COAL LIQUEFACTION USING DEUTERIUM-LABELED ANTHRACENE OIL SOLVENT

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ABSTRACT

In order to better understand the reactions of heteroatom-containing organics which occur during liquefaction of subbituminous coal, it is necessary to distinguish between coal-derived and solvent-derived species. A coal-derived liquefaction solvent, A04, was deuterium-labeled by a method developed at the University of North Dakota Energy and Minerals Research Center and found to be stable under liquefaction conditions. The deuterium-labeled A04 was reacted in the presence of unconverted coal (tetrahydrofuran-insoluble material from a previous autoclave liquefaction test), water, carbon monoxide, and hydrogen sulfide at 350°C and 1000 psia for 30 minutes. No significant degradation in isotopic purity was observed in the mass spectra of the individual deuterated species comprising approximately 95 wt% of the deuterated solvent. Tests were also conducted with raw coal under similar liquefaction conditions to determine the amounts of coal-derived compounds evolved, and whether these compounds will undergo deuterium exchange with the deuterated solvent. Distillable products are being analyzed using GC/MS, and soluble and insoluble products are being analyzed using liquid proton and solid state C-13 NMR. The deuterium-labeling method has also been used to synthesize 16 model compounds including O-, S-, and N-containing aromatics to be used in future liquefaction tests. Analytical results including product component identification, coal conversion as determined by tetrahydrofuran solubility, and changes observed in NMR spectra will be presented.

INTRODUCTION

The purpose of the described research is to study the reactivity of heteroatom-containing organics in Wyodak subbituminous coal under liquefaction conditions. The liquefaction solvent specified for use in the research is a coal-derived anthracene oil (A04). Several heteroatom-containing components of A04 (dibenzofuran, dibenzothiophene, and carbazole) are thought to be produced from coal during liquefaction. Other coal-derived liquefaction products such as phenol, cresols, and quinolines are also present in A04 as minor components. Clearly, a method is needed to distinguish between coal-derived and solvent-derived heteroatom-containing product species. By producing deuterium-labeled A04 and examining its behavior under liquefaction conditions, it should be possible to differentiate between coal-derived and solvent-contained species with gas chromatography/mass spectrometry (GC/MS) and nuclear magnetic resonance (NMR) techniques.

SYNTHESIS OF DEUTERIUM-LABELED A04 LIQUEFACTION SOLVENT

Approximately 30 grams of deuterium-labeled A04 was synthesized

using a 1.0 liter autoclave constructed of "Hastelloy C", an alloy resistant to chloride ion corrosion. A six hour reaction at 300°C was carried out using 30 grams A04, and a 250 mL solution of 4% deuterium chloride in deuterium oxide with 10 mg/mL dissolved chromium metal. After cooling the autoclave overnight, the product was removed from the autoclave, dissolved in ether, washed, dried, and weighed to yield an approximate 97% recovery. Figure 1 shows a gas chromatogram of A04 before and after deuterium-labeling. The similarity in the two chromatograms demonstrates that essentially no degradation or loss due to volatilization of any major components occurred as a result of undergoing the deuteration reaction. Figure 2 shows representative mass spectra of several individual A04 components before deuteration (upper spectrum of each set) and after deuteration (lower spectrum). The spectra were obtained with a Hewlett Packard 5985 GC/MS using a 70 eV electron impact ionization potential. In general, isotopic purities of the individual aromatic components of the A04 were approximately 95%, as determined using GC/MS with low voltage (10 eV) electron impact ionization.

Proton NMR spectra obtained of the non-deuterated and deuterated solvents are presented in Figures 3a and 3b. Since deuterium is not detected with proton NMR, the area of the aromatic region (7-9 ppm) is greatly diminished relative to the aliphatic region (0.7-4.5 ppm) in the deuterated sample. This is because aromatic protons are more easily exchanged than aliphatic protons under the synthesis conditions utilized. Using data in Table 1, a calculation was made to estimate the extent of deuterium-for-hydrogen substitution required to produce the observed spectral difference between the deuterated and non-deuterated solvents. Assuming no exchange of deuterium for aliphatic protons, approximately 91% of the aromatic protons observed in the spectra of the original solvent would have to be replaced with deuterium to produce the observed spectra of the deuterated solvent. This value is in reasonable agreement with the 95% isotopic purity value calculated using GC/MS analysis.

