

THE HYDROGEN TRANSFER CYCLE FOR COAL LIQUEFACTION --
PROCESS IMPLICATIONS*

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INTRODUCTION

Direct liquefaction of coal involves the conversion of a hydrogen-poor solid to a liquid richer in hydrogen by a complex set of bond ruptures and hydrogen transfer reactions. This paper reports a portion of a continuing effort to understand the utilization of hydrogen in direct liquefaction by tracing the transfer of hydrogen from the gas phase to polynuclear aromatic hydrocarbon (PAH) solvent components, and from these donor components to coal. In this portion of the effort, experiments were performed to monitor the dehydrogenation of hydroaromatic components of a coal-derived solvent that results from donation of hydrogen to coal.

In a previous paper (1), results of experiments were reported that showed the impact of a hydrogen source, either from the gas phase or from solvent containing hydroaromatic compounds, on the yield of liquefaction products. Gas-phase hydrogen was required to produce high conversion of coal to liquids only if the solvent contained low concentrations of hydroaromatic donors. Furthermore, significant consumption of gas-phase hydrogen occurred only in reactions catalyzed to promote in-situ hydrogenation of PAHs to hydroaromatics. In related experiments (2,3,4), we have sought to define effective conditions for the hydrogenation of PAHs in coal-derived solvents. The results of these studies demonstrated that 1) use of catalytic hydrogenation at relatively low temperatures favored formation of hydroaromatics; 2) use of lower temperature allows the use of lower pressure; and 3) that CO/water mixtures are effective sources of hydrogen for hydrogenation of PAHs. These results were used to establish conditions for preparing a liquefaction solvent containing high concentrations of hydroaromatic hydrogen donors. This solvent was then reacted with coal, in the absence of gas-phase hydrogen, over a range of temperatures and times to monitor the transfer of hydrogen from the hydroaromatic derivatives of three key PAHs, phenanthrene, fluoranthene, and pyrene.

EXPERIMENTAL

Materials

Feed to the solvent production reactor was prepared from a pasting solvent produced from Illinois No. 6 (Burning Star) coal by the Lummus Integrated Two-Stage Liquefaction (ITSL) process development unit (5). This material, which was too viscous to be used in our laboratory reactor, had a boiling point range of approximately 550 to 850°F. Prior to its use, it was vacuum distilled with a spinning band apparatus. The 650 to 770°F fraction, which contained 3.3% by weight phenanthrene, 4.0%

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fluoranthene and 8.6% pyrene, was retained for these experiments. Illinois No. 6 high-volatile bituminous coal for these experiments was obtained from the Argonne National Laboratory Premium Coal Sample Program. The coal was found to have 7.3% by weight moisture and 17.5% mineral matter by low temperature ashing. Extrudates (0.8 mm diameter by 4 mm length) of Shell 324M, a 2.8% Ni, 12.4% Mo on alumina catalyst, were used for hydrogenation of the solvent. Prior to use, the catalyst was sulfided in situ with 10 mole % H₂S in H₂ at 390°C and atmospheric pressure.

Apparatus and Procedure

Solvent hydrogenation was performed in a trickle-bed reactor using steam and a 1:1 "syngas" mixture of hydrogen and carbon monoxide to simulate the products of a gasifier. The reactor consisted of six 1.0 cm ID by 15 cm long catalyst-filled stainless steel tubes connected in series. Each tube contained 9.5 g of catalyst. The reactor was thermostatted to $\pm 1.0^\circ\text{C}$ by a forced-air convection oven and pressure was controlled to ± 10 psig with a precision back pressure regulator. After pressurizing to 800 psig with the gas mixture, the reactor temperature was brought to 300°C and water flow was initiated. Upon detection of conversion of CO/H₂O to CO₂/H₂, the coal-derived solvent flow was started. The gas mixture was delivered to the reactor at a volume hourly space velocity of 325 and steam and solvent were delivered at weight hourly space velocities of 0.07 and 0.5 respectively. The amount of steam fed to the reactor was slightly in excess of the amount required to stoichiometrically convert all of the CO. During the operation of the reactor, 0.5 mole % of H₂S was added to the gaseous feed to maintain the catalyst in the sulfided state.

