

AN ISOTOPIC INVESTIGATION OF THE CHEMISTRY OF COAL HYDROLIQUEFACTION

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I. INTRODUCTION

We reported earlier on a deuterium tracer method for investigating the mechanisms of coal liquefaction.⁽¹⁻³⁾ The research involved the use of deuterium gas,⁽¹⁾ or deuterium gas and tetralin-d₁₂^(2,3) for hydrogenation, and the use of the deuterium as an isotopic tracer to follow the incorporation of hydrogen into the coal. After separation of the liquefaction products, the product fractions were analyzed for deuterium incorporation into different structural positions. It was found that when deuterium alone was used (without donor solvent) for liquefaction, the deuterium content of the products increased in the following order: oil < asphaltene < preasphaltene < residue. When deuterium and tetralin-d₁₂ were used, the deuterium contents of the product fractions were about the same. In both types of experiments, preferential incorporation of deuterium was found in the benzylic structural positions of each fraction. Similarly, preferential incorporation of protium was observed in the benzylic position of the recovered tetralin-d₁₂.

A number of related investigations have been reported on the use of deuterium as a tracer in coal hydrogenation research. Schweighardt, et al.⁽⁴⁾ examined a centrifuged liquid product from a Synthoil run after heating it to 450°C with deuterium gas; Kershaw and Barrass⁽⁵⁾ reported on the examination of products from the reaction of coal with deuterium gas using SnCl₂ as catalyst; Franz⁽⁶⁾ investigated the products from the reaction of a subbituminous coal with tetralin-1,1-d₂ at 427°C and 500°C; Cronauer, et al.⁽⁷⁾ reported on the interaction of deuterium-labeled tetralin with coal model compounds; King and Stock⁽⁸⁾ investigated the influence of coal and coal-related compounds on the exchange reaction between diphenylmethane and perdeuteriotetralin.

This paper presents the results of experiments which were conducted to investigate the respective roles of gas-phase and donor-solvent hydrogen in coal hydroliquefaction. Coal hydrogenation experiments were carried out with ²H₂/tetralin-h₁₂ and ¹H₂/tetralin-d₁₂ mixtures and tetralin-d₁₂ under N₂ pressure to study the mechanisms that are in operation.

II. EXPERIMENTAL

A. MATERIALS

A high-volatile A bituminous coal (80.1% C, 5.1% H, 1.6% N, 3.6% S, 9.6% O, by weight, daf basis, 7.7% ash) from the Loveridge Mine, Pittsburgh Seam was used. The coal was stored under nitrogen, ground to -200 mesh, and dried in vacuo for 4 hr at 115°C before use in each experiment. Technical-grade deuterium (>98 atom % deuterium, typical HD:0.5%) and high-purity nitrogen were utilized. Some of the tetralin-d₁₂ was prepared in our laboratories⁽³⁾, and some was purchased from the Aldrich Chemical Co., Inc. The isotopic purity of both materials was >99 atom % deuterium. The isotopic purity of tetralin-d₁₂ was determined by proton-NMR using p-dioxane as an internal reference.

B. EXPERIMENTAL AND ANALYTICAL PROCEDURES

A schematic outline of the experimental and analytical procedures is shown in Figure 1. Batch experiments were performed using a 1-liter stirred Autoclave Engineer's autoclave equipped with a coal injection system. In a typical experiment, the autoclave was charged with 25 g of tetralin, heated, and 25 g of coal was injected at temperature with the appropriate cover gas. After the scheduled reaction time had elapsed, the furnace was lowered from the autoclave, and the external surface was air-cooled. Also, water was circulated through the autoclave's internal cooling coils. After the autoclave had cooled to ambient temperature, the gas volume was measured using a wet test meter, and product gas samples were analyzed by GC-MS. The solvent was distilled from the product mixture and analyzed by NMR and GC-MS. The solid and liquid products were solvent fractionated into oil (hexane soluble, benzene soluble), asphaltene (hexane insoluble, benzene soluble), preasphaltene (THF soluble, benzene insoluble), and residue (THF insoluble) fractions. A portion of each fraction was combusted and its protium/deuterium ratio was determined by MS analysis of the resulting water. Each fraction was analyzed to determine its elemental composition. The fractions also were analyzed by proton and deuterium NMR spectrometry.

