

The Structure and Plastic Properties of Coals Following
Low-Temperature Catalytic Hydrogenation

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Abstract

Following earlier work, studies have been continued in examining the physical and chemical changes which occur in coals following low-temperature ($\leq 400^{\circ}\text{C}$) catalytic hydrogenation. Reactions were conducted with a series of coals ranging in rank from subbituminous to low volatile bituminous and using a dispersed Mo catalyst in the absence of solvent. With progressive hydrogenation, the yield of extractable liquids substantially increased for all coal samples except the low volatile bituminous coal. There were corresponding increases in the coal fluid properties. Low-temperature hydrogenation was also found to negate the adverse effects of air oxidation on coal fluid behavior.

Although hydrogenation improved coal fluidity, it essentially eradicated any swelling properties of the parent coal. Experiments using blends of hydrogenated coals and hydrogenated coal extracts with parent coals showed that dilatation could be greatly improved for a bituminous coal by the addition of hydrogenated bituminous coal extract. No other blends exhibited swelling properties. It is suggested that the phenomenon of swelling is due to a particular chemical interaction between the mobile liquids (indigenous or extraneous) and the chemical structure of the coal macromolecular network.

Introduction

It has been known for several decades that heating certain coals, at or near their softening point, may result in a several fold increase in the content of extractable liquids (1-8). Furthermore, it has been demonstrated that the fluid properties of the parent coals correlate with the yield of extractable liquids from the heat treated coals (most often when chloroform was used as the extracting solvent) and that both of these characteristics pass through a maximum in coals between 85 to 88% carbon content (5,6,9,10).

The effect of the low molecular weight, hydrogen-rich, chloroform-soluble material on the plastic behavior of coal has been explained by the hypothesis that the development of plasticity is a transient, in-situ, hydrogen-donor process (11). These lighter molecular weight substances not only play an essential role in plasticity development, but also are influential in coal liquefaction (12,13).

A decrease in the yield of extracts (14) and a significant decrease in plastic properties (14,15) can be effected by mild oxidation. Ignasiak et al. (16) have suggested that the incorporation of reactive oxygen groups (as phenolic, acidic, or ketolic oxygen) may act as the agents responsible for the formation of cross-linkages during the heating of the coal, leading to an overall reduction in the internal mobility of the coal molecules. Conversely, hydrogenation of oxidized or high oxygen content coals can result in the development of plastic properties (17-19).

In earlier reported research (13,20), which was directed towards deriving coal structural information through low-severity catalytic coal liquefaction in the

absence of solvent, it was found that, as the yield of extractable liquids increased, the coals became progressively more fluid. Further investigations have since been made of the relationship between the catalytically generated liquids and coal fluid properties for a series of coals of different rank. The findings are presented in this paper.

Experimental

1) Coal Properties and Preparation

The coals studied were obtained from the Pennsylvania State Coal Sample Bank and were selected to cover a range of rank from subbituminous to low volatile bituminous; each containing over 80% vitrinite. Properties of the coals are shown in Table 1.

The coals were ground to -20 mesh under conditions to minimize oxidation and were subsequently stored under nitrogen and used without drying. For catalytic hydrogenation experiments, the coals were impregnated with 1% wt (dmmf) Mo by slurring with an aqueous solution of ammonium tetrathiomolybdate. After slurring, the excess water was removed by drying under vacuum below 100°C.

A high fluidity coal (PSOC-1296) was chosen for studies to examine the effects of oxidation on plastic properties. The coal was oxidized under mild conditions by passing air through a bed of the finely ground coal (-40 mesh) at 50°C for four days.

2) Catalytic Hydrogenation

Hydrogenation reactions were conducted in tubing bomb reactors under an initial (cold) hydrogen pressure of 7 MPa and at temperatures between 250 and 400°C for times of 5 to 60 min. The yields of light gases were determined by volumetric measurement and gas chromatographic analysis.

In some cases, the reacted coals were extracted in chloroform, using a Soxhlet apparatus, to obtain a partition into soluble extract and residue. More detailed descriptions of the experimental procedures have been reported (13,20,21).

3) Analytical

The fluid properties of coals, hydrogenated coals and blends of coals with coal extracts were studied using an automated Gieseler plastometer, following the ASTM standard procedure (22), and a pressure microdilatometer. The latter was operated at a heating rate of 20°C min⁻¹ from ambient under 0.1 MPa of nitrogen.

