LOW SEVERITY CATALYTIC HYDROGENATION OF COALS IN THE ABSENCE OF SOLVENT

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Introduction

Historically, models of coal structure have been developed on the premise that its principal characteristics can be attributed to those of a complex solid phase. Attempts to describe and portray this phase have focused on embodying measured compositional parameters into an 'average' molecule which presents a statistical representation of the whole molecular assembly. The value of such an approach is very limited particularly in its ability to describe behavioral characteristics. Furthermore, it does not take account of the existence of comparatively low molecular weight extractable liquids which are present in all except anthracitic coals (1).

In bituminous coals, the chloroform soluble materials have been shown to directly influence coal fluid properties (2-4). The role of the 'bitumens' has been suggested to be that of solvating and hydrogen-donating agents for the remainder of the coal substance (2). By analogy, it has been proposed that extractable coal liquids can provide a similar function during coal liquefaction (5). Experiments have shown that the extraction of bituminous and subbituminous coals in chloroform prior to liquefaction adversely influences the net liquefaction yield (6).

At moderate temperatures only a small proportion of coal may be extractable in solvents such as chloroform. However, it has long been recognized that by preheating the coal up to temperatures of 400°C and above, the yield can be increased several fold (2,7-8). Brown and Waters (2) concluded that the normal yield of extract is related to the accessibility of the pores to solvent, which is enhanced by preheating (swelling). Similarly, it has been found that the yields of alkanes present in benzene/ethanol solvent extracts was higher by 8-10 times in the liquefaction products of the same coals, although the distribution of the various species was very similar in both cases. It was concluded that the increased yield of alkanes on liquefaction was due to their liberation from regions of the structure hitherto inaccessible to solvent (9).

The work of Vahrman (10) has shown that in the Soxhlet extraction of coals extended for several hundred hours, the quantity of extract progressively increases, albeit at very low rates, and ultimately approaches that of the tar produced in low temperature (450°) pyrolysis. These findings are consistent with more recent suggestions to the effect that proportion of coal which is potentially extractable is much larger than is generally assumed but that it is not readily available due its being contained in closed or restricted porosity (11).

There are at least two possible sources of extractable or trapped liquids; by reactions during coalification leading to the formation and accumulation of lower molecular weight material (2); by physical entrapment of relatively unmodified components of plant origin (9,12-14). The presence of these materials in the

coal mass and their influence on its properties have promoted a number of suggestions concerning coal structure (1,2) which have been revitalized in recent years (15-17). Essentially coal is considered to comprise a relatively rigidly bonded three dimensional network which acts as a host for lower molecular weight species contained in both open and closed or partially closed pores. In effect, the structural model is that of a multicomponent system which, in the light of present knowledge, appears to be a more consistent and realistic basis for coal research than the earlier single phase concepts.

With this background, research investigations have been initiated to examine the low temperature ($\leq 400^{o}C$) catalytic hydrogenation of coals. The general objectives are to determine if it is possible to increase the yield of extractable liquids through the breakdown or modification of the network under mild hydrogenative conditions. Through, so doing, it is hoped i) to derive information about the structures and interactions of the 'network' and 'mobile' phases and ii) to ascertain the influence of such a pretreatment upon the behavior of coal in subsequent reactions. Earlier research has shown that low temperature chemical reduction of coals (treatment with a solution of lithium in ethylamine) can increase the H/C ratio and solubility in pyridine (18).

The approach which has been adopted follows the work of Hawk and Hitsehue (19) and Weller (20) who investigated catalytic coal hydrogenation in the absence of solvent in order to reduce the number of variables in the system and the problems of interpretation. The principal difference in the studies reported here, compared to the earlier work, is that reactions have been conducted at substantially lower temperatures and pressures.

Experimental

Coal Preparation

Samples of a bituminous coal were obtained in undried 1/2" lump form from The Pennsylvania State University Coal Sample Bank. The coals were ground, without drying to minus 800×10^{-6} m in a glove box which was first purged and maintained under pressure using a flow of oxygen-free nitrogen. The total ground product was riffled and then divided into approximately 20 gram lots which were sealed into vials while still in the glove box. The origin and analysis of the ground coals are summarized in Table 1.

The molybdenum catalyst used in these experiments was impregnated onto the coals using an aqueous solution of ammonium hepta molybdate $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (supplied by courtesy of Climax Molybdenum, Co.). The procedure was to mix the prerequisite quantity of the molybdenum salt with the coal following which sufficient distilled water was added to form a thick slurry which was stirred for 30 minutes at room temperature. The excess water was removed by vacuum at room temperature overnight. (It was estimated that by this technique more than 98% wt of catalyst was retained on the coal.)