Proton NMR and deuterium NMR, spectra of soluble fractions, and recovered solvent mixtures were obtained by using a JEOL FX60Q FT NMR spectrometer. A flip angle of 45° was used which corresponds to $14 \mu\text{s}$ for ^1H and $75 \mu\text{s}$ for ^2H . The pulse repetition times were 6.0 and 9.0 s, respectively. Chloroform- d was used as the ^1H NMR solvent, and chloroform was used as the ^2H NMR solvent. Integrations were obtained using software supplied by JEOL, Inc. The GC-MS analyses were conducted by Shrader Analytical Laboratories, Inc., using a Pye-Unicam Model 105 chromatograph interfaced to an AEI Model MS-30 mass spectrometer.

III. RESULTS AND DISCUSSION

Three experiments were conducted to explore the roles of gas-phase and donor-solvent hydrogen on coal liquefaction. Tetralin- h_{12} , tetralin- d_{12} under $^2\text{H}_2$ or $^1\text{H}_2$, or N_2 pressure were used, as shown in the experimental matrix (Table 1). In each experiment, there was only one source of deuterium atoms: deuterium gas in Experiment 120 and tetralin- d_{12} in Experiments 121 and 122. In Experiment 122, nitrogen cover gas was used to eliminate those reaction pathways which involve gas-phase hydrogen.

TABLE 1
EXPERIMENTAL MATRIX FOR DONOR SOLVENT HYDROGENATION EXPERIMENTS

Experiment*	Coal +				
	Gas			Solvent	
	Protium	Deuterium	Nitrogen	Tetralin- h_{12}	Tetralin- d_{12}
D/P		X		X	
P/D	X				X
N/D			X		X

*Experiment name indicates gas isotopic composition/solvent isotopic composition (i.e., D/P refers to deuterium gas/tetralin- h_{12}).

A. PRODUCT YIELDS AND COMPOSITIONS

The product yields are shown in Table 2. It should be noted that the asphaltene and preasphaltene yields are lower than would be expected at 425°C and 15 MPa, particularly for the experiment in which nitrogen was the cover gas. We believe that this resulted from using unfavorably small amounts of reactants for the 1-liter autoclave to minimize the use of expensive tetralin-d₁₂. Nevertheless, previous coal hydrogenation experiments⁽²⁾ conducted with deuterium gas and tetralin-d₁₂ in a 1-liter and in a 250-ml autoclave showed that while higher soluble product yields were obtained in the smaller autoclave, the isotopic incorporation patterns were similar in both experiments.

TABLE 2
PRODUCT YIELDS FROM DONOR SOLVENT
HYDROGENATION EXPERIMENTS
(wt %)

Product	Experiment		
	D/P	P/D	N/D
Gas	10	11	9
Oil	24	19	16
Asphaltenes	8	4	1
Preasphaltenes	7	3	3
Residue	51	63	71

The deuterium contents of the product fractions are shown in Table 3. The deuterium content of the heavier fractions (asphaltenes, preasphaltenes, and residue) depend principally on the isotopic composition of the gas phase. These fractions have high atom % deuterium content in Experiment D/P, where ²H₂ gas and tetralin-h₁₂ were used, and low atom % deuterium content in Experiment P/D, where ¹H₂ gas and tetralin-d₁₂ were used. The atom % deuterium content of the heavy fractions is between these two extreme values in Experiment N/D where tetralin-d₁₂ was used under N₂ pressure. This indicates that the use of the inert gas, which precludes reactions with molecular hydrogen, allows pathways which are otherwise less significant to become more important in the reaction sequence. No obvious trend regarding the deuterium content was observed for the gas and oil fractions.

B. PRODUCT GAS COMPOSITIONS

The gas compositions, determined by gas chromatographic analysis, are shown in Table 4. The isotopic compositions of the product gases were determined by GC-MS analysis. The isotopic compositions of methane, ethane, and propane are shown in Table 5. The main results are summarized below:

- 1) The concentrations of the D₀ species can be correlated with the deuterium source used in the experiment. The D₀ species can form from the corresponding radicals by protium abstraction from the coal in any experiment, from the protium gas (Run P/D), or from tetralin-h₁₂ (Run D/P). The amount of D₀ species is reduced if the same radicals abstract deuterium from the tetralin-d₁₂ (Runs P/D and N/D) or ²H₂ gas (Run D/P). It appears that ²H₂ gas reacts more

TABLE 3
DEUTERIUM CONTENTS OF PRODUCTS
(Atom % of Total Hydrogen)