Results and Discussion

The yields of gases and chloroform-soluble extract obtained upon catalytic hydrogenation of the coals for 60 min at 350 and 400°C are given in Table 2. Reaction at 350°C caused a significant increase in the yields of chloroform-soluble extract over that obtained from the parent coal, the greatest response being obtained with the subbituminous coal, PSOC-1403. This observation is consistent with reported data showing that, under these reaction conditions, low-rank coals were more reactive than bituminous coals (13). At 400°C, high extract yields were obtained with all of the coals except the low volatile bituminous coal, PSOC-1325. It is supposed that the structure of a coal at this stage of metamorphism contains such a high proportion of strong covalent bonds that it is difficult to break down into lower molecular weight species, even in the presence of an active catalyst.

Mild oxidative treatment of the hvA bituminous coal, PSOC-1296, reduced the yield of extractable liquids, a commonly observed phenomenon. However, the subsequent catalytic hydrogenation of this coal appeared to have more than counteracted the effects of oxidation.

The results of Gieseler plastometer measurements on catalytically hydrogenated and unextracted coals are shown in Figures 1(a) - (c). The effect of reaction time on the fluidity of an hvA coal can be seen in Figure 1(a). With increasing reaction time at 400°C, which corresponds to a progressive increase in the content of extractable liquids, the coal softening temperature was lowered and the maximum fluidity was increased. For times longer than 15 min, the maximum fluidity exceeded the measurable range of the instrument. Similarly, reaction for 60 min at 400°C introduced fluid behavior to subbituminous coals which, in their parent state, produced no response in the Gieseler plastometer, Figure 1(b).

In parallel with the measured effects of oxidation of the hvA bituminous coal in lowering the yield of chloroform-extractable liquids, the fluid properties were also suppressed, Figure 1(c). Catalytic hydrogenation of the oxidized coal was instrumental in increasing the fluidity above that of the original coal.

The development of fluidity in these coals, as measured by the Gieseler plastometer, is not to be confused with the swelling behavior shown by coking coals. Examination of the treated coals in the microdilatometer showed that, consistent with the Gieseler measurements, the coal softening temperature had been reduced. However, all of the samples underwent a volume contraction with increasing temperature, even those which had exhibited a net volume expansion or dilatation prior to treatment. These results were interpreted to mean that the catalytic hydrogenation had increased the coal fluidity to such an extent that, in the melted state, the viscosity was so reduced that volatile pyrolysis products could freely escape without causing the coal to swell. In effect, the volume contraction meant that, upon becoming fluid, the density of the coal sample had increased.

A number of experiments were then conducted, using a bituminous and a subbituminous coal (PSOC-1266 and PSOC-1403, respectively) to determine whether blending the hydrogenated products with untreated coals could influence swelling behavior. Mixtures of unextracted hydrogenated coals with the parent coal, in which the concentration of the former was increased up to 50% wt did not appreciably influence the swelling behavior of either coal, although, for the bituminous coal, there was a steady reduction in softening temperature with increasing concentration of the treated coal.

Blending the extract from the hydrogenated bituminous coal with the parent coal had a dramatic effect upon swelling properties, Table 3. This effect was not found with any other combination of the parent bituminous or subbituminous coal with either extract from the hydrogenated coals, although blending did reduce the initial softening temperature and increase the volume contraction in each case.

It is assumed that the extracts from the hydrogenated coals and in particular the bituminous coal will contain a reasonable proportion of hydroaromatic structures. The presence of H-donor compounds is thought to enhance the plastic behavior of coals (11). The results presented here suggest that the phenomenon of swelling is attributable to a particular combination of (possibly) H-donor properties of the mobile liquids within coals (and added liquids such as the extract from the hydrogenated bituminous coal) together with the structural configuration of the coal macromolecular network.

