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Differential scanning calorimetry studies on coal. 2. Hydrogenation of coals

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Results of exothermic heats involved during hydrogenation of twenty U.S. raw coals of varying rank at 5.6 MPa (gauge) and temperatures up to 570°C are reported. The heat evolved during hydrogenation up to 570°C decreases with increase in coal rank. A part of the total heat released during hydrogenation of coals appears to be due to the exothermic reaction between H₂ and surface carbon-oxygen complexes removed during the reaction. The transition temperature, that is the temperature corresponding to the onset of exotherms, is markedly dependent on coal rank. A sharp increase in the transition temperature occurs for coals having a carbon content, on a dry-ash-free basis, in the 75–80% range. Demineralization of coals lower in rank than HVA bituminous decreases the heat of hydrogenation; in the case of higher-rank coals, exothermic heats increase upon demineralization. The presence of pyrite has a beneficial catalytic effect on coal hydrogenation.

There is considerable interest in the production of high-CV gas by coal hydrogenation. Perusal of the literature shows that most of the work on coal hydrogenation deals with coal chars, probably because of a need for pretreatment of raw coals to avoid agglomeration in most hydrogasifiers¹. However, pretreatment also represents a substantial loss of the very reactive volatile matter in coal². Hydrogenation data of Feldkirchner and Linden³ on three coal samples of lignite, bituminous coal and anthracite indicate that hydrogenation rates in the initial high-rate period are proportional to the standard volatile matter of coals. Other workers^{4,5} have also observed that the presence of volatile matter enhances hydrogasification rates. The Hydrane process⁶, recently developed by the U.S. Bureau of Mines, involves direct hydrogenation of raw coals.

The present study on coal hydrogenation uses a pressure-differential-scanning-calorimeter (DSC) approach. This approach, reported on earlier for quantitative evaluation of thermal effects involved during pyrolysis of coals in helium⁷, is intended to provide information on the reactivity of representative U.S. raw coals. It would be desirable to know if the amount of heat released during the hydrogenation reaction can be used as a relative measure of reactivity of coals during their hydrogasification or liquefaction under hydrogen pressure. Furthermore, information on the heats generated during the reaction can be useful in designing reactors for coal conversion processes.

Twenty U.S. raw coals of different rank have been selected for the present study. Heats of reaction with hydrogen at 5.6 MPa and temperatures up to 570°C have been measured. The effect of demineralization of coals upon heats of reaction has also been studied.

EXPERIMENTAL

Operating procedure

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. The experimental procedure followed was essentially the same as used in previous pyrolysis studies⁷. DSC scans for various coals (40 × 70 U.S. standard mesh) were obtained from 200 to 570°C at a constant heating rate of 5.4°C/min. Lower starting temperatures could not be used for the following reason. The cell temperature is controlled by a Platinel II thermocouple which chemisorbs hydrogen even at ambient temperature. This affects both temperature calibration as well as the heating rates. For instance, for a starting heating rate of 5°C/min, that is the heating rate indicated on the control panel of the 990 Thermal Analyzer, a rectilinear heating rate of 5.4°C/min was observed from 200 to 570°C. Since when correcting the DSC output curves for weight losses occurring during coal hydrogenation it is imperative to use a constant heating rate over the entire temperature range⁷, quantitative thermal effects could only be evaluated in the temperature range 200–570°C.

It was ascertained, in a few preliminary experiments, that for the amounts used in the DSC runs there were no significant temperature gradients within the coal samples over the temperature range studied. This was determined by spreading a mixture of small amounts (about 2 mg each) of indium, tin and zinc in the form of a thin layer on the sample pan and determining their melting points during a given scan. Melting points were determined under identical experimental conditions for approximately the same amounts of the three metals spread on top of 20 mg of a coal previously heat treated in N₂ at 1000°C. The melting point for each metal in the two sets of experiments agreed with each other within ±2°C.

Heats of reaction using the DSC technique were calculated from the following equation:

$$\Delta H = \frac{ABE\zeta}{m}$$

where ΔH = heat of reaction (mJ/mg); A = area of the exo-

therm or endotherm (mm^2); m = sample mass (mg); B = time-base setting (s/mm); E = cell calibration coefficient at a given temperature (dimensionless); and ζ = y-axis sensitivity [(mJ/s)/mm]. The calibration coefficient at different temperatures was determined in the manner described previously⁷. E increased monotonically from 2.10 at 200°C to 3.36 at 570°C.