Coal liquefaction reactions were performed in batch microautoclaves with slurry capacities of 8 cm³ and gas volumes of 35 cm³ (6). After the reactors were charged with 8g of a 2:1 ratio mixture of solvent and coal, they were pressurized to 300 psig with nitrogen. They were then heated to temperature in a fluidized sand bath while being agitated with a wrist-action shaker at 200 cycles/min. Following the heating period, the reaction vessels were quenched in water, the final temperatures and pressures were recorded, a gas sample was taken and the product slurry was quantitatively removed for analysis. All experimental variables for both the flow and batch reactors were monitored and recorded with a computer-controlled data acquisition system. Four coal liquefaction experiments were performed to correlate dehydration of the hydroaromatics with coal conversion. Reactions were performed at two temperatures, 425 and 450°C, and for times ranging from 10 to 40 minutes.

Product Analyses

Gas samples from the liquefaction reactions were analyzed for N₂, H₂, CO, CO₂, and C₁-C₃ hydrocarbons with a Carle Series 500 gas chromatograph with a hydrogen transfer system. The amounts of PAHs and hydroaromatics in the flow reactor feed and liquid product samples were determined with a Hewlett-Packard 5890 gas liquid chromatograph equipped with a capillary column. Coupled gas chromatography/mass spectrometry techniques were used to

identify the retention times of the PAHs and hydrogenated PAHs. Hydrogen content of the product was determined by elemental analysis. To calculate the amount of donatable hydroaromatic hydrogen, a portion of the coal-derived solvent that was catalytically dehydrogenated was also analyzed for hydrogen content. Conversion of coal to products was quantified by tetrahydrofuran (THF) and n-heptane solubility. Dry, mineral matter free (dmmf) basis conversions were calculated from the difference between the weight of organic coal and the insoluble organic matter resulting from THF or n-heptane extraction of the product. The n-heptane soluble materials, which contained the post-reaction solvent components, were examined by capillary column chromatography to determine the extent of dehydrogenation of solvent hydroaromatics.

RESULTS AND DISCUSSION

Solvent Hydrogenation

The extent of solvent hydrogenation can be seen in Figure 1, which is a comparison of the chromatogram of the trickle-bed reactor product to that of the feed. Analysis of the product solvent showed that 66% of the phenanthrene, 88% of the fluoranthene and 56% of the pyrene were converted to hydroaromatics. Table I gives the concentrations and distribution of the hydroaromatics resulting from hydrogenation of the PAHs. It was also noted from the chromatograms that the solvent contained significant amounts of alkylated phenanthrenes and pyrenes, which were also hydrogenated. However, the concentrations of these were not quantified. From the difference between the hydrogen content of the solvent (9.0%) and that of a catalytically dehydrogenated sample (8.2%), the donatable hydrogen content was calculated to be 0.8% by weight.

Coal Liquefaction and Hydrogen Donation

Table II presents a summary of the results of the coal liquefaction experiments in terms of insoluble organic material (IOM) remaining after reaction, n-heptane insoluble and soluble products formed, yield of hydrocarbon gases (C₁-C₃) and release of hydrogen to the gas phase. As can be seen from Table II, the highest reaction severity, 450°C for 40 minutes, produced a significant conversion of coal to n-heptane soluble products (44%) with only a small amount (16%) of hydrogen released to the gas-phase.

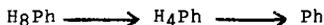
Figures 2-4 trace the concentrations of the PAHs and hydroaromatics as a function of conversion of coal to the sum of the yields of n-heptane soluble materials and hydrocarbon gases. Several observations can be made with respect to hydrogen donation by the hydroaromatic species.

