DIFFERENTIAL SCANNING CALORIMETRY STUDIES ON COAL HYDROGENATION

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INTRODUCTION

There is considerable interest in the production of high BTU gas by coal hydrogenation. The Hydrane process (1), recently developed by the U.S. Bureau of Mines, involves direct hydrogenation of raw coals. The present study on coal hydrogenation using the differential scanning calorimetry (DSC) approach is intended to provide some information on the reactivity of representative U.S. raw coals. Twenty U.S. raw coals of different rank have been selected for the present study, in which heats of reaction at 800 psig of hydrogen and temperatures up to 570°C have been measured. The effect of demineralization of coals upon heats of reaction has also been studied.

EXPERIMENTAL

A DuPont pressure DSC cell was used in conjunction with a cell base Module I and a 990 Thermal Analyzer to determine thermal effects involved during hydrogenation of coals. DSC scans for various coals (40x70 U.S. standard mesh) were obtained from 200 to 570°C at a linear heating rate of 5.4°C/min. Details of experimental procedure and calculations have been described elsewhere (2).

RESULTS AND DISCUSSION

Heats of hydrogenation of different coals, expressed as cal per unit weight of starting coal, are given in Table 1. Throughout the discussion which follows, carbon contents of coal are given on a dry-ash-free (daf) basis. The heat of hydrogenation ($-\Delta H$) increases, in general, with decrease in coal rank; the value varying from about 7 cal per gram, exothermic, for anthracite to about 150 cal per gram, exothermic, for lignites.

Weight losses at 570°C for various coals are included in Table 1. It is seen that weight loss decreases, in general, with increase in coal rank. However, in the case of PSOC 24, weight loss is far greater than that expected from its rank. Weight losses at 570°C for various coals are plotted against integral exothermic heats in Figure 1. It is seen that, except in the case of PSOC 24 and 95, data points for the rest of the coals fit on two straight lines of different slopes; the two lines intersect each other at a weight loss of about 45%. Considering the data in Table 1, it is seen that weight losses up to 45% are characteristic of coals with a carbon content greater than about 82%. For such coals, each one per cent of weight loss is seen to correspond to evolution of about 1.4 cal per gram weight of starting coal. This value increases to about 2 cal per gram for coals with carbon contents less than 82%.

The higher weight loss observed in the case of PSOC 24 may be due to the presence of a beneficial catalytic impurity. Out of all the samples investigated, PSOC 24 has the highest pyritic sulphur content (4.95%, daf); this may be responsible for its enhanced reactivity. However, in the case of PSOC 290 which has a pyritic sulphur content of 3.18% (daf), weight loss corresponds to that expected on the basis of its rank. DSC and TGA runs on the two coals were also made after partial removal of pyrite by a flotation technique using a halogenated hydrocarbon of density 2.85 g/cc. Following partial removal of pyrite, both coals exhibit a significant decrease in weight loss as well as exothermic heat (Table 2). These results suggest that pyrite or its reduction products, namely pyrrhotite or iron, catalyze hydrogenation.

Transition temperatures, that is the temperatures corresponding to the onset of the exotherms, are plotted as a function of carbon content in Figure 2. The transition temperature is strongly rank dependent, varying from about 230-250°C for lignites to about 535°C for anthracite. The plot in Figure 2 consists of four distinct parts. Coals associated with 63-75% carbon have about the same transition temperature. A sharp increase in transition temperature (about 200°C) occurs in 75-80% carbon range. Thereafter, up to about 90% carbon, the transition temperature increases only slightly. A further increase in transition temperature occurs beyond 90% carbon. It is noteworthy that variation of transition temperature with carbon content follows essentially the same trend as variation of average layer diameter and number of atoms per layer with carbon content (3).

The effect of demineralization on transition temperatures and exothermic heats for eight coals is illustrated by data in Table 1. It is seen that in the case of coals with carbon content less than 80%, demineralization increases the transition temperature and decreases the exothermic heat of reaction. This behavior again suggests that mineral matter associated with such coals catalyzes hydrogenation. However, in the case of coals with carbon contents greater than about 80%, removal of mineral matter decreases the transition temperature and increases the heat of hydrogenation. This is probably due to the fact that in such coals mineral matter removal opens up new feeder pores, thus increasing the accessibility of hydrogen into the pore structure. The development of additional porosity and enhanced accessibility to active sites more than offsets a decrease in reactivity which might result from the removal of catalytically active mineral matter. This is consistent with previous studies on the reactivity of coal chars with air (4). That is, mineral matter removal from lignites decreased gasification rates whereas mineral matter removal from an LV bituminous coal increased gasification rates.

