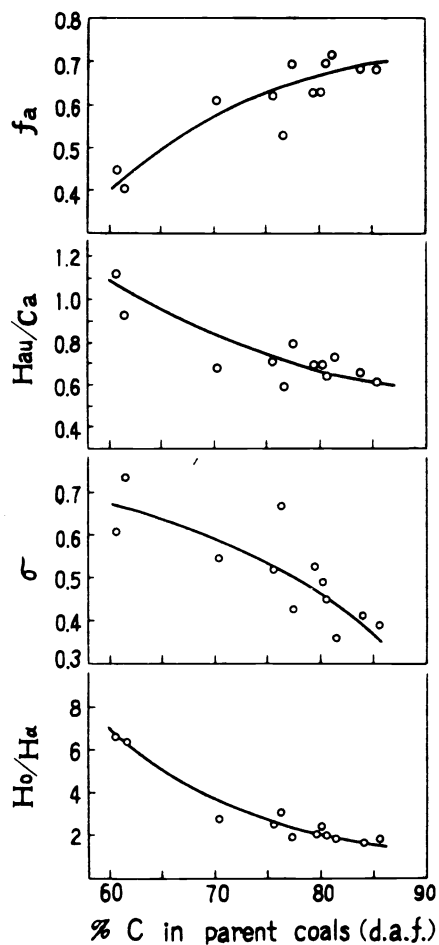


Fig. 3 Plots of f_a , H_{au}/Ca , σ and H_o/H_α for the pyridine extracts against the carbon content of the parent coals

An attempt was made to estimate the structural parameters of the sample coals. In pyridine extracts, a good linear relationship was found between the content of aliphatic hydrogen estimated from NMR analysis and the peak intensity of the absorption band 2920 cm^{-1} on IR spectra of the pyridine extracts (Fig. 4), (Ref. 10).

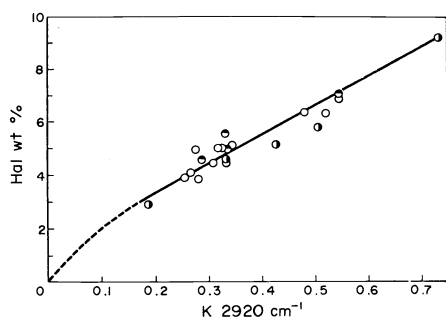


Fig. 4 Relationship between the aliphatic hydrogen content, H_{al} , obtained by NMR analyses and $K_{2920\text{ cm}^{-1}}$ in IR spectra for pyridine extracts of coals and their solvent fractionation products.

○ : Pyridine extracts, ● : Fractionation of Sumiyoshi coal extract, ● : Fractionation of Yubari coal extract.

The measurement of content of aliphatic hydrogen of the 12 parent coals was attempted by means of IR analysis as well as using the relationship between NMR and IR analysis, assuming that the relationship would be applicable to coal. The structural parameters f_a and H_{av}/Ca of the average structural unit of coals, including the 12 parent coals, were calculated based upon the content of aliphatic hydrogen of the coals and the values of elementary analysis of the same coals (Ref. 10). The results are shown in Fig. 5.

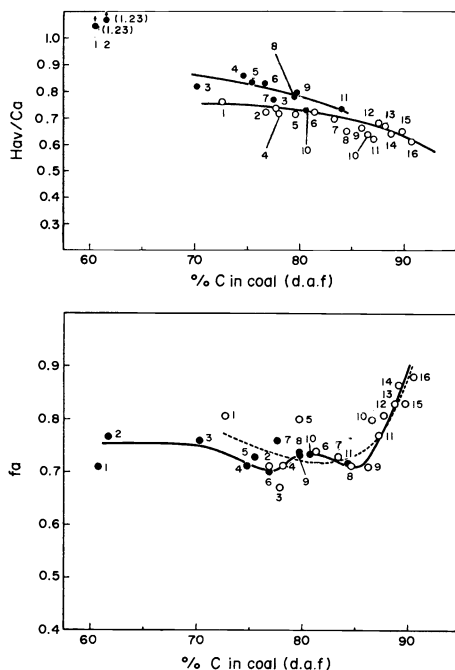


Fig. 5 Plots of H_{av}/Ca and f_a against the carbon content of coals. ● : Hokkaido coals ○ : Vitrinit portion of other sample coals. --- : Results reported by Fujii obtained by helium densimetric method (Ref. 11).