In order to evaluate quantitatively the thermal effects involved during hydrogenation of coals, it is essential to correct the DSC output curves for weight losses occurring at different temperatures⁷. Weight losses under conditions simulating those in the DSC runs were determined by using a DuPont TGA unit in conjunction with a 990 Thermal Analyzer. Details of the experimental procedure have been described elsewhere⁷. A platinum bucket was used to contain the coal samples. It was ascertained in a few

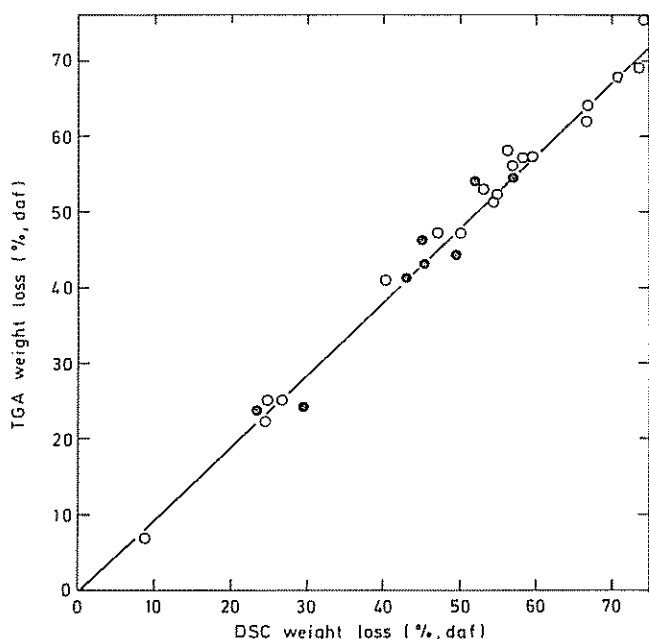


Figure 1 Relation between weight loss in DSC and TGA runs for raw and demineralized coals. Solid points denote demineralized samples

preliminary experiments that the use of a quartz bucket for a given coal gave essentially the same weight loss at different temperatures as the use of a platinum bucket. This indicates that the platinum bucket did not catalyse the coal hydrogenation reaction. The effect of starting-sample weight on weight losses at different temperatures revealed that for the starting-sample weights used in the present study there was little or no resistance to hydrogen diffusion down through the bed. The excellent agreement observed (Figure 1) for the cumulative weight loss up to 570°C obtained from the TGA and DSC runs in the case of twenty raw and eight demineralized coals lends support to the accuracy of the TGA results.

In our previous DSC studies on coal pyrolysis in the temperature range 100–580°C, base lines were determined individually on the residual coal chars following completion of the scan at 580°C⁷. A subsequent scan on the residual char between 100 and 580°C did not exhibit any additional thermal effects and was used as the base line. However, following hydrogenation at 570°C, the residual char was still reactive so that during a subsequent scan additional exothermic effects were observed. In the present study we have used the base line obtained for a graphitized carbon black Sterling MT, which is an ultra-clean carbon devoid of essentially all volatile and mineral matter, as the reference base line for all the coal samples. We believe that this choice of reference base line does not introduce any significant error in the values of ΔH . This is so because in our pyrolysis studies we observed that base lines obtained for Sterling MT and various coal samples were essentially the same above 200°C.

The DSC output curves for the various samples were corrected for weight changes occurring at different temperatures in the manner described earlier⁷.

Coals studied

Table 1 presents ultimate and proximate analyses of the coals studied. The sulphur contents of coals represent on the organic sulphur, that is sulphur bound in the coal matrix, and does not include pyritic and sulphatic sulphur. Volume percentages of vitrinites in the coals, as estimated