STABILITY TESTING OF DEUTERIUM-LABELED A04

Following the synthesis of deuterium-labeled A04 it was necessary to determine the stability of the individual deuterated species in the solvent under liquefaction conditions. To do this, a reaction system was needed that simulated as closely as possible conditions that exist during liquefaction, without using coal. The absence of coal is required to ensure that possible degradation in the isotopic purity of a solvent-derived deuterated compound is not masked by the formation of the same compound from coal. In order to provide the system with the catalytic activity normally derived from the mineral content of coal, it was decided that the reaction mixture should contain tetrahydrofuran-insolubles (THFI) produced from an actual liquefaction reaction. To generate the THFI, an autoclave liquefaction reaction was run at 350°C and 1000 psia for 30 minutes using 383 grams Clovis Point Wyodak coal, 500 grams non-labeled A04, 36 psi H_2S, and 964 psi CO. (Based on moisture- and ash-content tests run prior to the autoclave reaction, 383 grams raw coal would provide 250 grams moisture- and ash-free (MAF) coal.) The product slurry contained 15.3% THFI, 19.4% of which was ash. The stability of deuterated A04 was tested by performing duplicate tubing bomb reactions using deuterated A04 (2.5 grams),

water, and THFI from the autoclave run. Water and THFI were added in quantities that would be supplied by a MAF coal charge of 1.25 grams. The amount of water added (0.36 grams) was calculated based on a moisture content of 20.99 wt% raw coal, as determined immediately prior to the tubing bomb tests. The amount of THFI added (0.65 grams) was calculated based on the THF solubility of the product slurry resulting from the autoclave run. All other reaction conditions including H_2S and CO pressures, and reaction time and temperature were identical to the conditions of the autoclave run.

The most important result of the stability tests on deuterated AO4 is the finding that the deuterated species comprising approximately 95 wt% of the solvent underwent no significant degradation in isotopic purity. Figure 4 displays mass spectra (70 eV) of 4 major components of deuterated AO4 before and after exposure to liquefaction conditions. The fact that the before and after spectra are essentially identical will enable distinction to be made between coal-derived and solvent-derived species found in future liquefaction product slurries resulting from reactions with deuterated AO4 and coal. For example, the assumption can be made that any non-labeled dibenzofuran resulting from the liquefaction of coal using deuterated AO4, must be derived from the coal, since all solvent-derived dibenzofuran should remain deuterium-labeled throughout the reaction.

Several minor component species displaying various degrees of degradation in isotopic purity based on mass spectral data include phenol, two cresol isomers, quinoline, and carbazole. These compounds, while displaying molecular ions of smaller mass after stability testing than before, are still distinguishable from non-labeled isotopes. Figure 5 displays the mass spectra of deuterium-labeled phenol as it appears in deuterated AO4 prior to stability testing (top spectra), deuterium-labeled phenol as it appears in deuterated AO4 following stability testing (middle spectra), and non-labeled phenol as it appears in non-labeled AO4 (bottom spectra). Coal-derived phenol (molecular ion at 94) produced during future liquefaction tests in which deuterated AO4 is used, should be easily distinguishable from solvent-derived phenol (molecular ion at 96).

Another result of the stability testing of deuterated AO4 is the conversion of approximately 24 wt% of the THFI (which by definition is unconverted coal and ash) from one liquefaction reaction, to THF-soluble products through a second liquefaction reaction under nearly identical conditions. A partial explanation of this conversion may be the fact that the residence time for the THFI was double that of the raw coal. The 24 wt% conversion value was calculated based on the ash-free weight of THF-insolubles reacted.

LIQUEFACTION OF WYODAK COAL WITH DEUTERATED AO4

After demonstrating that deuterium-labeled AO4 is stable under the previously described liquefaction conditions, duplicate tubing bomb reactions were run using labeled AO4 with Wyodak (Clovis Point) coal. The feed slurry contained a 2/1 weight ratio of labeled AO4 to MAF coal. All reaction conditions were identical to those used in the previously described tubing bomb and autoclave reactions. Liquefaction conversion of the organic content of the coal was determined by THF solubility to be approximately 41 wt%.

The product slurries obtained were analyzed using GC/MS, and liquid proton NMR.