An investigation was conducted on the size and distribution of structural units and their state of polymerization for the pyridine extract. The chloroform and petroleum ether-soluble part (γ_1), and the remaining portion (γ_{2-4}) of the pyridine extract from Akabira coal were separated into fractions according to molecular weight by gel permeation chromatography. Average structural units and mean molecular structure were estimated for the fractions from their NMR analysis, elementary analysis and mean molecular weight measurement of each fraction (see Fig. 6). From these results it may be concluded that the fractions of the γ_1 -part with average molecular weights lower than 400 consist of single structural unit varying in size, whereas the fractions of molecular weight higher than about 500 consist of a dimer or trimer of structural units. The mean molecular weight (M) was measured by vapour pressure osmometry and the weight of mean structural unit ($M_{(us)}$) was calculated from its structural parameters and oxygen containing groups. In the case of γ_{2-4} portion, the average molecular structure of most of the fractions consist of dimer or trimer of units (Ref. 12, 13).

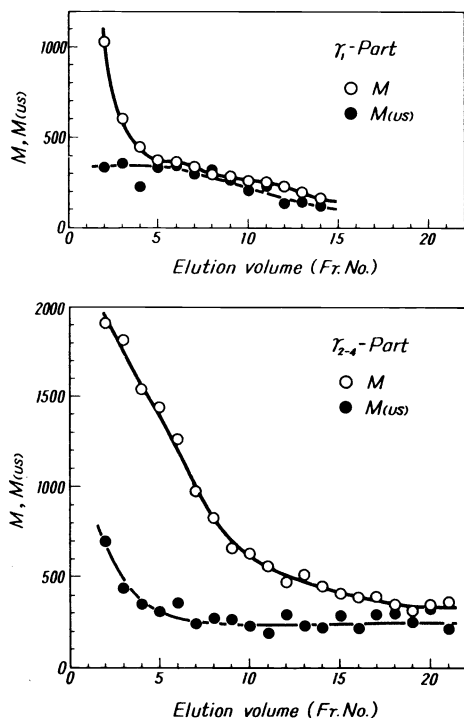


Fig. 6 Comparison of molecular weight (M) and weight of structural unit ($M_{(us)}$) in relation to the elution volume (fraction number)

Structure of coal derived heavy oils

Recently, by using a computer a method was developed for the estimation of numerous structural parameters of carbonaceous soluble matters, such as highly condensed aromatic heavy oil, coal tar, coal liquid and so on. This computer-aided structural analysis is derived from the method developed by Hirsch and Altgelt (Ref. 14). The computer method for obtaining structural parameters uses such data as molecular weight, density, proton NMR and elementary analysis. By means of this procedure we have developed, it is possible to calculate not only the aromaticity but also the number of structural units, naphthenic rings or aromatic rings per molecule without relying on the assumptions related to the compactness of aromatic fused rings (Ref. 15).

The new method was applied to crude oil-cracking tar pitch, coal tar pitch and asphalt cracking pitch etc. (Ref. 16). Figure 7 shows the results of aromaticity of various pitches compared with those from densimetric and proton NMR methods. As you may see this computer method gives results which showed a satisfactory coincidence with those obtained by the Krevelen and Brown-Ladner methods. It is emphasized that the structural characters of such carbonaceous matters can be clarified by this method.

Our group has been trying to establish or set forth satisfactory conditions for ^{13}C -NMR analysis of hydrogenated oil. The measuring conditions have been finalized. Thus, we have come to the point where accurate fa of the above oil can be determined (Ref. 17). A mass spectroscopic analysis was applied to the n-hexane soluble part (Yield : 27%) of Yubari coal tar pitch using a GC-Mass spectrometer (Hitachi M52) (Ref. 18). As a result, about 60 aromatic compounds having from 2 to 6 aromatic rings were quantified. And the number and distribution of the methyl group attached to aromatic rings of these compounds were clarified (Table 4).