Product	Experiment		
	D/P	P/D	N/D
Gas	29	33	29
Oil	26	26	12
Asphaltenes	42	21	31
Preasphaltenes	34	15	28
Residue	<u>46</u>	<u>20</u>	<u>36</u>
Total Product	32	27	28

TABLE 4
PRODUCT GAS COMPOSITIONS
(Weight in Grams*)

Component	Experiment		
	D/P	P/D	N/D
CH ₄	1.10	1.36	0.94
C ₂ H ₄	0.01	0.01	0.01
C ₂ H ₆	0.58	0.63	0.43
C ₃ H ₆	0.01	0.01	0.01
C ₃ H ₈	0.35	0.35	0.24
i-C ₄ H ₁₀	0.01	0.03	0.05
n-C ₄ H ₁₀	0.08	0.10	0.08
i-C ₅ H ₁₂	0.02	0.01	-
n-C ₅ H ₁₂	0.02	0.02	0.02
CO	0.09	0.09	0.05
CO ₂	0.10	0.10	0.22
H ₂ S	<u>0.01</u>	<u>0.08</u>	<u>0.07</u>
Total	2.38	2.79	2.12

*Weights calculated on an all-protium basis

TABLE 5
ISOTOPIC COMPOSITIONS OF THE PRODUCT GASES
(%)

Component (Experiment)	D ₀	D ₁	D ₂	D ₃	D ₄	D ₅	D ₆	D ₇	D ₈
<u>CH₄</u>									
D/P	28	29	30	13	0	-	-	-	-
P/D	36	25	13	14	12	-	-	-	-
N/D	40	24	14	11	11	-	-	-	-
<u>C₂H₆</u>									
D/P	8	31	32	19	10	0	0	-	-
P/D	23	17	19	15	10	10	6	-	-
N/D	*	*	*	11	9	12	13	-	-
<u>C₃H₈</u>									
D/P	27	24	17	10	10	6	4	2	0
P/D	35	31	16	7	3	2	3	2	1
N/D	36	27	14	9	3	4	5	2	2

*Interference from other species causes uncertainty in these values.

effectively with the radicals than tetralin-d₁₂ does.* This tentative conclusion is supported by previous experimental data⁽³⁾ obtained on the hydrogenation of coal with deuterium gas at 380°C without added donor solvent. The D₀ components in that experiment were for CH₄:3%, for C₂H₆:0%, and for C₃H₈:12%, which shows that the ²H₂ gas is a more effective deuterium source for the conversion of methyl, ethyl, and propyl radicals to the corresponding deuterated hydrocarbons than is tetralin-d₁₂. Hydrogen exchange with the solvent probably contributes to a lesser extent to the formation of these species, because even by the end of the experiment no more than one-third of the solvent hydrogen in any position has been exchanged. This may be due to the greater access of the hydrogen gas molecules to the pore structure of the coal compared with that of the solvent molecules.

- 2) Only minor differences were observed between the isotopic compositions of the gas products of the tetralin-d₁₂ run made with N₂ cover gas in one case (Run N/D) and under ¹H₂ pressure in the other (Run P/D). These results show that very little isotopic exchange takes place in the gas phase between hydrogen and hydrocarbons.
- 3) Fully deuterated methane and ethane were detected only in those experiments in which tetralin-d₁₂ was used. No such species were found in Experiment D/P, where tetralin-h₁₂ was used, and the deuterium source was ²H₂. This indicates that the CD₄ and C₂D₆ species were formed from the tetralin-d₁₂ only. It also appears that at least some of the CD₄ and C₂D₆ were formed from the solvent prior to the injection of the coal. Additional investigations are in progress to clarify this point.

*Alternately, isotopic exchange reactions may occur with the radical precursors.

C. COMPOSITION OF THE RECOVERED SOLVENT

1. GC-MS Analyses

The GC-MS analyses of the recovered solvents are shown in Table 6. In Experiment D/P, tetralin- h_{12} was used and the source of deuterium was 2H_2 gas. The isotopic distributions in the recovered tetralin and naphthalene are very similar. In both compounds, D_1 and D_2 species predominate, but sizable concentrations of D_3 and D_4 species are also present. The predominance of the D_1 and D_2 species, coupled with information from the NMR analysis of the solvent (Table 7), which show that 76% of the incorporated deuterium is in the α -aliphatic position, indicates that the α -tetralinyl radical has a significant role in the transfer of deuterium from the gas phase into the coal.

