

DEUTERIUM TRACER METHOD FOR INVESTIGATING THE CHEMISTRY OF COAL LIQUEFACTION

Raymund P. Skowronski, Laszlo A. Herydy
Rockwell International, Atomic International Division
8900 De Soto Avenue, Canoga Park, California 91304

Joseph J. Ratto
Rockwell International, Corporate Science Center
1049 Camino Dos Rios, Thousand Oaks, California 91360

INTRODUCTION

Conversion of coal to liquids by hydrogenation involves an increase of the hydrogen content of the coal. The effective use of this costly gas is, therefore, of significant importance to commercial hydrogenation processes. An intensive research effort has been under way to obtain a better understanding of the hydrogenation reaction mechanisms and thereby to improve hydrogen utilization and the efficiency of the process. This paper describes the development of a deuterium tracer method for the investigation of the mechanism of coal hydrogenation.

The deuterium tracer method consists of conducting coal hydrogenation experiments with deuterium, or deuterium and a deuterated donor solvent, separating the products by solvent-fractionation and analyzing the fractions for protium and deuterium structural types by proton and deuterium NMR spectrometry. In an alternative application of the method, which has been investigated, pairs of hydrogenation experiments are conducted, one with protium and one with deuterium, under identical experimental conditions. The hydrogenated products are separated by solvent-fractionation and the fractions are analyzed for hydrogen structural types by proton NMR spectrometry. The difference between the two spectra gives a quantitative measure of the hydrogen which is incorporated into different structural positions in the coal.

In the past, relatively little use has been made of deuterium as an isotopic tracer for investigating coal chemistry.^(1,2) Very recently, however, renewed interest in the applications of deuterium to coal science has been evident.⁽³⁻⁵⁾

EXPERIMENTAL

A high volatile A bituminous coal (81.8% C, dmmf basis) from the Loveridge Mine, Pittsburgh Seam, was used. The coal was ground to -200 mesh and stored under dry nitrogen until used. It then was dried at 115°C for 4 h before use.

High-purity (99.95% according to the supplier's specifications) protium and technical grade (>98.8 atom % deuterium and total hydrocarbons <1 ppm according to the supplier's specifications) deuterium were used. The benzene, hexane isomer mixture, and methanol utilized for the solvent-fractionation analyses were all Baker reagent grade. Chloroform-d was used as the solvent for the NMR spectrometric analyses.

The experiments were performed in a 1-liter stirred autoclave (Autoclave Engineers). The combined solid and liquid products from each of the hydrogenation experiments were solvent-fractionated into oil, asphaltene, benzene-methanol soluble, and residue fractions. Samples of fractions from those experiments in

which deuterium was used were combusted, and the resulting water was collected. The water samples then were analyzed by mass spectrometry (MS) to determine the protium and deuterium contents of each.

The product gases were analyzed by gas-solid chromatography coupled with mass spectrometry (GC-MS) to determine both the amount of each component in the gas phase and its isotopic composition. Both the MS and GC-MS were performed by Shrader Analytical and Consulting Laboratories, Inc.

The NMR spectra of the soluble fractions were obtained using a JEOL FX60Q Fourier Transform NMR Spectrometer. Elemental analyses were conducted with a standard combustion train.

RESULTS AND DISCUSSION

Exploratory hydrogenation experiments were conducted to establish baseline conditions for the systematic investigation of deuterium incorporation. The criterion that was established for baseline conditions was that the benzene-soluble portion of the products be 25-50 wt % of the total products. Moderate conversion to benzene solubles was desired because it was expected that isotopic scrambling and nonspecific deuterium incorporation could be kept to a minimum under such reaction conditions.

The results of the exploratory experiments indicated that an experiment performed at 400°C, 3200 psig, for 1 h, with a 100 rpm stirring rate, should give the desired quantity of soluble products. Accordingly, the first pair of protium/deuterium experiments (4 and 5) was conducted under these conditions. The second pair of hydrogenation experiments (6 and 7) was performed at a lower temperature and for a shorter reaction time in order to investigate deuterium incorporation at a very low conversion. The parameters for each experiment were 380°C, approximately 3000 psig, and 15 minutes reaction time. The yield of soluble products and the degree of deuterium incorporation were considerably lower than in the first pair of experiments.

The results of both pairs of experiments are summarized in Table 1. In both experiments, the atom percent deuterium content of the fractions increased from the oil (hexane soluble) to the less soluble fractions and it was highest in the insoluble residue.

Table 2 lists the deuterium/protium ratios for the structural positions of the various fractions from Experiment 4. These numbers indicate the relative deuterium content in each position. The higher the number, the greater the deuterium incorporation in this position relative to other structural positions. The term ${}^2\text{H}_x$ refers to the quantity of deuterium that is in a specific structural position and, therefore, $({}^2\text{H}_x/{}^2\text{H})$ refers to the fraction of the total deuterium that is in a given structural position. Similarly, $({}^1\text{H}_x/{}^1\text{H})$ refers to the fraction of the total protium that is in a given structural position.

Significant specific deuterium incorporation is noted in the α -alkyl (benzylic) positions in all the fractions and in the γ -alkyl positions of the asphaltene fraction. Large specific incorporation of deuterium in α -alkyl positions is illustrated in Figure 1, where the proton and deuterium NMR spectra of the oil fraction from Experiment No. 4 are compared. The deuterium incorporation in the γ -alkyl position of the asphaltenes is quite interesting because protium-deuterium exchange is expected to be relatively low in such a structural position. Further research will be conducted to establish whether this finding is related to the mechanism of asphaltene production.