Reaction and Product Workings

Reactions were carried out using standard tubing bombs (20 cc capacity) constructed out of 316 stainless steel which were loaded with approximately 5 g of sample. The bombs were first purged of air several times with nitrogen and, if required, purged of nitrogen and sealed with the reactant gas to a cold pressure of 1000 psig. The bombs were heated by immersion in a preheated fluidized sandbath heater which rapidly raised the contents of the bomb to reaction temperature. Agitation was provided by oscillating the bomb through a vertical displacement of 5 cm at a frequency of 50 sec^{-1}. At the end of the reaction period, the bomb was

removed from the sandbath and quenched by immersion in water.

The excess pressure in the bomb was released by venting at room temperature during which time gas samples were collected for analysis. The reactor contents were completely removed to a predried ceramic Soxhlet thimble using chloroform as wash solvent. Soxhlet extractions were then carried out for 12 hours in boiling chloroform under a protective blanket of nitrogen. The resulting residue was dried in vacuo at 110°C for 12 hours to remove remaining solvent.

The chloroform extracts were filtered (Whatman 42 filter paper) under a nitrogen blanket and the excess chloroform removed on a rotary evaporator at 40°C. The resulting product was then further dried in vacuo for 1 hour at 110°C. The residual and extract products were sealed under nitrogen and stored under refrigerated conditions.

The total yields of chloroform soluble extract and gases were calculated from the mass of dried chloroform insoluble residue and reported as a percentage of dmmf coal. In those cases where catalyst had been added, the assumption was made that the molybdenum in the residue had been converted to a 50-50 mixture of MoO_3 and MoS_2. This assumption requires verification but any resulting inaccuracy does not affect the general trend shown in the data. The reproducibility of the total yields was found to be within 2%.

Analytical

The chloroform soluble extracts, the insoluble residues and nonextracted coals were analyzed for elemental composition. The extracts were also analyzed by ^1H n.m.r. spectroscopy (using pyridine as solvent) and by high resolution mass spectrometry (KRATOS M-50 spectrometer, resolution 1:30,000). The mass spectrometric method employed direct probe sample introduction which allows analysis of materials which are volatilized at 350°C and a pressure of 10^{-6} mm of mercury.

The parent coals and nonextracted, reacted samples were analyzed by ^{13}C n.m.r. using two independent methods to detemine differences in aromaticity; cross-polar magic angle spinning and the Bloch decay technique.(21)

Results and Discussion

Extract Yields

The total yields of chloroform extracted liquids and gases obtained under different reaction conditions are shown in Table 2 and are presented in Figure 1. It can be seen that the extract yield obtained in nitrogen increases with temperature from 0.9% at 61°C to a value of 9.2% at 400°C. The effects of heating on extract yield are consistent with those reported previously (1,2,7,8) and the value at 400°C is of the same order as has been measured for coals of similar rank (2).

More notably, at temperatures above about 325°C, the total yield is increased to some degree by the presence of hydrogen gas and more appreciably by the combination of hydrogen and impregnated catalyst. In the latter case, the yield at 400°C amounted to 43.1% of dmmf coal which is more than a factor of two higher than obtained in hydrogen alone and over four times that in nitrogen. Accurate figures for the gas make are not yet available although from preliminary estimates the quantity does not appear to be higher than about 5% dmmf coal at the maximum total yield measured. Consequently, it can be seen that by catalytic hydrogenation a substantial proportion of the coal substance has been rendered soluble and

TABLE 1

COAL ANALYSIS

Coal Identification	
Rank	Bituminous HVA
Sample Band I.D.	PSOC 1266
Seam	Ohio #5 (Lower Kittanning)
Mine	East Fairfield C
Analysis	
Moisture % a.r.	3.36
Mineral Matter % m.f.*	6.09
Elemental Analysis (dmmf)	
C	83.20
H	4.97
O (by diff)	8.64
N	2.06
S	1.35
H/C atomic ratio	0.76

*by low temperature ashing

TABLE 2

TOTAL YIELDS (CHLOROFORM SOLUBLES AND GASES) FROM BITUMINOUS COAL REACTED FOR 1 h, 1000 psig GAS (COLD)

Reaction Temperature, °C	Yield % dmmf+ Noncatalyzed	Yield % dmmf+ Catalyzed*
250	0.9	0.3
300	1.2	1.3
350	6.3	9.2
400	19.3	43.1

+Yields are the average of at least two results. Estimated error ±1%.