TABLE 6
ISOTOPIC DISTRIBUTIONS IN TETRALIN AND NAPHTHALENE
IN THE RECOVERED SOLVENTS
(%)

Component (Experiment)	D_0	D_1	D_2	D_3	D_4	D_5	D_6	D_7	D_8	D_9	D_{10}	D_{11}	D_{12}
<u>Tetralin</u>													
D/P	28	32	22	11	5	1	1	0	0	0	0	0	0
P/D	1	1	3	3	4	3	3	4	6	11	21	23	17
N/D	1	1	2	3	3	2	3	1	4	9	23	30	18
<u>Naphthalene</u>													
D/P	30	32	21	10	4	2	1	0	0	-	-	-	-
P/D	4	6	7	11	14	20	18	13	7	-	-	-	-
N/D	1	2	4	7	11	17	21	22	15	-	-	-	-

TABLE 7
ISOTOPIC COMPOSITION OF THE RECOVERED TETRALIN

Experiment	Incorporated Isotope	Atom % Isotope	Isotope Distribution (%)		
			H_{ar}	H_{α}	H_{β}
D/P	2H	13.5	10	76	14
P/D	1H	23.4	8	75	17
N/D	1H	18.6	9	74	17

The data from Experiment D/P also indicate that there is direct incorporation of deuterium gas into the coal. At the end of Experiment D/P there was only 13.5% deuterium in the tetralin. The α -aliphatic position of tetralin contained 31% deuterium ($13.5 \times 0.76 \times 3$) at the end of the experiment. Nevertheless, some of the coal products (asphaltene, preasphaltene, and residue), which formed throughout

the duration of the reaction, contained considerably more deuterium. This large amount of deuterium incorporation into the coal products strongly indicates that there is also a direct route for deuterium incorporation into the coal without the participation of tetralin.

In Experiments P/D and N/D, tetralin- d_{12} was used. The following observations can be made regarding these experiments:

- 1) In these experiments, the D_{11} and D_{10} (that is, H_1 and H_2) species predominate in the recovered tetralin. This is similar to Experiment D/P, in which the D_1 and D_2 species predominate. The predominance of the D_{11} and D_{10} species, together with the NMR analysis of the solvent indicating that 74-75% of the incorporated protium is in the α -position (Table 7), indicates that the α -tetralinyl radical has an important role in the hydrogen transfer. This is true for hydrogen transfer from the gas phase into the coal (Experiment P/D) as well as for hydrogen transfer from one site in the coal structure to another (Experiment N/D).
- 2) In contrast to Experiment D/P, where no species containing more than six deuterium atoms were detected, species with fully exchanged hydrogen (D_0) were found in each experiment. The extent of isotopic exchange was greater in these experiments because in contrast to Experiment D/P, isotopic exchange between the coal and the donor solvent could take place.
- 3) There is only a small difference between the isotopic distribution of the recovered tetralin obtained in Run P/D on the one hand, and Run N/D on the other. This indicates that the extent of isotopic exchange between the coal and the solvent is greater than it is between the hydrogen gas and the solvent. This same result is further substantiated by the data shown in Table 7.
- 4) The isotopic distribution found in the naphthalene is similar to that observed in the tetralin in Experiment N/D in that the least exchanged species (D_4 - D_8) are predominant. The isotopic distribution of the recovered naphthalene from Experiment P/D shows relatively large values for each of the species of low deuteration (D_0 through D_4), which indicates that a significant amount of the gas-phase protium exchanged with the naphthalene.

2. NMR Analyses

The recovered solvents were analyzed by proton and deutron NMR spectroscopy. As an example, the deutron NMR spectrum of the recovered solvent from Experiment D/P is shown in Figure 2. The tetralin α -aliphatic and β -aliphatic absorptions are shown at 1.8 ppm and 2.8 ppm, and the aromatic absorption of tetralin at 7.1 ppm. The aromatic absorptions at 7.4 and 7.8 ppm correspond to the β - and α -positions in naphthalene. There are additional absorptions in the spectrum (at 0.9, 1.3, 2.3, and 6.9 ppm) corresponding to deuterated alkylbenzenes, indan, methylindan, and cis- and trans-decalins, which form in small amounts during the reactions.

The isotopic composition data of the recovered tetralin, as determined by NMR analysis, are shown in Table 7. In Experiment D/P where tetralin- h_{12} and deuterium gas were used, 13.5 atom % deuterium was found in the recovered tetralin. In the other experiments, where fully deuterated tetralin was used, the protium incorporation ranged from 18.6% to 23.4%. The amount was larger in the tetralin from the experiment with the protium atmosphere (P/D) than from the experiment with the nitrogen atmosphere (N/D)--23.4 versus 18.6 atom % 1H .

