LOW-RANK COAL LIQUEFACTION H-DONOR STUDIES USING ^2H NMR

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Several batch autoclave experiments were carried out using natural abundance 30.7 MHz ^2H NMR spectroscopy of product fractions to assess H-donor activity during lignite liquefaction. ^2H NMR observations of deuterium enrichments and measurement of ^2H NMR distributions have been used to investigate liquefaction reactions (1-3).

The development of high field superconducting magnets that operate in the Fourier transform mode with high sensitivity probes has made it possible to monitor liquefaction reactions by natural abundance ^2H NMR (0.0156% natural abundance). It is, therefore, no longer necessary to add large amounts of deuterated solvents or even large amounts of deuterated H-donors which swamp out critical aspects of the liquefaction reaction. The use of natural abundance ^2H NMR allows the investigator to examine typical liquefaction reactions without disturbing the system by the addition of large amounts of extraneous materials.

Martin et al. demonstrated recently that very important and often very spectacular variations may be found in the internal distribution of deuterium within molecules (4, 5). Measurement of the naturally abundant ^2H NMR distribution may be used to provide valuable information on the selectivity of ^2H repartition. Martin et al. applied measurements of this type to determine the origin of natural products such as alcohols in which samples from various sources with different histories had different ^2H NMR distributions (4).

It may be inferred from the work of Cronauer et al (6) and of Brower (7), that the method of Martin may be applied to the investigation of the reactions of H-donors during coal liquefaction. Brower (7) reported that the H/D kinetic isotope effect for the reaction of coal with tetralin containing deuterium at the alpha positions is 2.1 ± 0.1 at 335°C. The reaction mixture was 1 g of deuterated or undeuterated tetralin with 1 g of subbituminous coal in glass ampules. Rates of reaction were compared by monitoring the naphthalene/tetralin ratios.

When Cronauer (6) carried out liquefaction of Powhatan No. 5 coal in 100% 1,2,3,4-d_4-tetralin solvent and in 100% d_{12}-tetralin, he also showed clearly that the abstraction of ^1H from a hydroaromatic carbon having one ^2H and one ^1H substitutent is greatly preferred. Since the natural abundance of ^2H is only 0.015%, the probability that a carbon would have two ^2H substituents is very, very small. It is therefore possible to use the natural system as an *in situ* probe for comparing reactivities of H-donors under actual liquefaction conditions.

If reactions occur which involve a hydroaromatic carbon, and ^1H is preferentially abstracted each time, the ^2H distribution will show an increase in that spectral region. If a large amount of H-donor activity in the regions α and β to aromatic rings (H_α and H_β) occurs during liquefaction, the ^2H distribution should reflect this by showing a corresponding increase in the 5.0 - 1.8 ppm region of the natural abundance ^2H NMR spectrum.

Since the natural abundance ^2H NMR spectrum reflects the reactive history of the sample, adequate blank experiments must be performed to determine original or non-affected ^2H distributions. They always differ from the proton NMR distributions

when the sample has reactive history that involved H-transfer reactions. Since we used a process coal-derived liquid as our solvent, the blank autoclave run was essential.

Another aspect of liquefaction involves the interaction of processing gases with the solvent or directly with the coal or coal fragments. This question has been addressed by several investigators (1, 3, 8, 9, 10). The types of molecules that are active during liquefaction either through exchange reactions, through hydrogenation, hydrogen transfer, or through direct reaction with H_2 gas may be inferred by substituting deuterium gas $^2H_2$ for the H_2 in the reactive gas mixture. The reactive sites are then located by ^2H NMR of the enriched reaction mixture.

Experimental

Autoclave experiments were designed to simulate processing conditions in our continuous process bottoms recycle liquefaction unit.