Table 1 Analysis of coals

PSOC Sample No.	ASTM rank	State	Proximate analyses (wt %)			Ultimate analyses (wt %, daf)					Vitrinite content (vol.%, mmf)
			Ash (dry)	Fixed C (daf)	VM (daf)	C	H	N	S	O (by diff.)	
85	Anthracite	Pa.	8.3	92.3	7.7	91.3	3.9	0.60	0.83	3.4	97.5
130	MV	W.Va.	6.4	77.0	23.0	90.6	4.3	1.1	0.51	3.5	72.7
127	LV	Pa.	5.7	79.4	20.6	89.6	5.0	1.0	0.52	3.9	77.7
135	MV	Ala.	5.0	75.2	24.9	88.4	4.9	0.25	0.59	5.8	83.1
137	MV	Ala.	7.1	73.6	26.4	86.9	4.8	1.5	0.81	5.9	73.8
4	HVA	Ky.	2.1	61.7	38.3	83.8	5.8	1.6	0.66	8.2	55.1
95	HVA	Wash.	21.1	57.9	42.1	81.6	6.1	1.1	0.95	10.3	79.3
290	HVB	Ill.	13.9	52.8	47.2	79.7	5.4	1.4	2.3	11.3	82.5
197	HVC	Ohio	12.4	58.0	42.0	78.9	5.3	1.7	0.63	13.5	79.7
22	HVC	Ill.	10.1	57.2	42.8	78.8	5.8	1.6	1.8	12.1	88.4
151	HVC	N.M.	5.1	54.3	45.7	77.8	5.8	1.2	0.42	14.7	78.6
26	HVC	Ill.	10.8	54.6	48.5	77.3	5.6	1.1	2.3	13.6	82.7
190	Sbb-B	Ill.	8.5	58.5	41.5	75.6	5.3	1.1	2.1	15.9	84.1
97	Sbb-A	Wyo.	9.8	45.6	54.4	75.0	5.5	0.58	0.93	18.0	80.3
138	Lignite	Tex.	10.3	52.9	47.1	74.3	5.0	0.37	0.51	19.8	75.1
100	Sbb-C	Wyo.	5.0	39.3	60.7	72.1	5.3	0.81	0.34	21.5	64.7
93	Lignite	Mont.	10.7	48.4	51.6	71.9	4.6	0.78	0.24	22.5	49.9
141	Lignite	Tex.	9.0	50.9	49.2	71.7	5.2	1.4	0.74	21.0	74.0
87	Lignite	N.D.	8.2	45.8	54.2	71.2	5.3	0.56	0.46	22.5	84.2
89	Lignite	N.D.	11.6	42.7	57.3	63.3	4.7	0.48	0.98	30.6	58.7

Table 2 Exothermic heats and transition temperatures^a for various coals

PSOC Sample No.	-ΔH (J/g, daf)		Transition temp. (°C)	
	Raw	Demineralized	Raw	Demineralized
85	28.8	—	536	—
130	200.6	—	450	—
127	152.2	177.7	478	457
135	129.2	174.3	487	462
137	155.9	—	468	—
4	239.9	—	446	—
95	155.1	267.1	468	455
290	285.1	—	412	—
197	333.1	—	315	—
22	350.3	249.1	324	431
151	357.8	—	421	—
26	276.7	217.4	340	445
190	466.1	215.3	285	457
97	395.4	—	343	—
138	504.1	372.9	230	363
100	525.4	—	232	—
93	510.8	—	266	—
141	503.3	—	246	—
87	633.7	514.6	232	272
89	639.9	—	256	—

^a Temperatures corresponding to the onset of the exotherms

by reflectance measurements, are also listed in Table 1. With the exception of coals PSOC-4, 100, 93 and 89, the remainder of the coals have vitrinite contents in excess of 70%.

Eight coals were demineralized using a hydrochloric acid/hydrofluoric acid mixture following which the samples were washed free of chloride ions and finally dried.

RESULTS AND DISCUSSION

Heats of hydrogenation of coals can be expressed either per unit weight of starting coal or per unit weight of coal left unreacted at a given temperature. In the discussion of results which follows, we have considered, for reasons discussed elsewhere⁷, values of ΔH expressed per gram weight of starting coal. Throughout the discussion, the carbon content of coal has been considered on a dry-ash-free (daf) basis.

Effect of coal rank

Exothermic heats of hydrogenation for various coals are given in Table 2 and are seen to vary from about 29 J/g for anthracite to about 640 J/g for lignites. When exothermic heats for various coals are plotted as a function of carbon content (Figure 2), it is seen that the heats decrease, in general, with increase in coal rank.

It is of interest to compare the thermal effects involved during pyrolysis in helium and hydrogenation of coals of different rank. During pyrolysis, endothermic heats were observed for practically all coals; sub-bituminous and lignitic coals exhibited some exothermic effects as well⁷. During hydrogenation, most of the coals gave exothermic effects only. Small endothermic heats (<8 J/g) were observed for lignites at temperatures less than 230°C. In addition, two other coals, PSOC-26 and 290, also showed endothermic effects. The former gave an endothermic effect (31.4 J/g) in the temperature range 200–300°C, while the latter exhibited a slight endothermic effect (8 J/g) in the range 300–400°C.