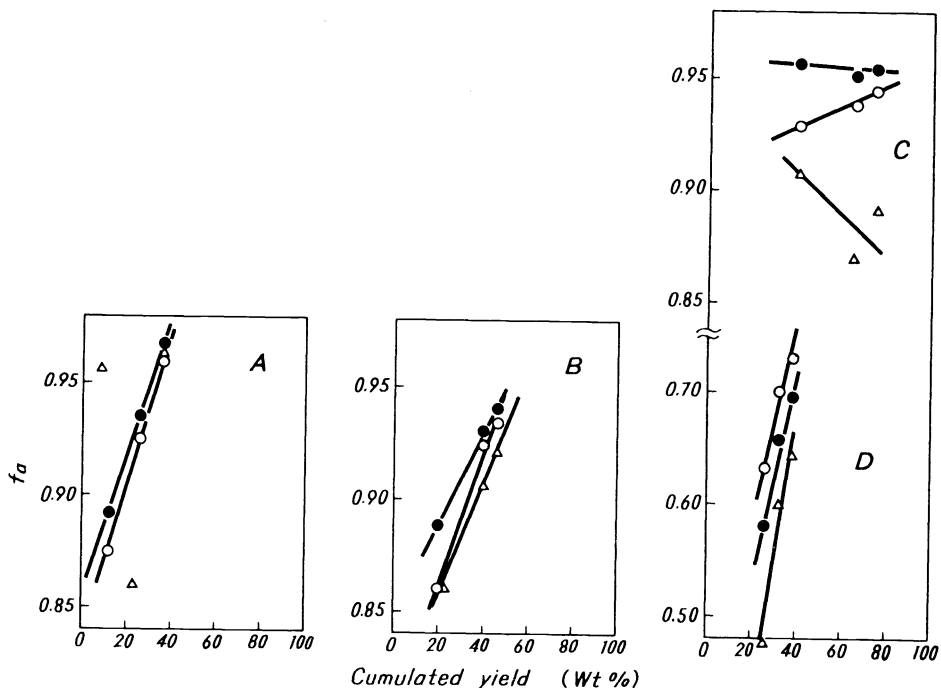


Fig. 7 Relationship between aromaticity (f_a) obtained by three methods and the yield of the fraction from each pitch.
 ● : New-method, Δ : Krevelen-method, \circ : Brown-Ladner-method.

TABLE 4 Analytical results of each fraction*

Fraction No.7

Compound	n	Yield %
<chem>Cc1ccc2ccccc12</chem>	3	0.04
<chem>Cc1ccc2ccccc12</chem>	4	0.13
<chem>Cc1ccc2ccccc12</chem>	0	0.16
<chem>Cc1ccc2ccccc12</chem>	1	0.16
<chem>Cc1ccc2ccccc12</chem>	2	0.32
<chem>Cc1ccc2ccccc12</chem>	3	0.17
<chem>Cc1ccc2ccccc12</chem>	0	0.36
<chem>Cc1ccc2ccccc12</chem>	1	0.14
<chem>Cc1ccc2ccccc12</chem>	2	0.70
<chem>Cc1ccc2ccccc12</chem>	3	0.80
<chem>Cc1ccc2ccccc12</chem>	4	0.44
<chem>Cc1ccc2ccccc12</chem>	0	2.43
<chem>Cc1ccc2ccccc12</chem>	1	2.97
<chem>Cc1ccc2ccccc12</chem>	2	2.00
<chem>Cc1ccc2ccccc12</chem>	3	4.96
<chem>Cc1ccc2ccccc12</chem>	0	0.73
<chem>Cc1ccc2ccccc12</chem>	1	1.05
<chem>Cc1ccc2ccccc12</chem>	0	0.20
<chem>Cc1ccc2ccccc12</chem>	1	0.30
<chem>Cc1ccc2ccccc12</chem>	2	0.02
<chem>Cc1ccc2ccccc12</chem>	0	0.73
<chem>Cc1ccc2ccccc12</chem>	1	3.40
<chem>Cc1ccc2ccccc12</chem>	2	5.82
<chem>Cc1ccc2ccccc12</chem>	3	3.45
<chem>Cc1ccc2ccccc12</chem>	4	2.77
<chem>Cc1ccc2ccccc12</chem>	5	1.14
<chem>Cc1ccc2ccccc12</chem>	6	0.39
<chem>Cc1ccc2ccccc12</chem>	1	0.15

Compound	n	Yield %
<chem>Cc1ccc2ccccc12</chem>	0	2.41
<chem>Cc1ccc2ccccc12</chem>	1	4.64
<chem>Cc1ccc2ccccc12</chem>	2	3.01
<chem>Cc1ccc2ccccc12</chem>	3	2.32
<chem>Cc1ccc2ccccc12</chem>	4	0.28
<chem>Cc1ccc2ccccc12</chem>	0	0.70
<chem>Cc1ccc2ccccc12</chem>	1	1.01
<chem>Cc1ccc2ccccc12</chem>	2	2.84
<chem>Cc1ccc2ccccc12</chem>	3	2.31
<chem>Cc1ccc2ccccc12</chem>	0	1.39
<chem>Cc1ccc2ccccc12</chem>	1	3.00
<chem>Cc1ccc2ccccc12</chem>	2	3.46
<chem>Cc1ccc2ccccc12</chem>	3	1.34
<chem>Cc1ccc2ccccc12</chem>	0	2.71
<chem>Cc1ccc2ccccc12</chem>	1	0.24
<chem>Cc1ccc2ccccc12</chem>	2	0.18
<chem>Cc1ccc2ccccc12</chem>	0	1.45
<chem>Cc1ccc2ccccc12</chem>	1	2.26
<chem>Cc1ccc2ccccc12</chem>	2	2.52
<chem>Cc1ccc2ccccc12</chem>	3	0.36
<chem>Cc1ccc2ccccc12</chem>	0	2.03
<chem>Cc1ccc2ccccc12</chem>	1	3.01
<chem>Cc1ccc2ccccc12</chem>	2	3.10
<chem>Cc1ccc2ccccc12</chem>	3	1.53
<chem>Cc1ccc2ccccc12</chem>	4	0.79
<chem>Cc1ccc2ccccc12</chem>	1	0.68
<chem>Cc1ccc2ccccc12</chem>	2	1.04
<chem>Cc1ccc2ccccc12</chem>	4	0.33
Total		86.55
Unknown		13.45