The experiments were carried out in a 1-liter hot-charged autoclave (11). The coal (65 g maf) solvent (120 g) slurry was hot-charged into the preheated autoclave, reaching the operating temperature of 450°C in less than two minutes. The reactant gas (40 g, unlabeled) was 50/50 H_2/CO or $^2H_2/CO$ at a pressure of 3700 psig under reaction conditions. Residence time was 20 minutes after which the entire contents of the autoclave were transferred into a quench vessel, cooled and depressurized at room temperature. Gases were analyzed and the product slurry was distilled (ASTM D-1160). The trap contents (mainly water), the ASTM D-1160 distillate, and vacuum bottoms were subjected to separations and NMR analyses.

Mass balances were obtained using a different portion of the slurry and analyzing it for water, ash, tetrahydrofuran (THF) solubility, and vacuum distillate at 5 torr. The additive, when used, was 1,2,3,4-tetrahydrophenanthrene (THPhen) (0.33 g). The run matrix is shown in Table I.

TABLE I

AUTOCLAVE TESTS WITH BIG BROWN LIGNITE, RECYCLE SLURRY DISTILLATE, 450°C and 3400-3700 PSI TOTAL PRESSURE

Run No.	Processing Gas	Additive
3	H_2/CO	None
4	H_2/CO	THPhen
5	$^2H_2/CO$	THPhen

The coal and solvent chosen for these tests were a Texas lignite from the Big Brown mine and a recycle slurry ASTM D-1160 distillate from a continuous processing unit (CPU) run carried out at UNDERC using the same coal. The solvent was distilled from slurry collected on the thirteenth bottoms recycle pass. A cold trap was used during distillation to assure the collection of all volatile oils and water.

The ASTM D-1160 distillate of the autoclave product was further separated into alkanes, aromatics, and polars by open column chromatography on neutral silica gel with pentane, methylene chloride, and methanol as elution solvents. The fractions were cleanly separated as shown by examination of their 200 MHz ^1H NMR spectra. The vacuum bottoms (10 g) were Soxhlet extracted with refluxing $CHCl_3$ (500 ml) for 20 hours, followed by THF (500 ml) for 20 hours. The residue consisting of inorganic

material, insoluble organic matter and unreacted coal amounted to 65-70% of the vacuum bottoms. Chloroform extracted 25-30% while the remainder of 3-4% was extracted with THF.

NMR spectra were obtained at 200 MHz in CD_2Cl_2 for protons and at 50.3 MHz in $CDCl_3$ for ^{13}C using pulsing conditions appropriate to the sample. ^2H NMR spectra were pulsed at 30.7 MHz 1-30,000 times depending on the sample. A 45° flip angle was used with an acquisition time of 4 seconds and a delay of 4 seconds. The solvent used was methylene chloride, CH_2Cl_2.

^2H enrichments of the fractions from Experiment 5 were determined by standard addition of CD_2Cl_2 to a preweighed oil sample. The standard addition line gave a linear regression value of r = 0.993. The sample was weighed tightly covered and diluted immediately with CH_2Cl_2. The enrichment of the water samples from the distillation trap was determined directly against a standard D_2O in H_2O curve whose linear regression value of r was 0.9999.

RESULTS AND DISCUSSION

Effect of Added H-Donor

Test numbers 3 and 4 were identical except that a small amount of an H-donor, THPhen, was added to Test 4 (Table I). Total percent conversion was essentially the same for Runs 3 and 4 (72%, 70%). Conversions to THF solubles were 56% and 60%, respectively.

The 50 MHz ^{13}C spectra for the light oils, the distillable oils, and their fractions and the $CHCl_3$ soluble vacuum bottoms were very similar for Runs 3 and 4. The 200 MHz ^1H NMR spectra of the products were likewise indistinguishable from run to run with corresponding fractions showing the same spectral features.

The natural abundance 30.7 MHz ^2H NMR distributions are, however, quite different from each other for the autoclave tests with and without the addition of small amounts of the H-donor, THPhen (Table II). These differences are mainly seen in the alpha + beta and in the aromatic regions of the spectrum (Figure 1). The change in the alpha + beta region gave a run 4/run 3 ratio of 1.25, clearly indicating increased H-transfer activity during Run 4.