*5% Mo on a.r. coal added as ammonium hepta molybdate.

extractable in chloroform. The lesser improvement in yield found in hydrogen alone may be attributable to catalysis by dispersed mineral matter.

From these data it is not possible to ascertain whether the chloroform soluble materials realized under hydrogenative conditions are derived solely from the more efficient liberation of trapped species or whether there is some accompanying decomposition of the 'network.' Nevertheless, the high yields obtained with impregnated catalyst suggest that a proportion of the extractable products may be produced through reactions which involve breaking relatively strong chemical bonds.

Coal and Extract Composition

The coal aromaticities measured by ^{13}C n.m.r. are shown in Table 3. The results obtained by the two methods differ significantly in absolute terms, reasons for which are currently being investigated. The differences are, however, systematic and depict the same relative changes in f_a, which show that under both sets of reaction conditions the aromaticity increases. In the presence of catalyst the extent of aromatization is reduced but the net chemical reactions evidently involve dehydrogenation rather than hydrogenation.

The hydrogen contents and the H/C ratios of the coals and residues, Table 4, are consistent with the ^{13}C n.m.r. analyses. The results for the chloroform soluble extracts do not reflect the same trend, the hydrogen content of the extracts derived following reaction being similar to or higher than that from the parent coal. In the absence of gas analyses, it is difficult to draw any inference from these data, although it is noteworthy that the hydrogen content of the extracts is little influenced hy the substantial changes in yield.

The role of the added catalyst is not at all clear. Its addition results in a two-fold increase in an extractable material while apparently there is only a small effect on net hydrogenation.

Further compositional analyses of the extracts were undertaken to attempt to elucidate the function of the catalyst and the origins of the additional chloroform soluble liquids. The hydrogen type distributions by ^{1}H n.m.r. of extracts, derived from hydrogenative reactions in the presence and absence of added catalyst, were found to be virtually indistinguishable, Table 5.

A comparison of the distribution of hydrocarhon fractions of these same samples obtained by high resolution mass spectrometry (HRMS) and subsequent data reduction is shown in Figure 2. The format for this figure is simply a plot of ion intensity vs Z number class (C_xH_{2x-z}) with each Z number class ordered by carbón number. (Thus, benzenes contribute to Z=6 napthalenes to Z=12 phenanthrenes to Z=18 and pyrenes to Z=22.) The yield of hydrocarbons (as a fraction of total extract) was approximately the same for the two extracts (32% for catalyzed, 35% noncatalyzed) and the similarity of the HRMS profiles indicates that the distribution and composition of the bydocarbons is also very similar. This close correspondence of HRMS profiles was also observed for other compound classes in the extracts ($C_xH_yO_2$, C_xH_yO, C_xH_yN).

A number of minor differences were detected in all of the profiles but it is not yet known if they are reproducible or significant. A further and possibly important distinction was that in the monoxygenate profile (C_xH_yO) the extract from the catalyzed reaction showed a higher concentration of monoaromatic phenols. Examination by dispersive infrared spectrometry confirmed that this extract contained a measurably higher concentration of phenolic -OH groups. This particular phenomenon which has been noted in earlier studies of low temperature coal reduction (18) is the subject of continuing investigation.

TABLE 3

AROMATICITIES OF NONEXTRACTED COALS BY ^{13}C n.m.r.

	Parent Coal	Reaction at 400°C, 1 h, 1000 psig H_2 (cold)	
		No Added Catalyst	Mo Impregnated
f_a (CP-MAS)	0.71	0.78	0.74
f_a (Block Decay)	0.75	0.84	0.79

TABLE 4

HYDROGEN CONTENT AND H/C ATOMIC RATIO OF COALS, EXTRACTS AND RESIDUES

Sample		Parent Coal	Reaction 400°C, 1 h, 1000 psig H_2 (cold)	
			No Added Catalyst	Mo Impregnated
Coal	H wt% dmmf	4.97	4.51	5.06
	H/C Atomic ratio	0.72	0.65	0.71
Residue	H % dmmf	4.86	4.00	4.61
	H/C atomic ratio	0.71	0.58	0.63
Extract	H % dmmf	6.52	7.25	6.95
	H/C atomic ratio	1.01	1.05	1.00

TABLE 5

HYDROGEN TYPE DISTRIBUTION OF CHLOROFORM SOLUBLE EXTRACTS BY ^{1}H n.m.r.
(coal reacted at 400°C, 1000 psig H_2)

Sample	H_α	H_β	H_γ	H_{Ar}
No added catalyst	0.36	0.25	0.06	0.32
Mo impregnated	0.34	0.24	0.07	0.30

Overall (and excepting the possible production of phenols) although the catalyst has been found to have a major influence upon the release and/or production of chloroform soluble material, the available compositional information indicates that its mechanism is unusually subtle. The additionally extractable liquids, whether originally trapped or derived from the 'network' are very similar in structure to those generated in the absence of catalyst.