Comparison of the PAH and hydroaromatic concentrations resulting from experiments 2 and 3 shows that the extent of donation is directly proportional to conversion of coal to products. Though experiments 2 and 3 were performed for different times and at different temperatures, the product distributions were

nearly identical, as were the post-reaction concentrations of PAHs and hydroaromatic solvent components.

Examination of the concentration curves shown in Figures 2-4 indicates the relative ease with which the various hydroaromatics donate hydrogen during the conversion of coal. Three groups of hydroaromatics can be distinguished: First are those which donate early in the coal conversion process, as indicated by sharply decreasing concentrations at the lowest coal conversion. Tetrahydrofluoranthene, di-, tetra- and 1,2,3,6,7,8-hexahydropyrene can be placed in this group. The second group consists of hydroaromatics that donate later in the coal conversion process, as indicated by sharply declining concentrations at higher conversions. Tetrahydrophenanthrene, hexahydrofluoranthene and decahydrofluoranthene belong to this group. The third group are hydroaromatics that show a steady decrease in concentration over the entire range of coal conversion. Three compounds, dihydrophenanthrene, octahydrophenanthrene, and 1,2,3,3a,4,5-hexahydropyrene (isohexahydropyrene in Fig. 4) exhibit this behavior.

Examination of the concentration profiles for the hydrogenation of octahydrophenanthrene indicates the existence of a multiple step donation for octahydrophenanthrene. Initially, as the concentration of octahydrophenanthrene (H_8Ph) decreases, the concentration of tetrahydrophenanthrene (H_4Ph) increases. The concentration of H_4Ph does not decrease much until the concentration of H_8Ph is substantially lower. This is consistent with the following dehydrogenation pathway which results from hydrogen donation:



Implications for Coal Liquefaction Processes

This study of the hydrogen transfer cycle for coal liquefaction suggests more effective ways to utilize hydrogen. The results of these experiments clearly demonstrate that an excellent coal liquefaction solvent can be produced by reaction of a coal-derived liquid with a H_2/CO /steam mixture at relatively low temperature and pressure. The resulting solvent contains a sufficient concentration of hydroaromatics to be used as the sole source of hydrogen for the liquefaction of coal. Applying these techniques for transfer of hydrogen to coal in a liquefaction process could provide several advantages: First, use of CO/H_2 /steam mixtures, instead of purified hydrogen, for the hydrogenation of the solvent would eliminate the need for gas purification units. Second, operation of the solvent production reactor at a lower temperature and pressure would allow reduction of the wall thickness of the reactor vessel, thus reducing vessel cost. Third, the 650-770°F distillate cut used as a recycle solvent contains significant concentrations of the important three- and four-ring hydroaromatic donor precursors, but does not contain compounds that cause extensive catalyst deactivation. Finally, the requirement for gas-phase hydrogen and high pressure in the thermal liquefaction step would be eliminated.

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TABLE I Distribution of phenanthrene, fluoranthene, pyrene and hydroaromatic derivatives in hydrogenated coal-derived solvent.

<u>Compound</u>	<u>Conc. in Solvent (Wt %)</u>	<u>Percent of PAH Mixture</u>
Phenanthrene	1.03	34
9,10-dihydro-	0.38	13
1,2,3,4-tetrahydro-	0.79	26
1,2,3,4,5,6,7,8-octahydro-	0.81	27
Fluoranthene	0.51	12
1,2,3,10b-tetrahydro	1.96	46
6b,7,8,9,10,10a-hexahydro-	0.71	17
1,2,3,3a,6b,7,8,9,10,10a-decahydro-	1.06	25
1,2,3,3a,4,5,6,6a,10b,10c-decahydro-		
Pyrene	3.81	44
4,5-dihydro-	2.49	29
4,5,9,10-tetrahydro-	0.53	6
1,2,3,6,7,8-hexahydro-	0.98	11
1,2,3,3a,4,5-hexahydro-	0.77	9