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TABLE 1

COAL PROPERTIES

Penn State Sample Bank Number	PSOC-1325	PSOC-1296	PSOC-1022	PSOC-1266	PSOC-1403	PSOC-1414
Seam	L. Kittanning	L. Kittanning	L. Kittanning	L. Kittanning	Anderson	Beulah-zap
County	Somerset	Armstrong	Lawrence	Mahoning	Campbell	Mercer
State	Pennsylvania	Pennsylvania	Pennsylvania	Ohio	Wyoming	N. Dakota
ASTM	LV	HVA	HVA	HVA	SUBBIT B	SUBBIT C
Mean-Maximum Reflectance of Vitrinite (R _{max} , %)	1.63	0.87	0.80	0.83	0.40	no data
Moisture Content (a.r., % wt)	1.2	1.1	3.8	3.4	17.8	25.4
Mineral Matter (dry, % wt)	13.5	20.3	17.2	6.1	11.9	10.8
Elemental Composition (% dmmf)						
Carbon	90.0	85.7	82.9	83.2	73.0	71.0
Hydrogen	5.0	5.5	5.7	5.0	4.5	6.6
Oxygen	2.8	5.8	7.7	8.6	20.4	21.1
Nitrogen	1.6	1.5	1.6	2.1	1.2	0.7
Organic Sulfur	0.6	1.4	0.6	0.5	0.9	0.6
Petrographic Composition (mineral-free, % vol)						
Vitrinite	96	88	81	91	87	83
Exinite	0	2	13	3	2	2
Inertinite	4	10	6	6	11	15

TABLE 2

YIELDS OF GASES AND CHLOROFORM-SOLUBLE EXTRACT (% dmfm) FROM CATALYTICALLY HYDROGENATED COALS
(1% wt Mo (dmfm); no solvent; 60 min reaction; 7 MPa cold H₂ pressure)

Coal	ASTM Rank	CHCl ₃ Extract for raw coal	Reaction Temperature (°C)					
			350			400		
			CHCl ₃ -solubles	CO _x	C ₁ -C ₄	CHCl ₃ solubles	CO _x	C ₁ -C ₄
PSOC-1325	lvB	0.6	12.9	0.2	0.4	12.8	0.1	0.7
PSOC-1266	hVA	0.9	8.8	0.2	0.0	59.1	0.3	0.8
PSOC-1022	hVA	2.5	13.3	0.7	0.3	54.3	1.8	1.5
PSOC-1296	hVA	5.0	--	-	-	49.6	0.5	0.8
PSOC-1403	Sub. B	4.3	33.4	7.2	0.8	52.3	12.4	4.0
PSOC-1414	Sub. C	2.3	--	-	-	37.0	17.2	4.1
*PSOC-1296	hVA	0.6	--	-	-	54.5	1.3	4.1

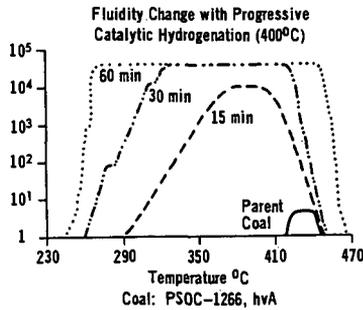
* Pre-oxidized coal

TABLE 3

DILATOMETRIC PARAMETERS FOR MIXTURES OF BITUMINOUS COAL (PSOC 1266)
WITH THE CHLOROFORM-SOLUBLE EXTRACT OF THE HYDROGENATED COAL

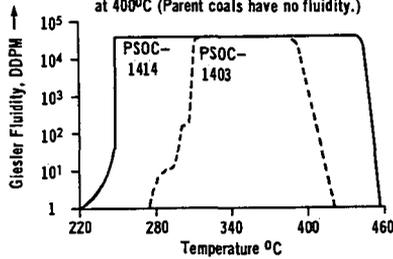
wt% hydrogenated extract in mixture	0	5	10	20
Softening temperature, °C	435	410	395	367
Temperature of maximum contraction, °C	477	460	450	435
Temperature of maximum expansion, °C	500	487	480	485
Resolidification temperature, °C	---	---	500	495
% maximum volume* contraction	21	24	21	26
% maximum volume* expansion (net)	23	52	129	349
% volume expansion* on resolidification (net)	---	---	80	349

* measured relative to original coal volume



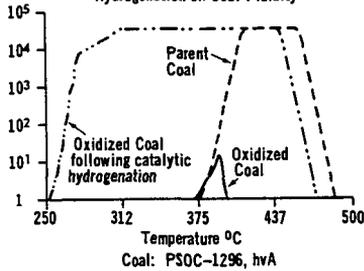
(a)

**Fluidity of Subbituminous Coals Catalytically Hydrogenated
at 400°C (Parent coals have no fluidity.)**



(b)

**Effects of Mild Oxidation and Subsequent Catalytic
Hydrogenation on Coal Fluidity**



(c)

**Figure 1. GIÉSELER PLASTOMETRY MEASUREMENTS OF HYDROGENATED
AND PARENT COALS.**