Fraction No.8

Compound	n	Yield %
<chem>Cc1ccc2ccccc12</chem>	1	1.1
<chem>Cc1ccc2ccccc12</chem>	2	0.8
<chem>Cc1ccc2ccccc12</chem>	0	17.9
<chem>Cc1ccc2ccccc12</chem>	1	7.3
<chem>Cc1ccc2ccccc12</chem>	0	24.3
<chem>Cc1ccc2ccccc12</chem>	1	4.3
<chem>Cc1ccc2ccccc12</chem>	0	11.6
<chem>Cc1ccc2ccccc12</chem>	1	6.1
<chem>Cc1ccc2ccccc12</chem>	0	6.9
<chem>Cc1ccc2ccccc12</chem>	1	1.0
		3.2
Total		84.5
Unknown		15.5

Fraction No.9

Compound	n	Yield %
<chem>Cc1ccc2ccccc12</chem>	0	8.3
<chem>Cc1ccc2ccccc12</chem>	1	2.2
<chem>Cc1ccc2ccccc12</chem>	0	22.0
<chem>Cc1ccc2ccccc12</chem>	1	4.5
<chem>Cc1ccc2ccccc12</chem>	0	15.6
<chem>Cc1ccc2ccccc12</chem>	1	4.0
<chem>Cc1ccc2ccccc12</chem>	0	15.3
<chem>Cc1ccc2ccccc12</chem>	1	16.2
		2.1
Total		90.3
Unknown		9.7

* n-Hexane soluble part of Yubari coal tar pitch.

STUDIES ON COAL HYDROGENATION PROCESS

Basic research on the coal hydrogenation process has been carried out since 1956. Our research subjects are as follows: reaction rate, reaction mechanism, products of coal hydrogenation in a laboratory-scale continuous apparatus, development of the high pressure differential thermal analytical apparatus (DTA) and its application to coal hydrogenation (see Table 2).

Reaction rate and reaction mechanism

A 500 ml batch autoclave study was made on the kinetics of high pressure hydrogenation of Japanese coals of different ranks (Ref. 19-24). The reaction rate was measured under the conditions of reaction rate controlling. The difference in coal hydrogenation reactivity was investigated in relation to the various analytical indices of the sample coals (Ref. 22).

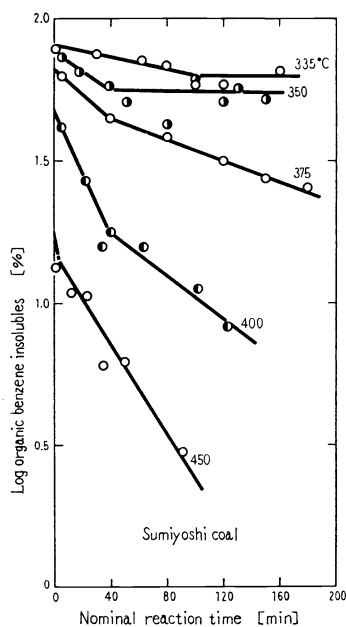


Fig. 8 Conversions of Sumiyoshi coal plotted as a first order reaction

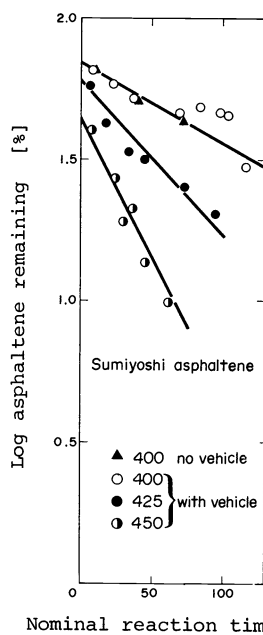


Fig. 9 Conversions of Sumiyoshi asphaltene plotted as a first order reaction

The rate of decrease of unreacted coal (d.a.f. basis) was taken as the rate of coal hydrogenation. From the semi-logarithmic plots of the benzene insolubles of residues (unreacted coal) versus the nominal reaction time at each reaction temperature level, it was concluded that the coal hydrogenation reaction involves two steps. The rate of reaction in the first step was high,

and the second step was much slower. Both steps of the reaction can be expressed as a first order reaction at each temperature. (Hydrogen pressure of 200-220 atmospheres were employed.)

