

## Studies on Coal Hydrogenation Reaction Using High Pressure Differential Thermal Analysis

S. Yokoyama\*, S. Ueda\*, Y. Maekawa\* and M. Shibaoka\*\*

\*Government Industrial Development Laboratory, Hokkaido  
41-2, Higashi-Tsukisamu, Toyohiraku,  
Sapporo, 061-01, Japan

\*\*CSIRO, Fuel Geoscience Unit, P.O.Box 136, North Ryde,  
N. S. W. Australia 2113

### Introduction

High pressure hydrogenation reaction of coal is an exothermic reaction accompanied by heat generation and hydrogen consumption. As compared against autoclave experiments, when high pressure DTA is applied it is possible to conduct a rapid and simple follow up of the course of reaction over a wide thermal range, and the results obtained are of considerable interest.

Up till the present, utilizing a 2 cell high pressure DTA apparatus developed by the present workers<sup>1)</sup>, we have conducted measurements of the heat of coal hydrogenation<sup>2)</sup> and desulfurization reaction of heavy oil<sup>3)</sup>. Following the above we have carried out comparative studies of catalytic activity and reactivity with regard to hydrogenation of aromatic compounds and coals<sup>4)-6)</sup>.

In the present paper, first we will describe a newly developed single cell DTA apparatus. This single cell apparatus, as compared against the conventional 2 cell DTA apparatus, was designed in such a way as to have a simpler heating rate control and a higher measurement sensitivity.

Next, in the hydrogenation reaction of coal, generally it is not quite so easy to maintain or obtain a contact of hydrogen and the coal sample. Thus, in the present work we did not use stirring, but instead we made an even mixture of the unreacted solid, namely  $\alpha\text{-Al}_2\text{O}_3$  was mixed at various rates with the coal sample, and by gradually changing the hydrogen availability, we investigated the relationship of mesophase formation and hydrogenation.

Next, under the condition of a sufficient hydrogen availability necessary for the coal hydrogenation reaction, the exothermic peaks were measured and the reaction course of coal hydrogenation was investigated.

### Experimental

#### Sample

The present work was undertaken as part of a series of studies on hydrogenation of the petrographic composition of coal, in the study vitrinite concentrate hand-picked from Bayswater and Liddell seam coal (N.S.W., Australia) with a high volatile bituminous rank were used. The particle size was under 100 mesh. The petrographic and chemical analysis of the hand-picked samples are given in Table 1.

#### Apparatus

The essential part of the single-cell DTA apparatus comprises two sheath thermoconples (1.6 mm diameter) and a heat-sink, which are placed in an ordinary autoclave (25 mm i.d., 50 ml capacity). One thermocouple is inserted into a hole

in the heat-sink and the other into the sample. Exothermic or endothermic reactions can be detected by measuring the temperature difference between the heat-sink and the sample. This temperature difference can be recorded on a chart as a DTA curve. The pressure change can also be recorded on a chart simultaneously by using a pressure transducer and an amplifier.

#### Experimental conditions

The sample coal was impregnated with accurate 10%  $ZnCl_2$  using an ethanol solution and was subsequently evaporated to dryness in a vacuum dryer. 5.5 g of this sample was used for each high pressure DTA experiment. In order to vary the hydrogen availability, to each sample 0~5.5 g of unreacted solid, namely  $\alpha-Al_2O_3$  of 80 mesh was mixed in evenly. Hydrogen initial pressure 100  $kg/cm^2$  was charged into the autoclave, and at a heating rate of  $3^\circ C/min$ , the temperature was raised to a given point and the DTA and pressure change curve was measured. After reaching a given temperature, the autoclave was immediately removed from the furnace and allowed to cool in air and the temperature was lowered at a rate of  $35^\circ C/min$ . After cooling down to room temperature, the reaction products were analysed using a Soxhlet extractor and a gaschromatography. Oil is defined here as a hexane-soluble fraction and asphaltene as benzene-soluble, hexane-insoluble fraction. The solid residues were examined under a reflected light microscope.

### Results and discussion

#### 1. The effect of hydrogen availability on coal hydrogenation and DTA

Previous work<sup>7)</sup> by the present author showed that the formation of the mesophase during coal hydrogenation was controlled not only by temperature and time but also by hydrogen availability.