TABLE II Summary of Results of Coal Liquefaction Experiments

Exp. No.	Temp (°C)	Time (min.)	Product Distribution (% dmmf coal basis)				Hydrogen Released to Gas Phase (% of donatable hydrogen)
			IOM	Hept. Sol's.	Hept. Insol's.	C ₁ -C ₃	
1	425	10	9.5	22.4	66.9	0.8	3.9
2	425	30	6.7	36.3	54.5	1.5	6.9
3	450	10	6.8	36.3	53.3	2.5	7.5
4	450	40	4.1	43.5	45.9	6.4	16.1

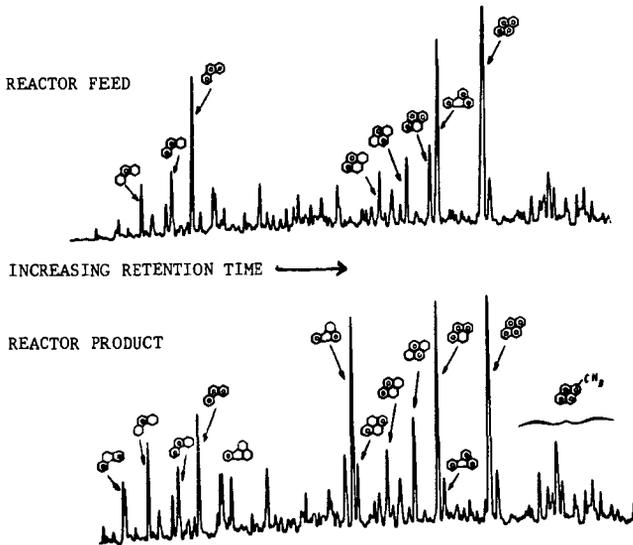


FIGURE 1. Comparison of Chromatograms of Trickle Bed Reactor Feed and Product

Fig. 2. Concentration of phenanthrene and hydrophenanthrenes vs coal conversion.

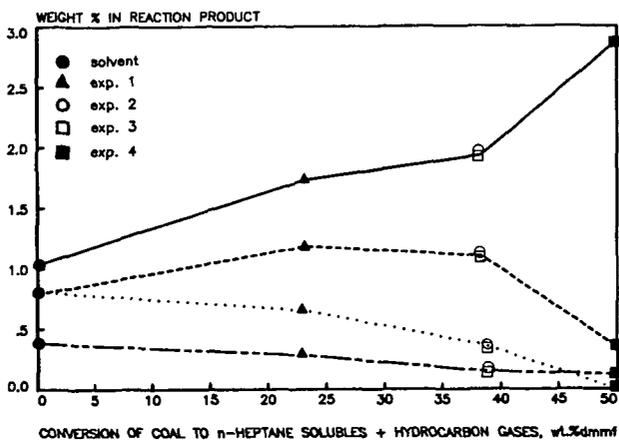


Fig. 3. Concentration of fluoranthene and hydrofluoranthenes vs coal conversion.

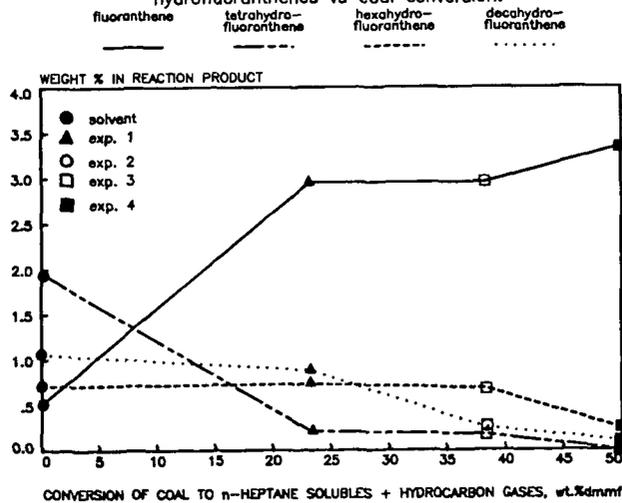


Fig. 4. Concentration of pyrene and hydroxyrenes vs coal conversion.