From the solvent extraction of coal hydrogenation products, asphaltene appears to be an intermediate product between coal and oil. Likewise asphaltene hydrogenation was studied with the same procedure. The hydrogenation reaction of asphaltene consists of one step which may be expressed as a first order reaction (Ref. 19 & 23).

The results for Sumiyoshi coal and Sumiyoshi asphaltene are shown in Fig. 8 and Fig. 9, respectively. The rate constants and the activation energies for Sumiyoshi coal and the asphaltene are shown in Table 5 and Table 6, respectively (Ref. 19).

TABLE 5 Reaction rate constants (min)⁻¹ and activation energies for Sumiyoshi coal hydrogenation

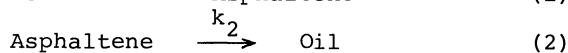
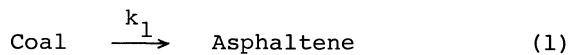
Reaction step	Reaction Temp. (°C)					Activation energy (Kcal)
	335	350	375	400	450	
1st step	0.0032	0.0077	0.0102	0.025	0.057*	19.6
2nd step			0.0045	0.0093	0.018	16.3

* Extrapolated value

TABLE 6 Reaction rate constants and activation energy for Sumiyoshi asphaltene hydrogenation with and without vehicle

Temperature (°C)	400	425	450	Activation energy (Kcal)
Rate constant (min ⁻¹)	0.0066	0.013	0.026	25.9

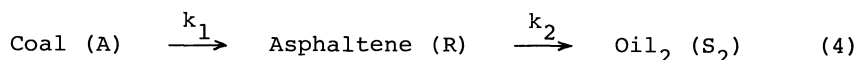
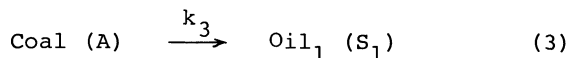
From kinetic studies, Weller et al. (Ref. 25) suggested that coal hydrogenation may be represented schematically as consecutive reactions:



They also suggested that the rates of these two reactions differ markedly, in other words normally reaction (2) is much slower than reaction (1).

In the case of Japanese coals, the distribution of asphaltene in the hydrogenation product greatly differed from some foreign coals (Ref. 19).

The reaction taking place for Hokkaido brown coal may be presented schematically as parallel reactions:



That is to say a part of the coal is converted directly to oil (S₁) and a greater part of raw coal is converted to oil (S₂) through asphaltene.

Assuming that reaction (3) is negligible in the second step reaction and that each of these reactions were simple first order, the reaction may be expressed as follows:

for the first step reaction

$$-dC_A / dt = (k_1 + k_3) C_A \quad (5)$$

$$dC_R / dt = k_1 C_A - k_2 C_R \quad (6)$$

$$dC_{S_1} / dt = k_3 C_A \quad (7)$$

$$dC_{S_2} / dt = k_2 C_R \quad (8)$$

for the second step reaction

$$-dC_A / dt = k_1 C_A \quad (9)$$

$$dC_R / dt = k_1 C_A - k_2 C_R \quad (6)$$

$$dC_{S_2} / dt = k_2 C_R \quad (8)$$

where

C_A : concentration of coal (benzene insolubles)

C_R : concentration of asphaltene

C_{S_1} : concentration of oil produced directly from coal

C_{S_2} : concentration of oil produced through asphaltene

The comparison between observed and calculated data at 400°C and 450°C for Sumiyoshi coal are shown in Fig. 10 and Fig. 11, respectively (Ref. 19).

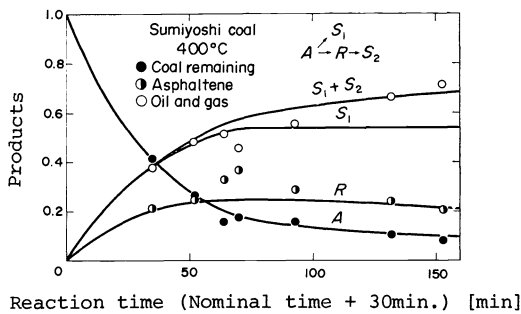


Fig. 10 Products distribution at 400°C on Sumiyoshi coal

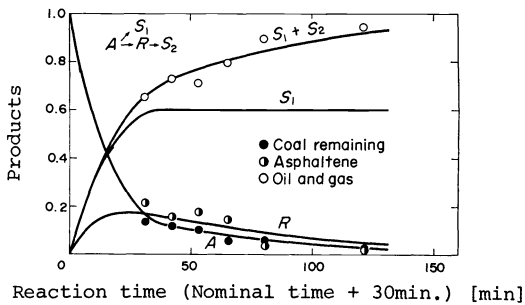


Fig. 11 Product distribution at 450°C on Sumiyoshi coal

A very good agreement between the calculated and the experimental results suggested that the new reaction mechanism given above may be applied to the hydrogenation reaction of Hokkaido brown coal.