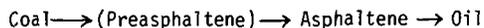
In the cases where coal hydrogenation was carried without the use of vehicle oil, since stirring is difficult, in the present case a new technic was attempted, namely by mixing unreacted solid,  $\alpha-Al_2O_3$ , evenly into the sample under various ratios, the hydrogen availability was gradually changed. In Fig. 1, the DTA curve and pressure change curve obtained by mixing in 0~5.5g of  $\alpha-Al_2O_3$ , and raising the temperature to  $450^\circ C$ , are shown. Fig. 2 shows the results of analyses of the reaction products after cooling down to room temperature. From microscopic observations of the extraction residues, in the case where less than 2.5 g of  $\alpha-Al_2O_3$  is mixed in, it was shown that while the mesophase formed, when the addition of  $\alpha-Al_2O_3$  was increased over 3.3 g the mesophase was not formed. In the former, from microscopic observations during the exothermic peak formation, it was considered that the reaction proceeds in the following manner. In the former half of the exothermic peak on the lower temperature side, the coal particles are independent of each other, and since the contact with hydrogen is good, the hydrogenation reaction proceeds rapidly accompanied by heat generation and hydrogen consumption. However, on the high temperature side of the exothermic peak, because of the melting point aided by a slight liquefaction, it was noted that the coal particles melted and agglomerated. Because of this, the contact of coal and hydrogen became poor and the hydrogenation was terminated. As the temperature is raised higher, mesophase formation proceeds accompanied by dehydrogenation and the evolution of carbon dioxide. In the case where more than 3.3 g of  $\alpha-Al_2O_3$  is mixed in, from the results of DTA and microscopic observation together with analyses of the products, it was shown that hydrogen availability was in sufficient quantity.

#### 2. Reaction course of coal hydrogenation

In order to investigate the reaction course of coal hydrogenation, the temperature rise was terminated at 10 points of the exothermic peak and after cooling down to room temperature, the reaction products were analysed as shown in Fig. 3. These

exothermic peaks were measured under the conditions of an adequate hydrogen availability necessary for the coal hydrogenation reaction, produced by an addition 4 g of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>.

From these results, the following reaction course was derived.



#### References

- 1) Takeya,G., Ishii,T., Makino,K., and Ueda,S., J. Chem. Soc. Japan, Ind. Chem. Sect., 69, 1654 (1966)
- 2) Itho,H., Makino,K., Umeda,N., Takeya,G., and Ueda,S., J. Fuel Soc. Japan, 50, 919 (1971)
- 3) Ueda,S., Yokoyama,S., Ishii,T., Makino,K., and Takeya,G., Ind. Eng. Chem., Process Des. Dev., 14, 493 (1975)
- 4) Ishii,T., Sanada,U., and Takeya,G., J. Chem. Soc. Japan, Ind. Chem. Sect., 71, 1783 (1968)
- 5) Ueda,S., Yokoyama,S., Ishii,T., and Takeya,G., *ibid*, 74, 1377 (1971)
- 6) Ueda,S., Yokoyama,S., Nakata,Y., Hasegawa,Y., Maekawa,Y., Yoshida,Y., and Takeya,G., J. Fuel Soc. Japan, 53, 977 (1974)
- 7) Shibaoka,M., and Ueda,S., Fuel In Press

Table 1 Petrographic, Proximate and Ultimate Analyses of Sample Coals

Sample	Maceral analysis (%)				Proximate analysis (%)				Ultimate analysis (% d.a.f.)					
	Vitrinite	Exinite	Miorinite	Semi-fusinite	Fusinite	Moisture	Ash	Volatile matter	Fixed carbon	C	H	N	S	O
Bayswater, Vitrinite concentrate	99	0.5	0.5	tr	tr	3.4	1.6	32.9	62.1	83.0	5.3	2.0	0.5	9.2
Liddell, Vitrinite concentrate	99	0.5	tr	0.5	tr	7.3	0.7	31.6	60.4	84.0	5.3	1.8	0.6	8.3

