

A Study of Catalytic Coal Liquefaction in the Absence of Solvent

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Abstract

In attempting to gain insight into the reactions involved in coal liquefaction and their relationship to coal structure, an approach has been adopted in which coals are reacted only with hydrogen gas in the presence of an impregnated molybdenum catalyst. The products from reaction at 400°C and lower have been characterized in terms of the yields of light gases and chloroform-soluble extracts. The composition of the latter has been examined by a number of analytical techniques. The extent of conversion has been measured as a function of time and temperature. Unlike liquefaction in a solvent medium, conversion increases progressively with reaction time. Consistent with other research, the molybdenum should be present in the sulfided form for high activity. Following reaction, unextracted coal samples were examined by reflected fluorescent light microscopy. The vitrinite fluorescence was found to correlate with the yield of chloroform-soluble extract and, essentially, to originate from these materials. This microscopic technique provided a direct visual observation of the chemical changes taking place within the coal structure.

Introduction

Early propositions concerning the structure of coal¹⁻² have formed the basis for the development of a concept in which coal is considered as a three-dimensional macromolecular network containing lower molecular weight species (the so-called mobile phase) accommodated in open, closed or partially closed pores.³⁻⁴ We have initiated research to investigate this concept and have adopted an approach used by other workers in coal liquefaction studies. To avoid complications in data interpretation only dry coal, hydrogen and catalyst were changed to the reactor.⁵

In the present research, coal samples have been impregnated with molybdenum salts and reacted in tubing bombs at temperatures up to 400°C, the objective being to attempt to convert the macromolecular structure into a soluble form while minimizing condensation and cracking reactions.

Experimental

Catalytic Hydrogenation

Samples of a high-vitrinite hvAb coal from the Lower Kittanning seam were obtained undried as lumps 12 mm top size from the Penn State Coal Sample Bank (PSOC-1266). Properties of the coal are shown in Table 1. The coal was crushed in a glove box under oxygen-free nitrogen to 0.8 mm top size and a number of approximately 20 g representative splits were sealed in vials without drying.

The procedure for catalyst impregnation was to mix a sample of coal with the quantity of ammonium heptamolybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (supplied by courtesy of the Climax Molybdenum Co.) necessary to give the desired molybdenum loading, and sufficient deionized water to form a thick slurry. The mixture was stirred for 30 min at room temperature and the excess water was then removed in a vacuum desiccator overnight.

For some experiments, the ammonium molybdate solution was first converted to one of ammonium tetrathiomolybdate by bubbling through H_2S at room temperature. Impregnation with this salt should lead directly to the formation of MoS_2 which is considered to be the active form of the catalyst.

Hydrogenations were carried out in tubing bomb reactors. The gaseous products were analyzed by gas chromatography to determine the yields of CO , CO_2 , and C_1-C_4 hydrocarbons. The nongaseous reaction products were separated by Soxhlet extraction into chloroform-soluble and chloroform-insoluble fractions. The procedure has been described in detail elsewhere.

Fluorescence Microscopy

Samples of hydrogenated unextracted coals, the chloroform-soluble extracts and chloroform-insoluble residues were examined using spectral fluorescence photometry. Details of the sample preparation and the experimental arrangement have been described.

Results and Discussion

Product Yields

The yields of gaseous and chloroform-soluble products from dry catalytic hydrogenation at different temperatures are summarized in Table 2. The yield of chloroform-soluble extract from the unreacted coal was 2.0% dmmf. The mass balances were obtained from the differences between the combined yield of gas and liquids, calculated from the weight of insoluble residue, and the sum of the gas and extract yields determined experimentally. In considering the insoluble residue it was assumed that the molybdate salt had been converted to MoO_3 , although some of the molybdenum probably exists as MoS_2 .⁹ The potential error in conversion arising from this assumption is less than 1%. As the extract yield increases so does the mass balance deficit, suggesting that, at high extract yields, proportionately more low-boiling liquids are produced by reaction and lost during product work-up.

In all cases the gas yields were low, the maximum total being 2.38% dmmf coal. Carbon dioxide was detected in all reactions and its yield increased with reaction temperature. Methane was only found in detectable quantities at 400°C; higher hydrocarbons were not detected. Above about 350°C, under the conditions investigated, there was a sharp increase in extract yield, which was accompanied by a change in coal particle morphology; the particles lost their original shape and tended to form sticky agglomerates.