Moreover, as shown in Fig. 12, the rate constants of the reaction in the first step decrease with the increasing rank of coals, and are closely correlated with classification parameters related to thermal reaction such as fixed carbon content, volatile matter content and fuel ratio; on the other hand, the rate constants of the reaction in the second step may be considered to be correlated with the ether-oxygen-bond in the remaining coal sample after removal of the constituents that appeared in the reaction of the first step, and are not correlated with the rank of coals (Ref. 22).

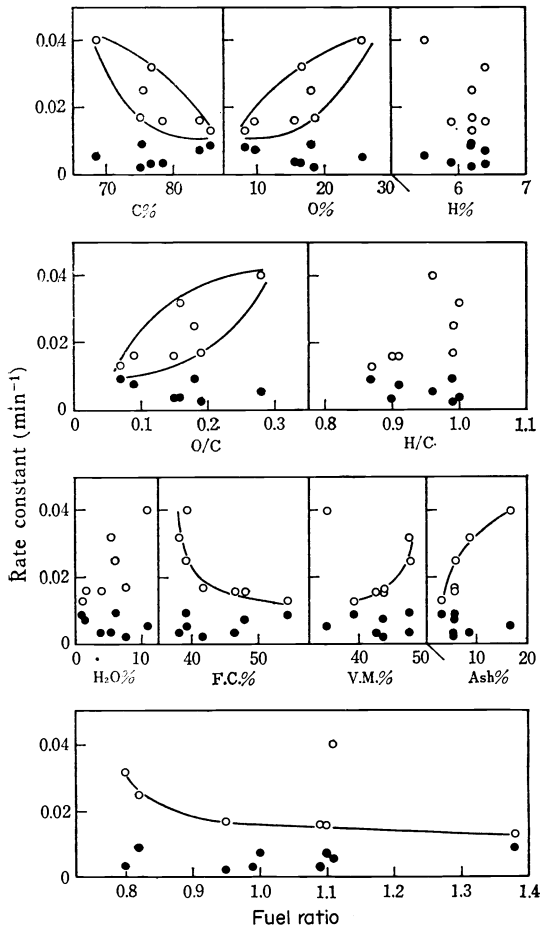


Fig. 12 Rate constants vs. ultimate analysis, proximate analysis and fuel ratio of parent coal. ○ : 1st step, ● : 2nd step.

Continuous coal hydrogenation process

As part of the studies on coal hydrogenation for the purpose of producing aromatic chemicals from coal, experimental work with a small scale continuous apparatus was carried out in our laboratory from 1956 to 1963 (Ref. 26 & 27).

The object of these experiments was to study optimum operating conditions for coal hydrogenation in a flow system, together with a detailed examination on various components of hydrogenated oils. An example of aromatic components in hydrogenated oil analysed in detail is shown in Table 7. About 50 components were identified or their existence was presumed (Ref. 27).

In addition to various points described above, as basic studies of high pressure coal hydrogenation reaction, we have conducted studies on the reaction process of mild treatment of coal under hydrogen pressure (Ref. 28 & 29) and stepwise hydrogen treatment of coal under pressure (Ref. 30) together with studies on the chemical structure of the products. Our obtained results showed a good clarification.

TABLE 7 Identified components or extrapolated components in primary oil produced by coal hydrogenation (Exp. No.12)

B.P. (°C)	Hydrocarbon Oils	Phenols
~ 150	 $n\text{-C}_7\text{H}_{16}$, $n\text{-C}_8\text{H}_{18}$, Xylene, (Dimethyl heptane)*	
150 ~ 190	 Hydrindene, (Indene)*, (Coumarone)*, (P-Cymene)*, (Trimethylbenzene)*, $n\text{-C}_{10}\text{H}_{22}$	
190 ~ 205	 Methylhydrindene, Trimethylbenzenes, Tetramethylbenzene	
205 ~ 225	 (CH_3) , $(\text{CH}_3)_2$	
225 ~ 230	 α -Methylnaphthalene, β -Methylnaphthalene	
115-130 (25 mmHg)	 α -Methylnaphthalene, β -Methylnaphthalene	
130-140 (25 mmHg)	 Dimethylnaphthalene	
140-150 (25 mmHg)	 Acenaphthene	
150 ~ 155 (25 mmHg)	 Fluorene, (Trimethylnaphthalenes)*, (Methyldiphenyl)*	

* Extrapolated component

Development of a differential thermal analysis apparatus under high pressure and its application

Studies on the production of liquid fuel and chemicals from coal and also on the chemical structure of coal were carried out using high pressure coal hydrogenation with a batch or a flow reactor.