ACKNOWLEDGEMENTS

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TABLE 1

HEATS OF HYDROGENATION

PSOC Sample No.	ASTM Rank	State	Coal analysis, % Ash (dry)	VM (daf)	C (daf)	Wt Loss at 570°C % (daf)	$-\Delta H$, cal/g (daf) Raw	Demin	Transition Temp. °C Raw	Demin
85	Anthracite	Pa.	8.3	7.7	91.3	8.7	6.9	-	536	-
130	MV	W.Va.	6.4	23.0	90.6	24.7	48.0	-	450	-
127	LV	Pa.	5.7	20.6	89.6	24.3	36.4	42.5	478	457
135	MV	Ala.	5.0	24.9	88.4	26.8	30.9	41.7	487	462
137	MV	Ala.	7.1	26.4	86.9	34.4	37.3	-	468	-
4	HVA	Ky.	2.1	38.3	83.8	40.3	57.4	-	446	-
95	HVA	Wash.	21.1	42.1	81.6	46.9	37.1	63.9	468	455
24	HVB	Ill.	11.8	41.9	80.1	73.6	66.2	52.7	340	445
290	HVB	Ill.	13.9	47.2	79.7	53.2	68.2	-	412	-
197	HVC	Ohio	12.4	42.0	78.9	50.4	79.7	-	315	-
151	HVC	N.M.	5.1	45.7	77.8	55.3	85.6	-	421	-
22	HVC	Ill.	10.1	42.8	78.8	55.4	83.8	59.6	324	431
190	Sbb-B	Ill.	8.5	41.5	75.6	59.3	111.5	51.5	285	457
97	Sbb-A	Wyo.	9.8	54.4	75.0	57.1	94.6	-	343	-
138	Lignite	Tex.	10.3	47.1	74.3	66.7	120.6	89.2	230	363
100	Sbb-C	Wyo.	5.0	60.7	72.1	57.0	125.7	-	232	-
93	Lignite	Mon.	10.7	51.6	71.9	56.6	122.2	-	266	-
141	Lignite	Tex.	9.0	49.2	71.7	66.1	120.4	-	246	-
87	Lignite	N.D.	8.2	54.2	71.2	70.8	151.6	123.1	232	272
89	Lignite	N.D.	11.6	57.3	63.3	74.5	153.1	-	256	-

TABLE 2

EFFECT OF PYRITE REMOVAL ON EXOTHERMIC HEAT AND WEIGHT LOSS DURING HYDROGENATION

PSOC Sample No.	Pyritic S % (dry)	Wt Loss at 570°C % (daf)	$-\Delta H$ cal/g (daf)
24	4.95	73.6	66.2
24 (d < 2.85g/cc)	3.56	56.7	61.8
290	3.18	53.2	68.2
290 (d < 2.85 g/cc)	1.87	47.0	40.7

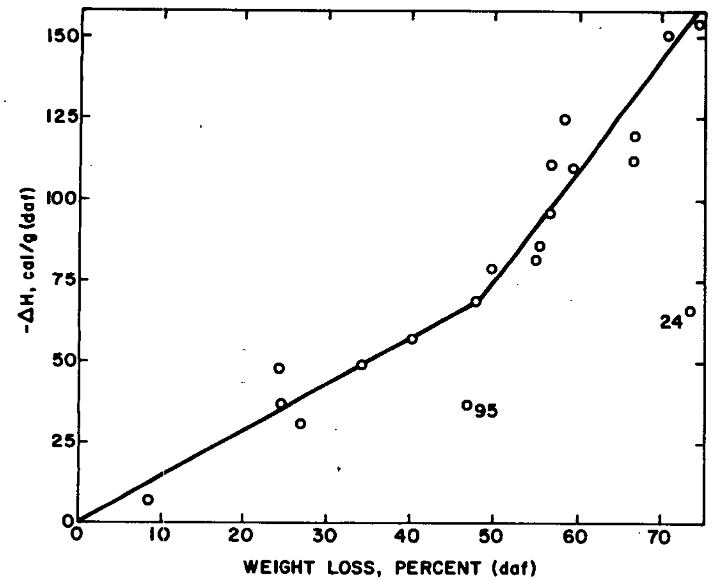

Figure 1 Exothermic Heat in Relation to Weight Loss During Hydrogenation.

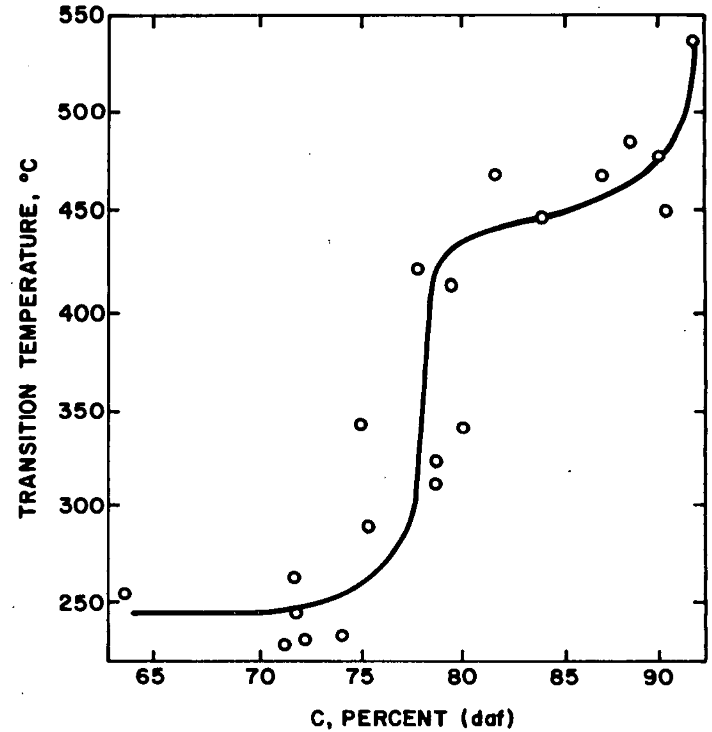

Figure 2 Transition Temperature in Relation to Carbon Content of Coals.