The extracts were characterized by elemental analysis, high resolution mass spectrometry, 1H n.m.r. and Fourier Transform Infrared Spectroscopy. Reaction in the presence of catalyst produced a higher concentration of mono-aromatic phenols than would otherwise be produced, suggesting that one of the catalyst functions involves ether cleavage. In general, however, no major compositional changes were observed as the yield increased from 2.0 to over 30% of dmmf coal. This is not to state that the products are similar at all levels of conversion or that important changes are not occurring. As more of the coal is converted to soluble form, compositional differences in successive conversion increments will be difficult to detect because of the weighting effect of the material which has already been converted to soluble form.

The extract yields obtained using the ammonium heptamolybdate salt are substantially lower than those reported in earlier work.¹⁰ One of the more likely reasons for this behavior is that only a fraction of Mo is converted to MoS_2 by reaction with sulfur in the coal. To ensure complete sulfiding of the metal, ammonium tetrathiomolybdate was employed as the catalyst precursor. The product

yields obtained from dry hydrogenation at 400°C with 1% Mo loading are summarized in Table 3 for reaction at different times.

A comparison of the results obtained after 60 min at 400°C, Tables 2 and 3, shows the much greater effectiveness of introducing Mo as ammonium tetrathiomolybdate; the extract yield was increased by about 70% while the Mo loading was reduced from 5 to 1%. In other experiments it has been found that the addition of a small quantity of CS₂ to coal impregnated with ammonium heptamolybdate was equally as effective as loading with the thio-salt.

It can be seen from Table 3 that a high proportion of coal can be converted to soluble form, with low attendant gas make, by reaction with an active dispersed catalyst under conditions of much lower severity than normally used in liquefaction systems. Conversion increases progressively with time, unlike solvent liquefaction which is usually characterized by two regimes; an initial rapid conversion of part of the coal followed by a much slower conversion rate. The mechanism of liquefaction by dry catalytic hydrogenation is not at all clear although presumably the liberated liquids play an integral role in the conversion of the remaining coal.

Fluorescence Microscopy

As the temperature of catalytic hydrogenation was raised, there was an increase in the maximum fluorescence intensity (I_{\max}) of the vitrinite in the unextracted coals. This intensity change closely parallels the increase in extract yield, Figure 1. The close correspondence between I_{\max} and the yield of chloroform-solubles suggests that the increase in fluorescence is directly related to the liberation of extractable liquids, which presumably occurs through breakdown of the macromolecular structure of the coal. After removal of the chloroform-solubles, the residue exhibited only a low level of fluorescence.

The fluorescence spectra for the hydrogenated vitrinites, normalized to a peak intensity of 100%, show a red shift in the wavelength at peak intensity, λ_{\max} , for the runs between 350-400°C, as shown in Figure 2. The shift may correspond to an increase in the concentration of condensed aromatics in the extractable liquids.

The fluorescence spectra of the hexane-soluble (oil) and hexane-insoluble (asphaltene) fractions of the extract obtained at 400°C were found to be quite different. The peak fluorescence intensity of the oil fraction occurred at about 550 nm whereas that for the asphaltene fraction was greater than 700 nm. These differences suggest that the red-shift observed in λ_{\max} for the spectra of the whole extracts on going from 350-450°C may be due to an increase in asphaltene concentration.

Summary and Conclusions

Dry catalytic hydrogenation of coal, using an impregnated Mo catalyst, has been found to considerably increase the yield of chloroform-soluble extract at temperatures of 400°C and less. For high activity the Mo should be present in sulfide form. Examination of the hydrogenated coals by fluorescence microscopy has shown that the intensity of vitrinite fluorescence increases in a parallel manner with extract yield. In the context of the mobile phase-network concept of coal structure, it is considered that, at high yields, a considerable proportion of the chloroform-solubles is derived from the breakdown of the macromolecular structure. The enhanced fluorescence would correspond to the liberation of smaller molecular fragments from a highly cross-linked network.