Since 1955, direct measurement of the reaction heat of coal hydrogenation was attempted by developing a new DTA apparatus under pressure which can be applied to the reactions of gas, liquid and solids.

Following the development of the first high pressure DTA apparatus, we continued our work and developed and improved on our first model. As a result, we finally developed 4 types of DTA apparatus which has made it possible to advance from direct heat measurement to such items as comparison of catalytic activity (Ref. 31 & 36), analysis of morphological changes of the catalyst under hydrogen pressure (Ref. 32) and determination of the reaction course under high pressure (Ref. 33-38). (see Table 2). The special features of the 4-types are given in Table 8.

Stirring of the sample is possible in Type I and Type II, while the measurement of DTA is being made, and at the same time the measurement of the pressure difference between the reference chamber and the reaction chamber, namely a differential pressure analysis (DPA) can be made.

TABLE 8 Comparison of 4 types of high pressure DTA apparatus

Type	Application	Autoclave (inner vol)	Max. working temperature (°C)	Max. working pressure (kg/cm ²)	Sample (g)	Stirring	Inner electric heater	Sensitivity (cal/min)
I	reaction between gas, liquid and solid	vertical (60 ml)	500 (700) ^a	200 (100) ^a	3-10	with magnetic stirrer	with	1-8
II	reaction between gas and solid or material of high viscosity	horizontal (200 ml)	500	200	20	with logrolling of autoclave	with	70
III	reaction between gas, liquid and solid	vertical (0.8 ml)	500	200	0.01 -0.06	without stirring	without	0.2
IV	reaction between gas and solid	vertical (15 ml)	800	100	1-3	gas flow or fluidization	without	—

a: Hastelloy-C autoclave and heater embedded in a cast iron block

The apparatus Type I is also equipped with a small electric heater by which the reaction heat can be calibrated. Schematic diagram of Type I is shown in Fig. 13.

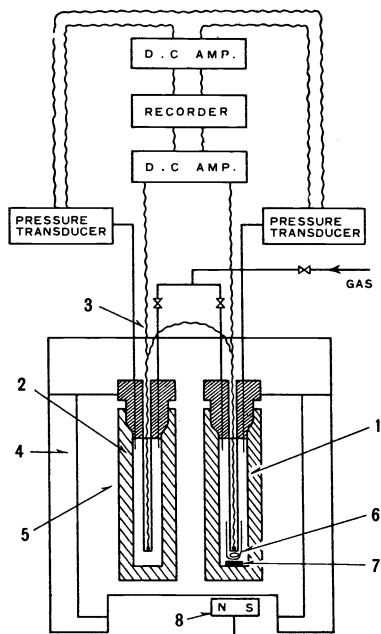


Fig. 13 High pressure DTA apparatus: (1) reaction chamber, (2) reference chamber, (3) differential thermocouple, (4) insulation, (5) heater embedded cast aluminum, (6) small electric heater, (7) magnet piece, (8) auto stirrer.

The measurements of the reaction heat were based on the relationship between the peak areas produced by means of the electric heater and the actual reaction heat (Ref. 33).

DTA curves using 3 different catalysts were shown in Fig. 14 for the measurements of the reaction heat of coal hydrogenation with the apparatus (Type I). These results clearly indicate that both the initiation temperature of the reaction and the heat of reaction depend upon the catalysts used (Ref. 35).

Secondly, DTA was applied to the study of coal hydrogenation with various catalysts under 200 atmospheric pressure.