TABLE II

^2H NMR AREA DISTRIBUTIONS FOR AUTOCLAVE TEST
WITH BIG BROWN TEXAS LIGNITE, H_2/CO, 450°C, MPa (3700 PSI)

	Run 3 (Area %)	Run 4 (Area %)	Run 4/3 (Area %)
Aromatic (9.6 - 5.8 ppm)	39.7	45.9	1.16
Alpha + Beta (5-1.8 ppm)	28.6	35.7	1.25
Other (1.8-0.1 ppm)	31.6	19.4	0.61

To test the effect of H-donor addition without liquefaction reaction, two portions of liquefaction recycle solvent distillate were equilibrated for three weeks at room temperature with and without the addition of the same amount of H-donor. When compared by ^2H NMR spectroscopy, there was no change in ^2H distribution.

The change in the ^2H distribution under liquefaction conditions therefore may be attributed to an increased cumulative isotope effect during liquefaction with small amounts of added H-donor. The small increase in THF soluble product, 60% as compared with 56% may be related to the H-donor activity increase but is not as notable during autoclave testing as it would be in CPU recycle operation.

Processing with $^2H_2/CO$

Autoclave Test 5 was conducted with deuterium-labeled 50/50 $^2H_2/CO$ and added THPhen. A deuterium-enriched product was obtained. Total conversion was 67% and conversion to THF solubles was 50%. The 50% conversion of lignite to THF solubles in Run 5 processed with $^2H_2/CO$ is significantly lower than the 60% conversion in Run 4 processed with $^1H_2/CO$. The deuterium isotope effect resulting from the use of $^2H_2$ rather than $^1H_2$, in the gas mixture would be expected to lower the yield of THF solubles since the rate of reaction of $^2H_2$ is expected to be slower than the rate of reaction of $^1H_2$ (7).

Examination of the product by ^2H NMR using the methods described in the Experimental section showed that ^2H entered every fraction of the product, including the H_2O, the ASTM distillate, and the soluble vacuum bottoms (Table III). The water was the most highly enriched fraction, probably due to the easy exchange of water hydrogens with the $^2H_2$ gas. Other hydrogens expected to exchange rapidly with $^2H_2$ gas are those ortho and para to phenolic OH groups and methylene hydrogens alpha and beta to aromatic rings. The fractions (polars, aromatics, ASTM D-1160 dist.) containing these types of bonds show appreciable enrichment (Table III). In the case of the aromatic fraction (Figure 2), it is even possible to assign some of the most exchangeable hydrogens to specific compounds. For example, the peaks at 3.9 ppm and 3.6 ppm in the proton NMR spectrum (Figure 2, top) can be plainly seen as enriched peaks in the deuterium NMR spectrum (bottom). These peaks are assigned to the methylene hydrogens of fluorene and acenaphthene respectively. It is notable that very little enrichment or exchange occurs on terminal methyl carbons of alkyl chains (0.9 ppm); however, the methylene region (~1.2 ppm) is enriched.

TABLE III

PRODUCTS FROM AUTOCLAVE TEST 5 (BIG BROWN TEXAS LIGNITE, $^2H_2/CO$, 450°C, 3400 PSIG), DETERMINED BY ^2H NMR

Product	No. Grams in Product	Wt % ^2H	Wt % H in Sample	*Enrichment Factor
Water	29.31	2.62	11.11	760
ASTM D-1160 Distillate	109.4	0.606	7.17	270
Fraction of Distillate:				
Alkanes	11.4	0.58 (by diff.)	14.88	120
Aromatics	44.9	0.542	7.20	240
Polars	30.9	0.967	7.81	400
ASTM D-1160 $CHCl_3$ Soluble Bottoms	25.74	0.605	5.84	330

$$* \quad \frac{\text{atom \% } ^2H}{0.0156\% \text{ (Natural Abundance)}}$$

Figure 3 shows the comparison of the ASTM D-1160 distillate polar fraction 200 MHz ^1H NMR spectrum (top) and the 30.7 MHz ^2H NMR spectrum (bottom). The aromatic region of the ^2H spectrum was more enriched than the rest of the spectrum.