It has been suggested⁸ that overall hydrogasification occurs in three independent consecutive stages: devolatilization, rapid rate methane formation, and low rate gasification. Since hydrogenation of coals is essentially exothermic in nature, it is difficult to conceive that devolatilization occurs as a separate and independent step. Because elimination of surface-oxygen groups occurs at lower temperatures in a hydrogen atmosphere than in vacuum or an inert atmosphere^{5,9}, it is more likely that devolatilization and exothermic hydrogenation reactions occur simultaneously, as suggested by Feldkirchner and Linden³, and that the exothermic heats more than offset the endothermic heats involved during release of volatile matter.

Cumulative weight losses at 570°C for various coals are plotted as a function of carbon content in Figure 3. It is seen that weight loss decreases, in general, with increase in coal rank. However, in the case of PSOC-26, weight loss is far greater than that expected from its rank.

When cumulative weight losses at 570°C for various coals are plotted against integral exothermic heats (Figure 4) it is seen that, except in the case of PSOC-26 and PSOC-95, data points for the remainder of the coals fit on two straight lines of different slopes. The two straight lines intersect each other at a weight loss of about 47%. Examination of Figure 3 shows that weight losses up to 47% are characteristic of coals with carbon contents greater than about 82%. For such coals, a weight loss of 1% is seen to correspond to a heat evolution of about 6 J/g of starting coal. This value increases to about 14 J/g for coals with carbon contents less than 82%. It is noteworthy that when oxygen contents of various coals are plotted against their carbon contents (Figure 5), two distinct straight lines are obtained which intersect each other at a carbon content of about 81%. The similarity in the shapes of the plots in Figures 4 and 5 suggests that at least a part of the total heat released during the hydrogenation of coals is due to the exothermic reaction between hydrogen and carbon-oxygen complexes evolved during the hydrogenation reaction giving

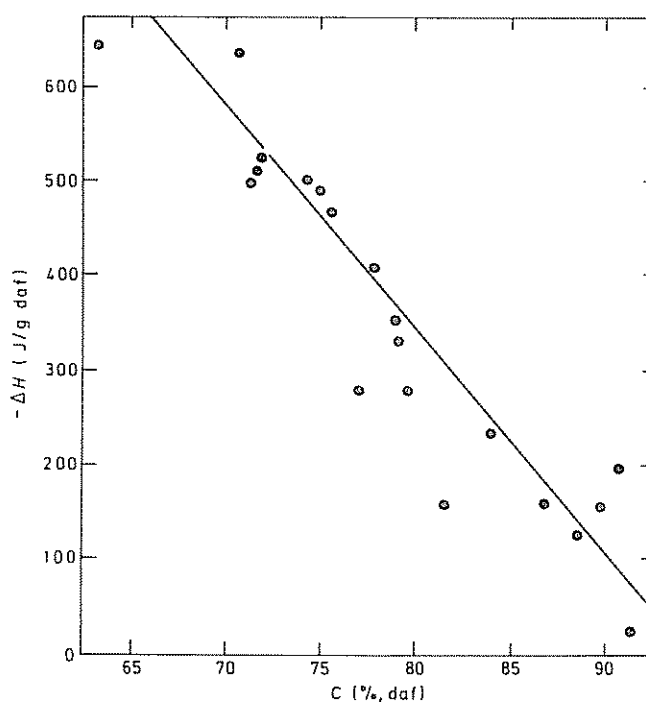


Figure 2 Exothermic heat of hydrogenation as a function of carbon content of raw coals