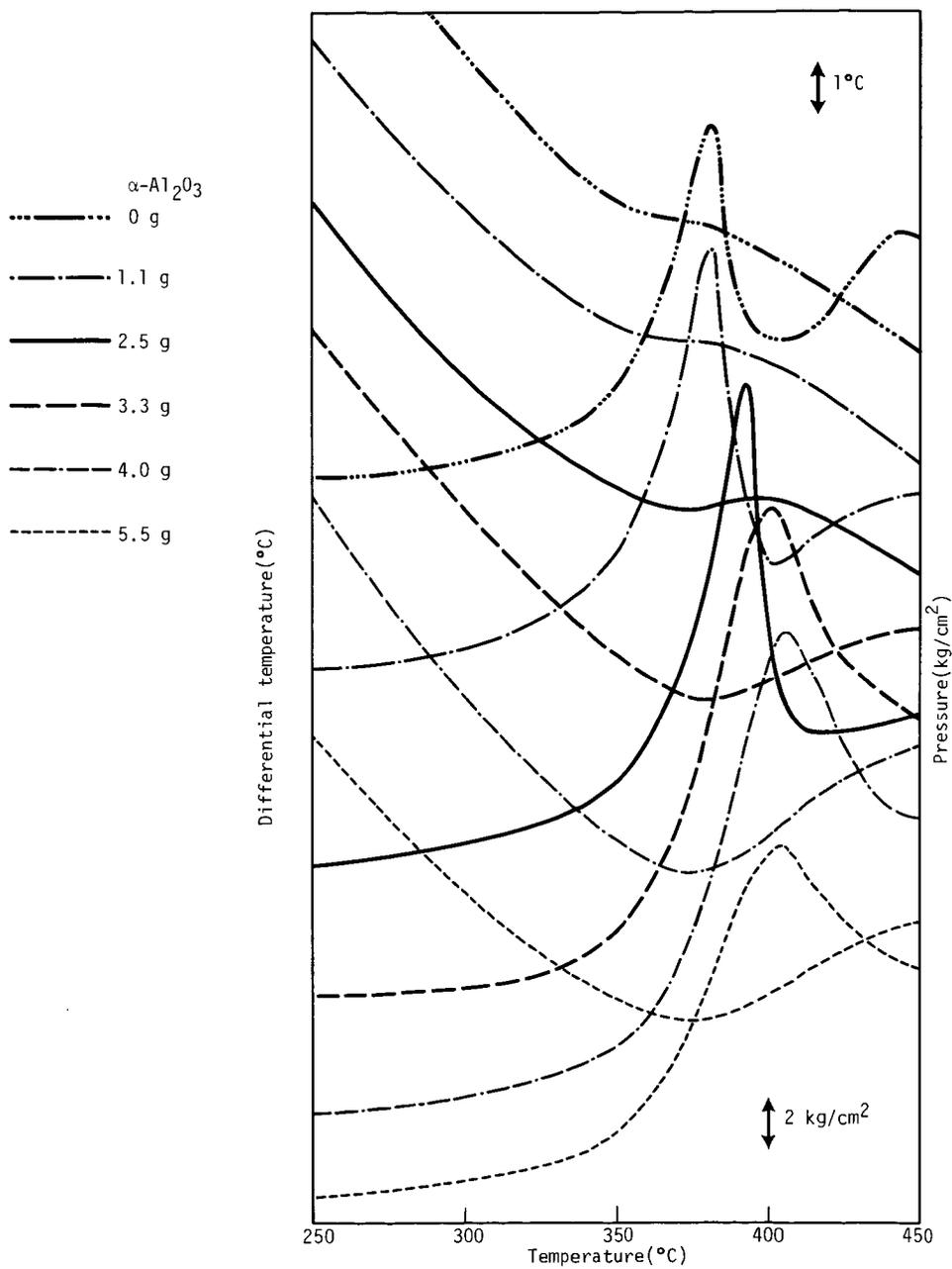


Fig. 1 DTA and pressure change curves in hydrogenation reaction of Bayswater seam coal