The distribution of the incorporated isotope among the three structurally different sites in the solvent was nearly identical in each experiment. Approximately 75% was incorporated in the α -aliphatic position, 16% in the β -aliphatic, and 9% in the aromatic position. These proportions did not change significantly regardless of whether the reaction was conducted under protium or nitrogen pressure. The N/D system was also tested using reaction times of 1/4 and 1/2 hour. It was found⁽⁹⁾ that the extent of isotopic exchange with the solvent increases with time; however, the ratio of exchanged hydrogen in the three different structural positions of the solvent remains constant within this reaction time range (1/4 to 1 hour).

The following conclusions have been drawn from these measurements: (1) the relative reactivities of the α -aliphatic, β -aliphatic, and aromatic C-H bonds of tetralin at 425°C for ^1H - ^2H isotopic exchange between tetralin and coal are: 75:16:9; (2) these ratios do not change significantly regardless of whether N_2 or $^1\text{H}_2$ cover gas or whether tetralin- d_{12} / $^1\text{H}_2$ or tetralin- h_{12} / $^2\text{H}_2$ reactant combinations are used.

ACKNOWLEDGEMENT

This work was conducted by Rockwell International for the U.S. Department of Energy under Contract DE-AC22-77ET11418.

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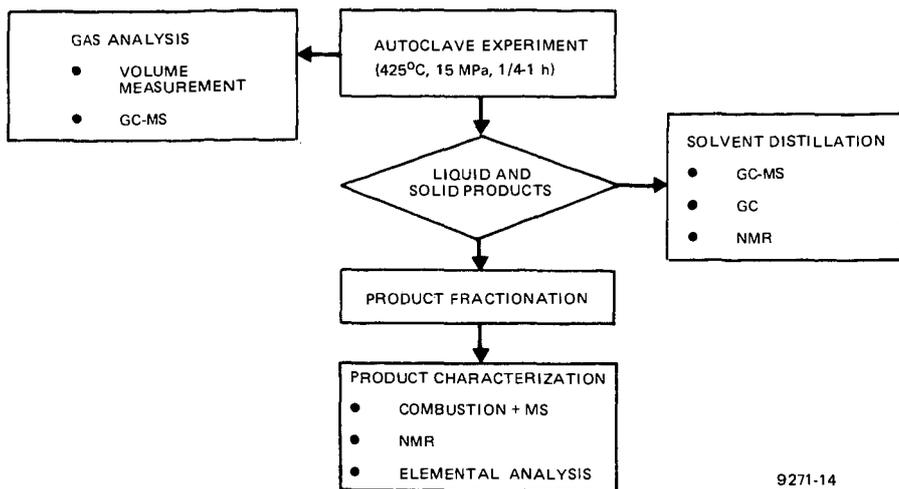


Figure 1. Experimental Procedure

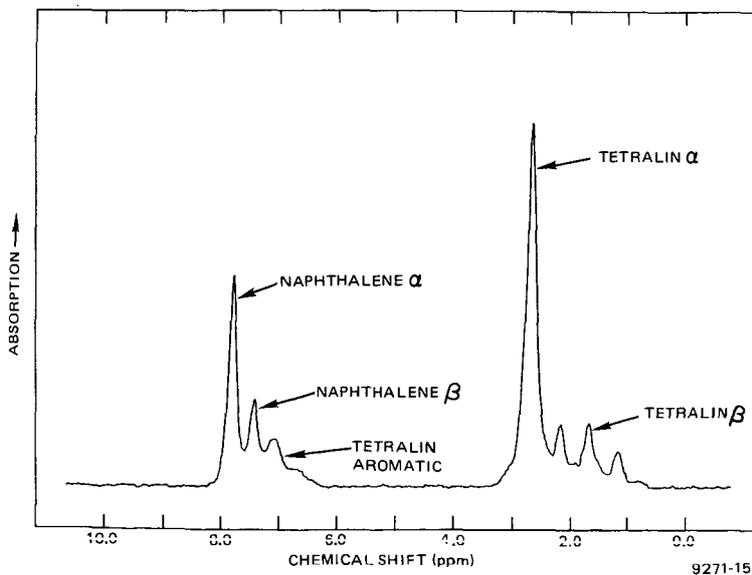


Figure 2. Deuteron NMR Spectrum of Recovered Solvent from Experiment D/P