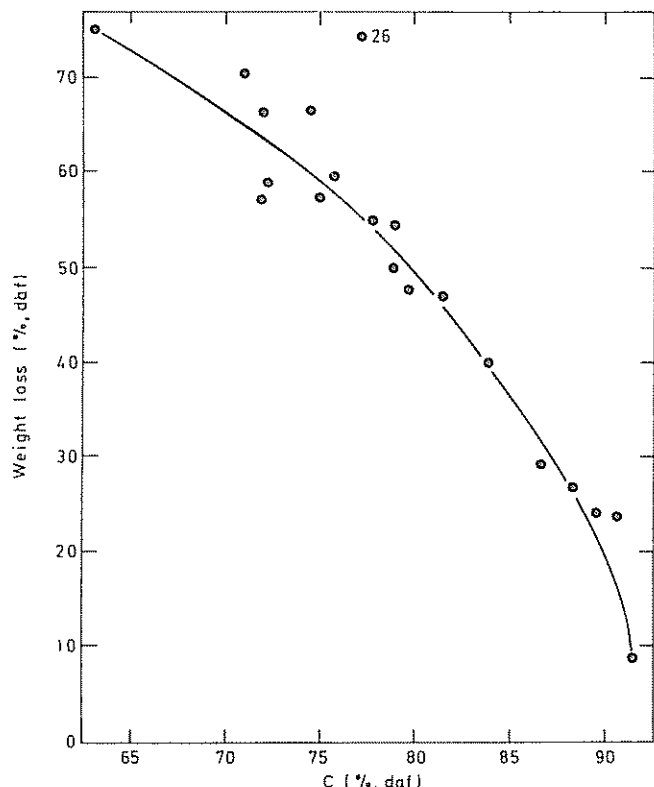


Figure 3 Weight loss during hydrogenation in relation to carbon content of raw coals

water and/or methane. The formation of methane by the methanation reaction (that is, $\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$) has previously been reported in the Hydrane process². In order that the heat released during the reaction between H_2 and carbon-oxygen complexes be measured by the DSC technique, it is essential that this reaction occurs within the sample pan. This is so because the DSC technique measures only the differential heat flow between the sample and reference pans. Any thermal changes occurring outside the sample pan cannot be measured by this technique.

Effect of pyrite removal

The higher weight loss in the case of PSOC-26 (Figure 3) may be due to the presence of a beneficial catalytic impurity. Of all the samples investigated, PSOC-26 has the highest pyritic sulphur content (4.9% on a dry basis) which may be responsible for its enhanced reactivity. However, when one considers results for PSOC-290 (pyritic sulphur content 3.2%), it is seen that the observed weight loss in this case corresponds to that expected on the basis of its rank (Figure 3). DSC and TGA runs on the two coals were also made after partial removal of pyrite by a flotation technique using Certigrav, a halogenated hydrocarbon of density 2.85 g/cm^3 . This treatment decreased the pyritic sulphur contents of PSOC-26 and 290 to 3.6 and 1.9%, respectively. It is unlikely that this treatment significantly alters the concentration of the remaining major mineral impurities. TGA curves showed that up to 400°C the two coals, after partial removal of pyrite, gave significantly more weight loss than the raw coals. This behaviour cannot be attributed to increase in porosity upon partial removal of pyrite because following demineralization by acid treatment PSOC-26 gave significantly less weight loss over the entire temperature range than the raw coal. It is more

likely that the observed behaviour is due to the desorption of Certigrav which might have been trapped within the capillary pores.

The observed weight losses at 570°C were corrected for the amounts of Certigrav desorbed on heat treatment. This was done in the following manner. For both PSOC-26 and 290 the difference in weight loss occurring during TGA runs on the two coals before and after partial removal of pyrite attained a constant value below temperatures at which the exothermic hydrogenation reaction commenced in the DSC runs. This constant weight difference was considered to be the total amount of Certigrav desorbed and was subtracted from the observed weight loss.

Considering the results in Table 3, it is seen that partial removal of pyrite decreases the exothermic heat and weight

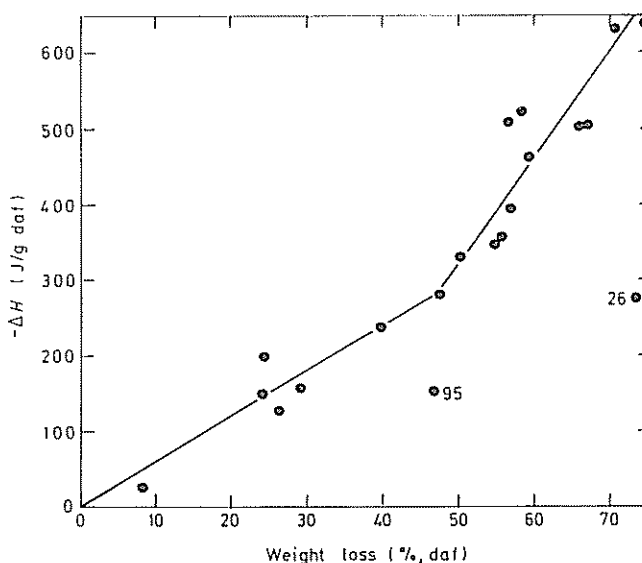


Figure 4 Exothermic heat in relation to weight loss during hydrogenation of raw coals