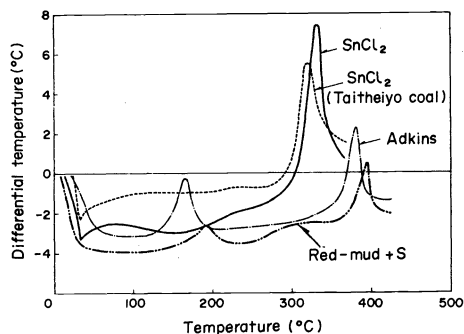


Fig. 14 DTA curves in hydrogenation of Sumiyoshi coal with various catalyst

The activities of catalysts used here were compared with each other directly from the temperature of appearance of an exothermic peak in a temperature range from 300 to 450°C. The order of catalytic activity was as follows: $ZnCl_2$ ($ZnCl_2$, 329°C) > $SnCl_2 \cdot 2H_2O$ (? , 339°C) > SnS (SnS+Sn, 372°C) > SnO_2 (SnO_2 +Sn, 386°C) > $(NH_4)_6Mo_7O_{24}$ (MoO_2 , 390°C) > red mud + S (? , 397°C) > ZnO (ZnO, 401°C) > red mud (? , 429°C) \approx ZnS (ZnS, 420-435°C) \approx no catalyst (420-436°C). The metallic compounds and temperature in brackets show the form of catalyst under the reaction conditions and the exothermic peak temperatures. In these tests also, $ZnCl_2$ was found to be the most active catalyst (Ref. 31).

Moreover, DTA was applied to determine the distribution of coal hydrogenation products. The DTA curve for hydrogenation of Taiheiyo coal in the presence of $SnCl_2 \cdot 2H_2O$ catalyst and the conversion to the reaction products, namely oil, gas and water, asphaltene and coal remaining is plotted in Fig. 15, at temperature ranging from 200 to ca. 460°C when the thermal peak appeared.

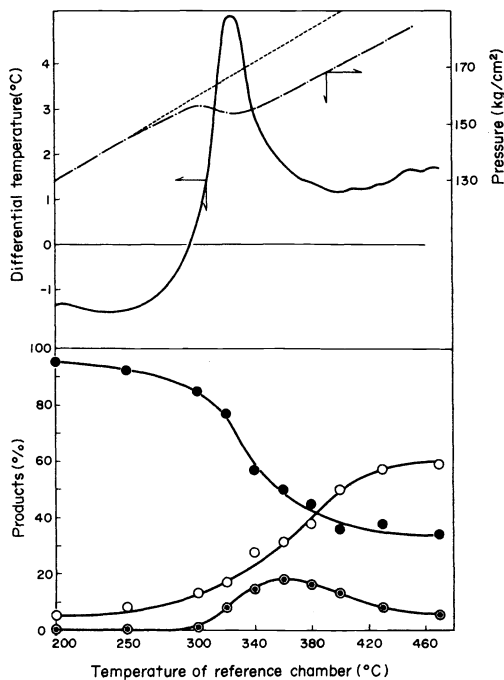


Fig. 15 DTA curve and distribution of products in Taiheiyo coal hydrogenation. ● Coal remaining, ● Asphaltene, ○ Oil+Gas+H₂O.

It may be noted that the maximum rate of decrease of residual coal can be found at a temperature roughly corresponding to the DTA peak temperature (Ref. 35).

Table 9 is a summary of our work at the Hokkaido University over the past twenty years.

TABLE 9 Studies on coal chemistry, Hokkaido University

Period	Basic research	Applied technique
1945 5 1956	<p>Chemical and physical properties of Hokkaido caking coal</p> <p>Coking properties of Hokkaido coal</p>	Metallurgical Coke Manufacturing
1956 5 1975	<p>Chemical structure of coal (Representative Japanese coals) (I)</p> <p>High pressure coal hydrogenation (Brown coal to bituminous coal) (II)</p> <p>Development and application of apparatus for DTA under high pressure (III)</p>	Coal Hydrogenation Process
	<p>I. Chemical Structure of Coal</p> <p>1. Structural characteristics</p> <p>(a) Average structural unit</p> <p>Aromatic cluster, Oxygen containing groups, Evaluation of aliphatic or alicyclic groups, Active hydrogen</p> <p>(b) Distribution of the structural units</p> <p>2. Depolymerization of coal (Solvent extraction, Hydrogenation under mild condition)</p> <p>3. Separation of coal derivatives (Liquid chromatography, GPC)</p>	<p>III. Differential Thermal Analysis Apparatus under Pressure</p> <p>1. Development of apparatus (Type I-IV) Reaction of gas, liquid and solid (up to 800°C and 200 kg/cm² pressure)</p> <p>2. Application Hydrogenation of aromatic compounds (Heat of reaction and course of reaction), Coal hydrogenation (Heat of reaction and course of reaction), Comparison of catalyst activity, Calculation method for kinetic data, Hydrodesulfurization of heavy oil</p>

REMARKS

By the above work, the average chemical structural units and hydrogenolytic characteristics of Japanese coals were clarified. However, in order to design a rational chemical reaction process with the coal structure in mind, it would be necessary to find the mode of aggregation of the chemical structural units and related configurations which make up the macro-structure of the coal in its entirety and coal derived liquids. It would also be necessary to devise analytical methods and procedures for this purpose as part of our fundamental research.

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