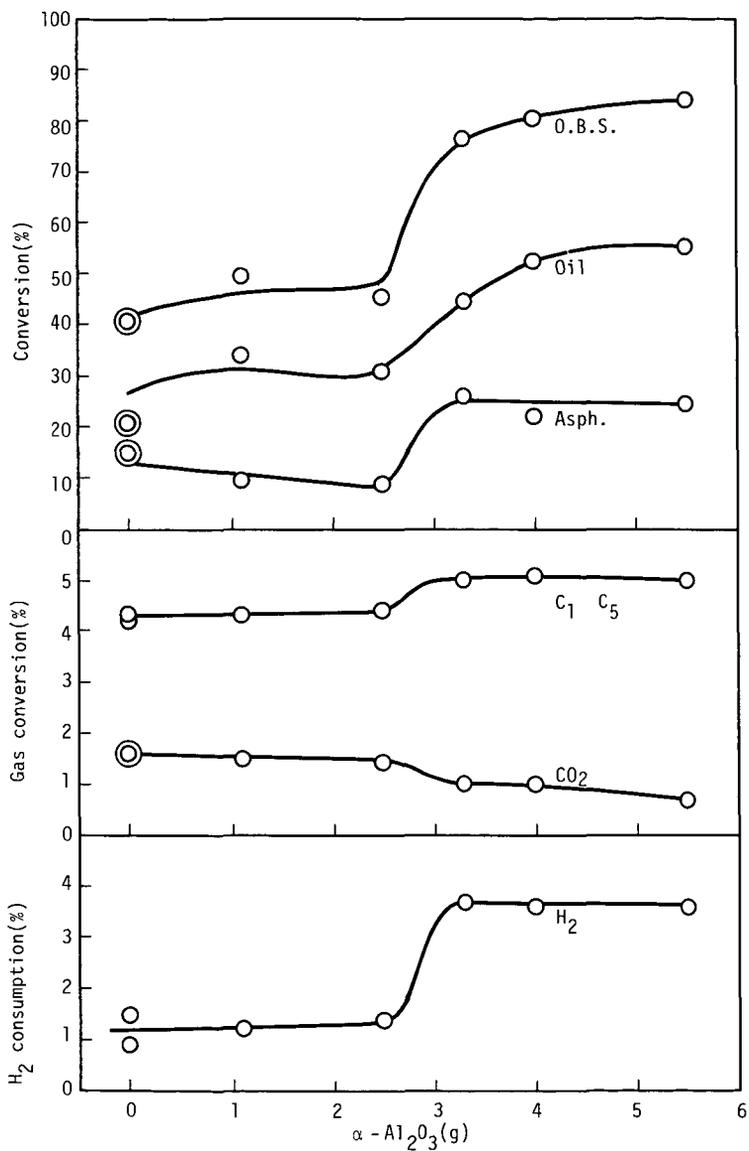


Fig. 2 Relationship between hydrogenation products and mixed  $\alpha\text{-Al}_2\text{O}_3$  for Bayswater seam coal

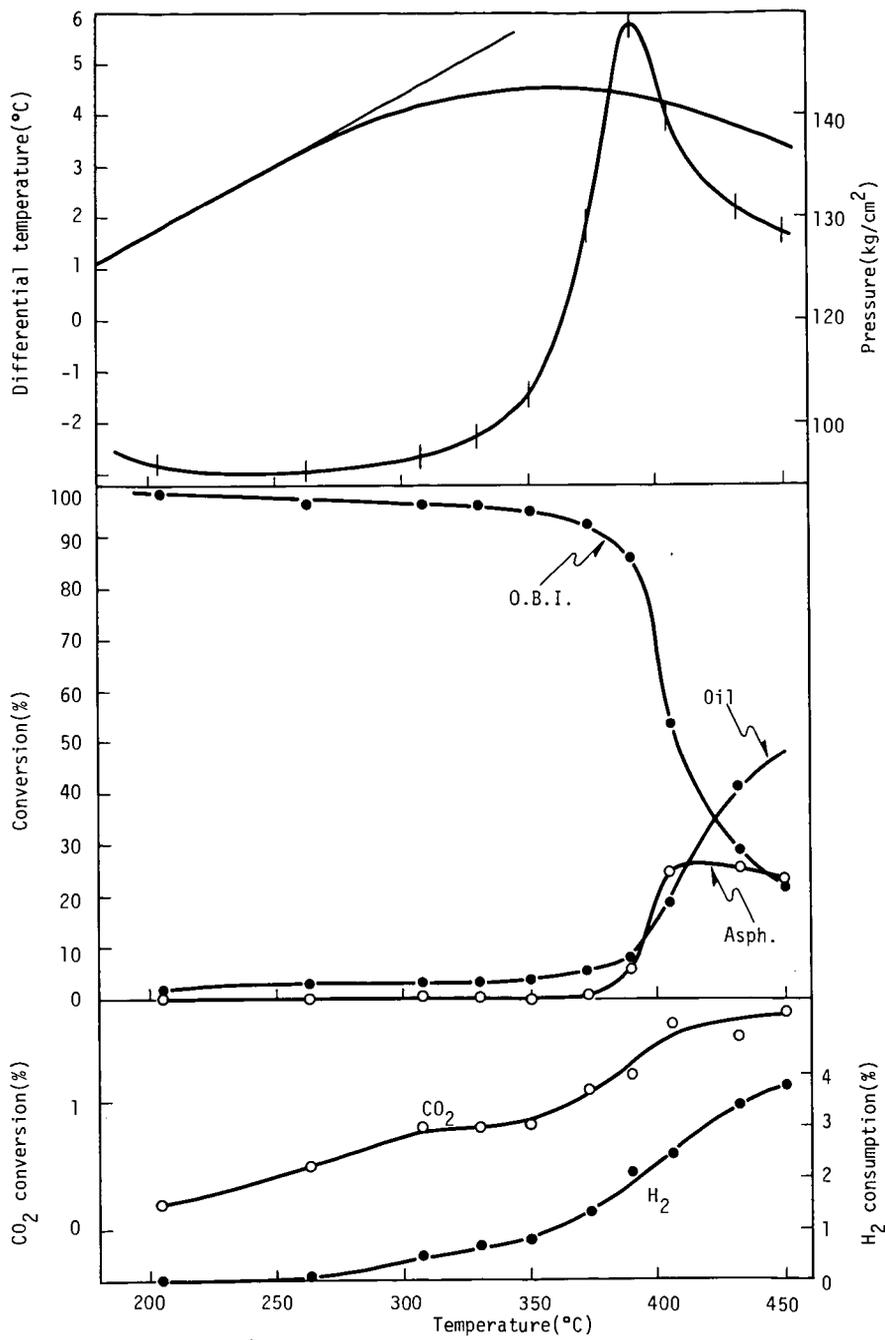


Fig. 3 DTA curve and products in hydrogenation reaction of Liddell seam coal