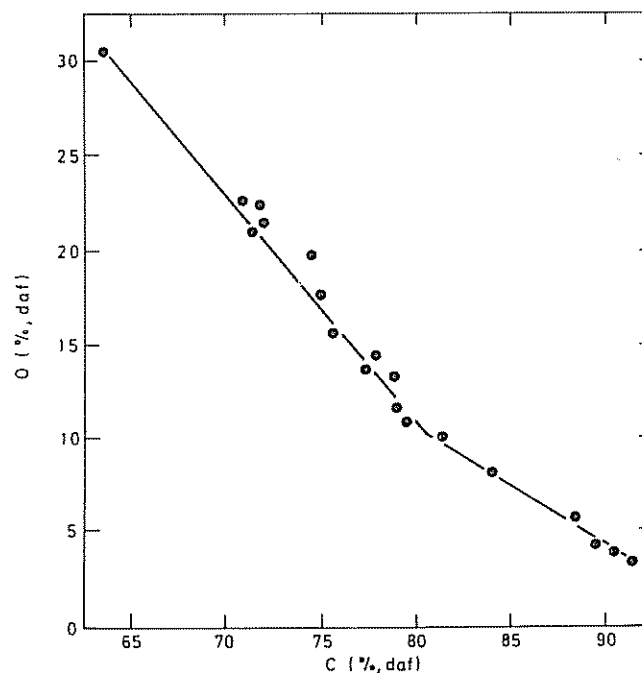


Figure 5 Oxygen contents of coals in relation to their carbon contents

Table 3 Effect of pyrite removal from coals by gravity separation on exothermic heat and weight loss during subsequent hydrogenation

PSOC Sample No.	Pyritic S (% dry basis)	Wt loss at 570°C (% daf)	$-\Delta H$ (J/g, daf)
26	4.9	73.6	276.7
26(d < 2.85 g/cm ³)	3.6	56.7	258.3
290	3.2	53.2	285.1
290(d < 2.85 g/cm ³)	1.9	47.0	170.1

loss upon subsequent hydrogenation of both coals. The decrease in weight loss is more pronounced for PSOC-26, while the decrease in $-\Delta H$ is more pronounced for PSOC-290. These results suggest that pyrite or its reduction product(s) catalyses coal hydrogenation. It has been suggested¹⁰ that during liquefaction of coal, pyrite is converted essentially completely to hexagonal pyrrhotite, $Fe_{1-x}S$ where $x = 0-0.15$. Defect structures may arise because of non-stoichiometric composition. It is well known that such structures can have exceptional catalytic activity. Iron also catalyses the hydrogasification of carbon¹¹. However, the reduction of pyrite to iron in hydrogen occurs only above 900°C¹². Therefore, the catalytic activity observed due to the presence of pyrite may be attributed to the formation of pyrrhotite. The authors realize that more coal samples rich in pyrite should be examined to establish unequivocally its beneficial catalytic effect on coal hydrogenation. The results of such an investigation will be reported in a subsequent publication.

Transition temperature

Transition temperatures, that is the temperatures corresponding to the onset of the exotherms, are plotted as a function of carbon content of the coals in Figure 6. The transition temperature is strongly rank dependent, varying from about 230–250°C in the case of lignites to about 535°C for anthracite. The plot in Figure 6 consists of four distinct parts. Coals containing 63–75% carbon have essentially the same transition temperature. A sharp increase in transition temperature (about 200°C) occurs in the 75–80% carbon range. Thereafter, up to 90% carbon, the transition temperature increases only slightly. A further sharp increase in the transition temperature occurs beyond 90% carbon. It is noteworthy that variation of the transition temperature with carbon content follows essentially the same trend as variation of average layer diameter and number of atoms per layer with carbon content¹³. This similarity suggests that the transition temperature is essentially a function of average layer diameter, that is the density of carbon sites (and oxygen complexes) at the edges of planar regions or crystallites.