The value for the β -alkyl region of the benzene-methanol fraction is equivalent to the γ -alkyl value for the asphaltene fraction. Data from a number of other experiments, however, indicate that the β -alkyl value is atypical, while the γ -alkyl value is typical.

A coal hydrogenation experiment was conducted with $^2\text{H}_2$ and tetralin- d_{12} at 400°C and 3000 psig. Significant specific deuterium incorporation was observed in the α -alkyl position in all fractions. Similarly, most of the protium in the recovered tetralin- d_{12} was concentrated in the α -alkyl position.

Another set of experiments was designed to test the reactions of coal with deuterium under 3000 psig pressure at different temperatures and under different degrees of contact opportunity. The gaseous products from each of these experiments were analyzed by GC-MS to determine their isotopic composition. Together with data on the composition of the solvent-fractionated liquid and solid products, this information is being used to develop a tentative mechanism for the coal hydrogenation reaction.

The two techniques used to determine into which structural positions in the coal deuterium is incorporated during hydrogenation were discussed in the introduction. The measured values of deuterium incorporation, obtained from deutron NMR spectrometry, were compared with the calculated values obtained from proton NMR spectrometry. In those cases where the ^2H content of the sample was over 10-15 atom % there was good agreement between the calculated and measured values for deuterium incorporation.

ACKNOWLEDGMENT

This research was supported by the U.S. Department of Energy under Contract EF-77-C-01-2781.

REFERENCES

1. Y. C. Fu and B. D. Blaustein, *Chem. Ind.*, 1257 (1967)
2. T. Kessler and A. G. Sharkey, Jr., *Spectrosc Lett.*, 1, 1977 (1968)
3. F. K. Schweighardt, B. C. Bockrath, R. A. Friedel, and H. L. Retcofsky, *Anal. Chem.*, 48, 1254 (1976)
4. A. F. Gaines and Y. Yürüm, *Fuel*, 55, 129 (1976)
5. J. R. Kershaw and G. Barrass, *Fuel*, 56, 455 (1977)

TABLE 1
SUMMARY OF RESULTS FOR EXPERIMENTS 4-7

Parameter	Expt. 4	Expt. 5	Expt. 6	Expt. 7
Reactant Gas	$^2\text{H}_2$	$^1\text{H}_2$	$^1\text{H}_2$	$^2\text{H}_2$
Reaction Time (h)	1.0	1.0	0.25	0.25
Temperature ($^{\circ}\text{C}$)	400	400	380	380
Pressure (psig)	3200	3200	2700	3000
Reactor	1 Liter 250 Milliliters			
Products (%)	Atom % ^2H (Expt. 4)		Atom % ^2H (Expt. 7)	
Oil	22	22	5	5
Asphaltene	25	25	<1	*
Benzene-Methanol Soluble Fraction	6	6	7	7
Insoluble Residue	47	47	87	87
				19.5

*Insufficient sample for analysis

TABLE 2
 COMPARISON OF PROTIUM AND DEUTERIUM
 DISTRIBUTIONS IN COAL HYDROGENATION PRODUCTS
 (EXPERIMENT 4)

Functional Region	$(^2\text{H}_x/^2\text{H})/(^1\text{H}_x/^1\text{H})$ Ratio		
	Oil	Asphaltene	BMS
	Experiment 4		
γ - Alkyl	0.6	1.2	0.9
β - Alkyl	0.5	0.6	1.2
α - Alkyl*	2.2	1.9	1.5
Aromatic**	0.9	0.8	0.8

*Includes α^2 - Alkyl Region
 **Includes Phenolic Region

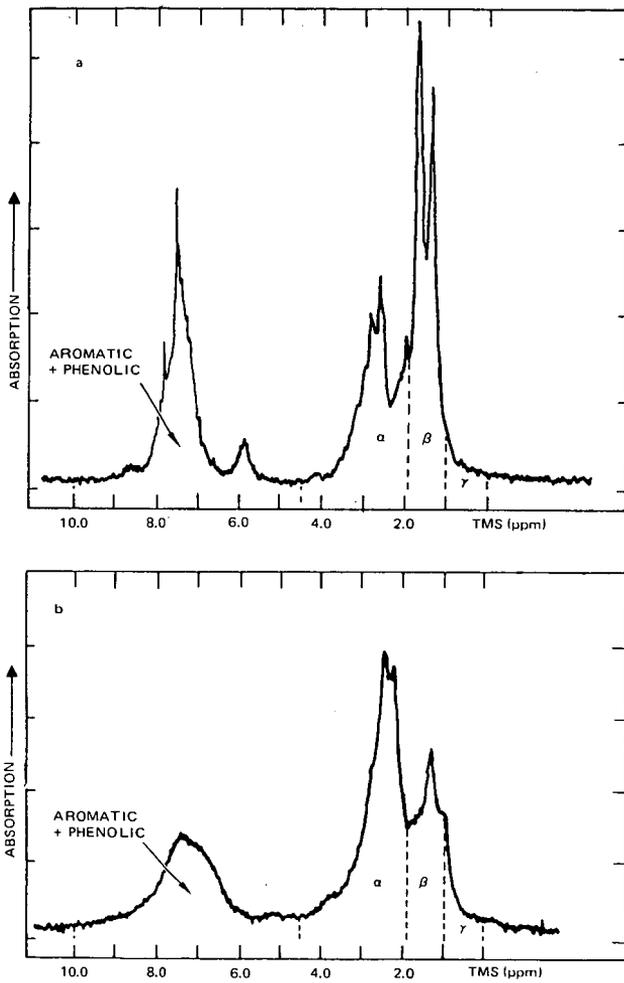


FIGURE 1. PROTON^(a) AND DEUTERON^(b) NMR SPECTRA OF THE OIL FRACTION FROM EXPERIMENT No. 4