Since considerable amounts of ^2H (about 35 wt. % of the $^2H_2$ added) entered the product, it is impossible to assign any of the incorporated ^2H to reaction product rather than exchange product. However, it is possible to note that some portions of the product that were enriched are materials that do not undergo exchange easily. The ^2H NMR spectrum of the alkanes separated from the ASTM D-1160 distillate shows incorporation of deuterium into both methylene and methyl regions of the spectrum and the overall enrichment of the alkane fraction is ~120 x natural abundance.

The most actively enriched portions of the alkanes, aromatics, and polars may be seen by comparing Autoclave Run 4 (H_2/CO) with Run 5 ($^2H_2$/CO), Table IV and to compare ASTM D-1160 distillate oils, Table V.

Summary

1. Differences in natural abundance ^2H NMR distributions resulted from differences in the processing history of the samples.

2. The addition of small amounts of H-donor to a liquefaction reaction changed the natural abundance ^2H NMR distribution with respect to an identical run without added donor. The ^1H distribution and ^{13}C distribution were unchanged. Changes were probably the result of increased hydrogen transfer activity and the cumulative deuterium isotope effects.

3. Tests made using $^2H_2$/CO showed product incorporation of ^2H to >270 times the natural abundance as determined by standard addition ^2H NMR. The ^2H distribution was not the same as in the unlabeled test.

4. ^2H entered all fractions of the product during the test with $^2H_2$/CO, including ASTM distillate alkanes, phenols and polars, H_2O and soluble vacuum bottoms. Polars and H_2O were the most enriched fractions, probably due to easy H-exchange.

5. Processing with $^2H_2$/CO resulted in decreased conversion to THF solubles when compared with an identical run with $^1H_2$/CO.

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TABLE IV

^2H NMR AREA PERCENTAGES OF SEPARATED FRACTIONS OF RUN 4 AND RUN 5 PRODUCT ASTM-1160 DISTILLATE

Integrated Area %, Column Fractions, ASTM Distillate		Run 4	Run 5	Run 5/4
Alkanes	^2H_o	100.0	100.0	N/A
Aromatics	$^2H_{ar}$	50.0	35.8	0.72
	$^2H_{\alpha+\beta}$	39.3	51.1	1.31
	^2H_o	10.7	13.1	1.19
Polars	$^2H_{ar}$	33.8	43.2	1.28
	$^2H_{\alpha+\beta}$	50.2	42.9	0.85
	^2H_o	16.0	13.9	0.87

TABLE V

COMPARISON OF RESULTS WITH LABELED AND UNLABELED SYNGAS ($CO/^2H_2$), (CO/H_2), ^1H NMR AREA PERCENTAGES, ^2H NMR AREA PERCENTAGES

Integrated Area, % ASTM D-1160 Distillate	Run 4 (unlabeled)	Run 5 (labeled)	Run 5/Run 4
$^1H_{ar}$	37.7	35.0	0.93
$^1H_{\alpha+\beta}$	31.4	34.3	1.09
^1H_o	30.9	29.9	0.97
$^2H_{ar}$	45.9	43.7	0.95
$^2H_{\alpha+\beta}$	35.7	43.1	1.21
^2H_o	19.4	13.2	0.68

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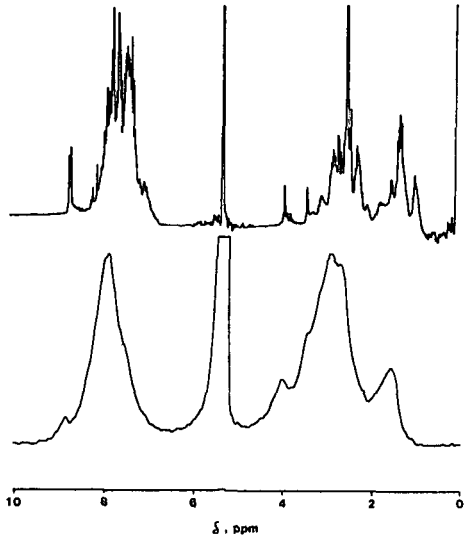