Given *et al.*¹⁴ have studied the liquefaction behaviour of vitrinite-rich coals as a function of rank. They observed that higher-rank coals with carbon contents greater than 80% are poor precursors for liquefaction. From Figure 6 it is not difficult to understand the reason. Transition temperatures for such coals are appreciably higher than those conventionally employed in coal liquefaction. Furthermore, since transition temperatures for lignitic and sub-bituminous coals are relatively very low, they could be liquefied at lower temperatures.

Effect of mineral matter removal

The effect of demineralization on transition temperatures and exothermic heats for eight coals is illustrated by data in Table 2. Considering the transition temperatures, it is seen that in the case of coals with carbon contents less than 80%, demineralization increases the transition temperature. This behaviour indicates that inorganic impurities associated with these coals catalyse their hydrogenation. It is noteworthy that in such coals the removal of inorganic impurities can increase the transition temperature by as much as 170°C. In the case of coals with carbon contents greater than 80%, transition temperatures decrease slightly upon demineralization. In such cases, it is suggested that the presence of mineral matter blocks some of the pores with the result that the entire mineral matter does not partake in catalysis and/or total area within the pores is not accessible for the reaction, as will be discussed shortly.

The results presented above elucidate the importance of mineral matter (some inorganic impurities) in catalysing the hydrogenation reaction, particularly for coals of rank lower than HVA bituminous. In the future, economic considerations could necessitate the development of improved catalysts which could decrease the required reaction temperature in various coal conversion processes. On the basis of results presented in this paper, the authors feel that DSC affords a simple experimental technique for evaluation of such catalysts.

When exothermic heats of hydrogenation for various coal samples before and after demineralization are considered (Table 2), it is seen that in the case of PSOC-127, 135 and 95 demineralization increases the heat of the reaction. This effect is most pronounced in the case of PSOC-95 where $-\Delta H$ increases from 155.1 to 267.1 J/g. Incidentally, this coal is associated with a maximum amount of mineral matter (cf. Table 1). The removal of mineral matter in the case of coals lower in rank than HVA bituminous decreases heats of the hydrogenation reaction.

It appears rather baffling that in the case of higher-rank coals mineral matter removal decreases the transition tem-

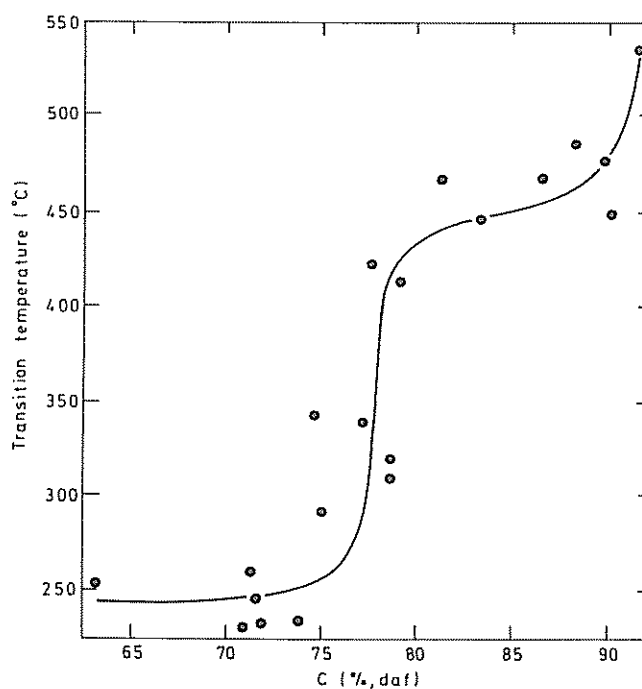


Figure 6 Transition temperatures for onset of exothermic heat in relation to carbon content of raw coals