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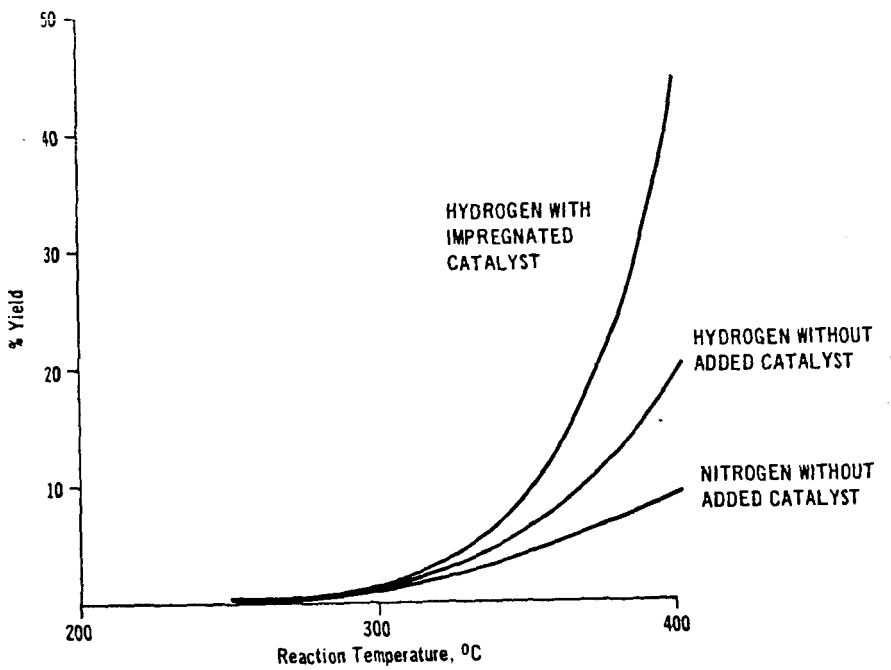

Figure 1. YIELD OF CHLOROFORM SOLUBLE LIQUIDS AND GASES AS A FUNCTION OF REACTION TEMPERATURE
(Bituminous coal, 5% M_0 loading on as-received coal, reaction 1h, 1000 psig cold pressure)

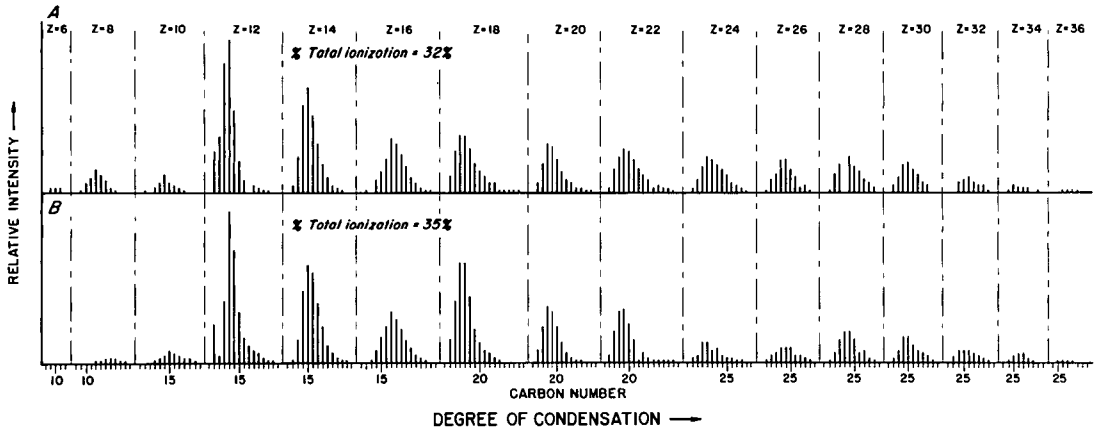

Figure 2. **HRMS Comparison of CH Formulas Identified in Coal Extracts (A) Catalyzed (B) Uncatalyzed**

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