FIGURE 2. ^{1}H NMR spectrum (top) and ^{2}H NMR spectrum of the aromatic fraction of autoclave Test 5 with Big Brown Texas lignite and $^{2}H_2/CO$.

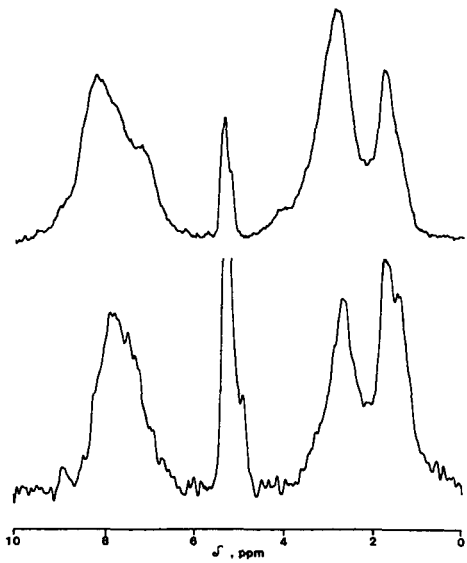

FIGURE 1. ^{2}H NMR spectra of (top) Run 4 (with added THPhen) and (bottom) Run 3 (without THPen). The peak at 5.2 ppm is the NMR solvent, CH_2Cl_2 (top) and CH_2Cl_2 with added CH_2Cl_2-d_2 (bottom). The aromatic region is designated as 9.6-5.8 ppm, the α and β region as 5.0 to 1.8 ppm and other region as 1.8 to 0.1 ppm.

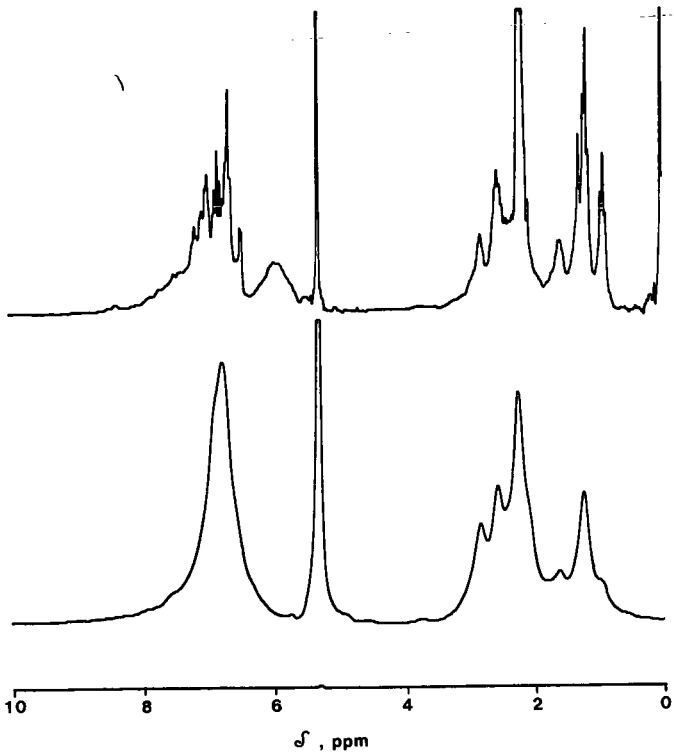

FIGURE 3. ^{1}H NMR spectrum (top) and ^{2}H NMR spectrum (bottom) of the polar fraction of autoclave Test 5 with Big Brown Texas lignite and $^{2}H_2/CO$.