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TABLE 1
COAL PROPERTIES

	<u>PSOC-1266</u>
Seam	L. Kittanning
County	Mahoning
State	Ohio
Province	Eastern
ASTM rank class	hvAb
Moisture content % wt (a.r.)	3.4
Mineral matter % wt dry coal	6.1
<u>Elemental Composition % dmmf</u>	
C	83.2
H	5.0
O**	8.6
N	2.1
S	1.3
<u>Sulfur Forms % Dry Coal</u>	
Organic	0.51
Sulfate	0.02
Pyritic	0.87
<u>Maceral Group Analysis % Vol.</u>	
Vitrinite	91
Liptinite	3
Inertinite	6

* Determined by low-temperature ashing

** By difference

TABLE 2

PRODUCT YIELDS FROM DRY CATALYTIC HYDROGENATION
(5% Mo as ammonium heptamolybdate, 1 h, 7 MPa
cold H₂ pressure)

Reaction Temperature (°C)	Gas ¹		Yields (% wt dmmf coal)		Mass Balance %
			CHCl ₃ -soluble ¹ extract	Gas+Extract ²	
250	CO _x	0.39	1.5	1.8	100.1
	C ₁ -C ₄	--			
300	CO _x	0.52	2.3	5.3	97.5
	C ₁ -C ₄	--			
350	CO _x	0.52	8.6	13.0	96.1
	C ₁ -C ₄	--			
400	CO _x	2.03	31.6	46.5	87.4
	C ₁ -C ₄	0.35			

¹Determined directly²Calculated from CHCl₃-insoluble residue

TABLE 3

PRODUCT YIELDS FROM DRY CATALYTIC HYDROGENATION
(1% Mo as ammonium tetrathiomolybdate,
400°C, 7 MPa cold H₂ pressure)

Reaction Time (min)	Gas ¹		Yields (% wt dmmf coal)		Mass Balance %
			CHCl ₃ -soluble ¹ extract	Gas+Extract ²	
5	CO _x	0.11	7.3	4.8	102.6
	C ₁ -C ₄	0.02			
15	CO _x	0.31	23.4	24.0	99.6
	C ₁ -C ₄	0.72			
30	CO _x	0.81	35.4	35.8	98.8
	C ₁ -C ₄	0.78			
60	CO _x	0.32	53.9	60.3	94.7
	C ₁ -C ₄	0.80			

¹Determined directly²Calculated from CHCl₃-insoluble residue

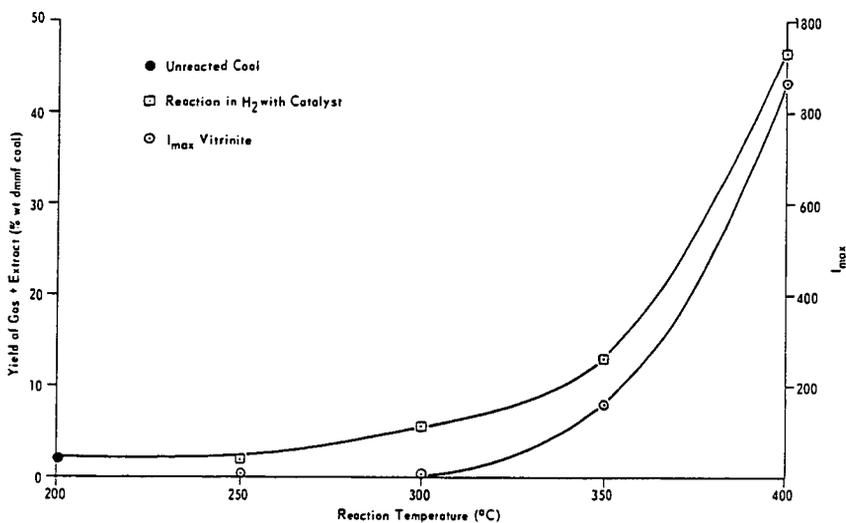


Figure 1. Correspondence between yield of chloroform-soluble extract and maximum fluorescence intensity of vitrinite.

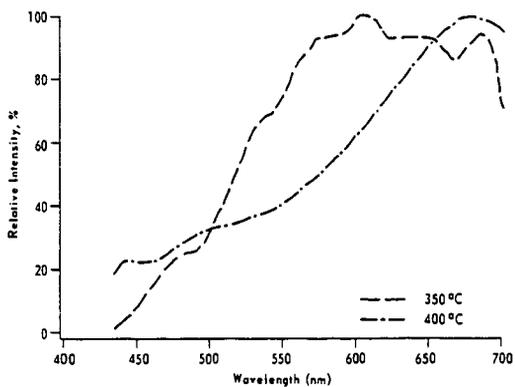


Figure 2. Fluorescence spectra of unextracted coals after dry catalytic hydrogenation.