perature and increases the magnitude of exothermic heats. In order to have higher gasification rates, it is desirable to have a large specific area of coal located in small pores but it is also important to have these micropores adequately connected to large voids so that reactant molecules can diffuse rapidly to the large internal area and reactive sites. In this context, it is known that if a coal char lacks macro or transitional porosity, that is large voids or 'feeder' pores, gasification rates in air and CO₂ are low^{15,16}. Gan *et al.*¹⁷ have shown that for coals with carbon contents greater than 80% or less than 70%, even though total surface area as measured by CO₂ adsorption is appreciable (150–400 m²/g), nitrogen surface area, which is a measure of transitional and macroporosity, is usually less than 1 m²/g. Nitrogen surface area is appreciable only for coals in the 75–80% carbon range. In the present study, any change in porosity and surface area will be the resultant of changes brought about by simple heat treatment as well as by hydrogasification. It has been reported¹⁵ that upon heat treatment up to 600°C, nitrogen surface area of coals with carbon contents less than 70% increases appreciably from an original value of 1 m²/g or less to as high as 100 m²/g. However, in the case of coals with carbon contents greater than 80% there is little or no increase in nitrogen surface area. The lower transition temperatures and higher exothermic heats for higher-rank demineralized coals suggest that in such coals mineral matter removal opens up the previously blocked feeder pores thus increasing the ease of accessibility of hydrogen into the pore structure. Apparently the development of additional porosity more than offsets any decrease in reactivity which might result from the removal of catalytically active mineral matter.

The fact that the removal of mineral matter has a different effect on the heat of hydrogenation of lower- and higher-rank coals may be due, apart from differences in their porosities referred to above, to another reason. The lower-rank coals are associated with surface carboxylic acid groups. Their concentration is a maximum in lignites and decreases with increasing carbon content till at about 83% carbon such groups essentially disappear¹⁸. Furthermore, in coals with carbon contents in the 65–80% range the hydroxyl oxygen content is essentially constant and is significantly higher than that in the higher-rank coals. That is, hydroxyl content decreases sharply in the 81–89% carbon range¹⁸. The hydroxyl groups are predominantly phenolic or at least acidic in nature. It is possible that hydrogen ions of the acidic functional groups in coals may have been exchanged, at least in part, for other cations such as Na⁺, K⁺, Ca⁺⁺, etc. as a result of extended contact of embedded coals with water containing different cations. Johnson¹⁹ has recently shown that the replacement of H⁺ ions of surface carboxyl groups in lignites by Ca⁺⁺ and Na⁺ ions appreciably increases hydrogasification rates. It is suggested that following decomposition of carboxylic and hydroxyl oxygen groups during hydrogenation of coals, the cations are converted to metals or oxides which are dispersed on the coal surface in the form of very fine particles.

In this context, it is known²⁰ that when supported metal catalysts are prepared by exchanging H⁺ ions in the surface acidic groups of the support with metal cations, the particle size of supported metals is very small. It is well known²¹ that the extent to which an impurity in carbonaceous solids is an active catalyst during gasification depends not only upon its amount and chemical form (that is, a metal, an oxide, etc.) but on its extent of dispersion (its particle size). The greater the degree of dispersion for a given amount of

the catalyst, the greater is its specific catalytic activity. From the foregoing discussion, it is suggested that because of a higher concentration of surface carboxyl and hydroxyl groups and, hence, of exchangeable cations in lower-rank coals, the decrease in the extent of hydrogasification and heat of hydrogenation upon removal of exchangeable cations by acid treatment will be more pronounced in such coals. Since higher-rank coals with carbon contents greater than about 80% are essentially devoid of acidic functional groups and, hence, of exchangeable cations, the decrease in heat of hydrogenation upon acid treatment will be minimal. Any decrease in heat of hydrogenation which might result from removal of exchangeable cations from higher-rank coals is more than offset by an increase in porosity as suggested earlier.

At this stage, it is instructive to emphasize that in addition to catalytic activity associated with exchangeable cations in the manner mentioned above, other inorganic impurities present in coals may also catalyse coal hydrogenation. In coals, there are two broad classes of inorganic impurities — the discrete mineral matter and the minor and trace elements. The mineral matter is usually present in particles greater than about 1 μm in size. The major minerals are usually kaolinite, illite, pyrite, calcite and quartz. A number of other minerals in smaller amounts can be present. Minor and trace elements are more or less associated with the organic phase or mineral phase of the coal. The elements are dispersed on a much finer scale in the coal; and, hence, even though they are present in smaller amounts than the major minerals they may be important catalysts because of their small particle size.

It is noteworthy that the exothermic heat of hydrogenation for demineralized PSOC-87 is the highest for any of the demineralized samples and is of about the same magnitude as that for the raw coals, PSOC-138 through PSOC-141 in Table 2. We have no explanation for this behaviour although it is possible that the higher exothermic heat may be due to the presence of residual amounts of catalytically active impurities still left after demineralization.

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