ANALYSIS OF PRODUCTS FROM COAL LIQUEFACTION WITH DEUTERATED AO4

All GC/MS analyses were performed using methylene chloride as the solvent. Comparison of the mass spectra of deuterated AO4 in product slurries from liquefaction runs made with and without coal, has indicated that the composition and isotopic purity of the deuterated solvent recovered from both reactions are essentially identical. In an effort to demonstrate the formation of coal-derived compounds, 8 compounds were selected for comparative quantitative analysis. The compounds chosen for study (phenol, 3 cresol isomers, tetralin, naphthalene, phenanthrene, and dibenzofuran) were selected primarily because they were present in detectable quantities in both the stability test and coal liquefaction product slurries. Since any coal-derived compounds would be non-labeled, to determine whether any of the 8 compounds were formed from coal, a method was needed to compare the quantity of each non-deuterated compound to the quantity of its deuterated counterpart in both product slurries. A mass spectral technique was employed which enables the relative quantitation of the amount of material having a specified molecular ion weight, using "area counts" as units of quantitation. For example, phenol has a molecular ion at 94 mass units, while deuterated (d_2-) phenol has a molecular ion at 96. The relative quantities (in area counts) of phenol and d_2-phenol can be obtained by integrating the area under each molecular ion peak. A ratio can then be calculated relating area counts of phenol to area counts of d_2-phenol. If this ratio is calculated for the phenol quantities in the product slurries from both the stability test reaction and the reaction with coal, it is possible to ascertain whether phenol was in fact produced from coal, simply by comparing the two ratios. Table 2 is a list of area counts for the 8 non-labeled and labeled compounds present in the product slurries from both reactions. Ratios of area counts non-labeled to labeled compounds are given in column E for both reactions. The fact that the ratio of area counts of non-labeled to labeled phenol produced from the reaction with coal is approximately 4 times greater than the same ratio for the reaction with THFI, is evidence for the presence of 4 times the quantity of non-labeled phenol in the coal reaction product slurry. Since conditions during the two reactions were identical, it is logical that the extra phenol came from the coal. There is also strong evidence pointing to low-temperature (350°C) production of cresol from the coal. Since the area counts are low for tetralin (see explanation at bottom of table) evidence suggests only the possibility of tetralin formation from the coal. Based on the ratios in column E, it appears that naphthalene, phenanthrene, and dibenzofuran are present in greater quantities in the THFI reaction products than in the coal reaction products. There are two explanations, both of which may be partially responsible for this result. The first centers on the longer residence time spent under liquefaction conditions by the THFI. Since the THFI were reacted twice as long as the coal, it is possible that species which take longer to form may be more concentrated in the product slurry of the longer reaction. The second explanation deals with adduction of AO4 solvent (non-labeled) to the solid THFI during the autoclave

reaction. When the A04-containing THFI were then subjected to liquefaction conditions a second time, A04 could have been released from the THFI and rendered soluble. The preparation of the THFI from the autoclave reaction involved their separation from THF-solubles through a vacuum filtration and extraction with THF. The insoluble fraction was then dried in an oven overnight at 120°C. The coarse powder remaining constituted the THFI which were then reacted a second time. In order to determine the contribution of solvent adduction to the presence of certain species in the THFI reaction, it may be necessary to use THFI which have been "cleaned", possibly through an extended Soxhlet extraction.

The product slurries from the reactions of THFI with deuterated A04, and coal with deuterated A04 were also compared using proton NMR. Figure 6 is the NMR spectrum of the deuterated methylene chloride solubles obtained from the reaction of deuterated A04 and THFI. (Since deuterium is not detected with proton NMR, reaction products were extracted with deuterated methylene chloride.) Figure 7 is the NMR spectrum of the deuterated methylene chloride solubles obtained from the reaction of deuterated A04 and coal. These spectra can be compared to the deuterated A04 spectrum in Figure 3b. The main peaks that stand out as unique are those associated with protons on bridge carbons found in fluorene at 3.9 ppm and acenaphthene at 3.4 ppm. The acenaphthene bridge protons make up 3.3% of the area in the spectrum of deuterated A04, 3.0% of the area in the spectrum of the THFI reaction products, and 7.1% of the area in the spectrum of the coal reaction products (see Table 1). Fluorene bridge protons make up 3.9, 12.8, and 9.8% of the three spectra areas, respectively. Protons (and deuterium atoms) in these bridge positions are labile. Higher percentages of hydrogen on bridge carbons in reaction products than in the deuterated solvent, could be due to hydrogen replacing bridge position deuterium during the reactions with THFI or coal. Sources of hydrogen could be non-substituted hydrogen from the solvent, hydrogen from the coal, or hydrogen from the hydrogen sulfide used in the reaction. According to GC/FID area percent data, acenaphthene comprises 3.6% and fluorene 3.5% of the total A04. According to GC/MS data, during the reaction with coal, approximately 75% of the acenaphthene and 90% of the fluorene bridge position deuterium was replaced with hydrogen. During the reaction with THFI, approximately 25% of the acenaphthene and 90% of the fluorene bridge position deuterium was replaced with hydrogen. This indicates that in the presence of coal, acenaphthene exchanges slightly less bridge deuterium than fluorene, and exchanges significantly less in the presence of THFI. Fluorene gives up its bridge deuterium with equal ease in the presence of THFI or coal. Based on this evidence it is likely that fluorene would be a more efficient hydrogen shuttler than acenaphthene.

THE FATE OF HETEROATOM-CONTAINING AROMATICS DURING LIQUEFACTION

Another aspect of this project involves monitoring the fate of heteroatom-containing species in coal under liquefaction conditions. A tubing bomb test was run with coal and non-labeled A04 which had been "spiked" with a set of 13 deuterated heteroatom-containing compounds and 3 deuterated aromatic hydrocarbons. All the heteroatom-containing organics used have been found in coal

liquefaction products, and many have also been identified as compounds emitted in substantial amounts during the pyrolysis of Wyodak coal (2). Analysis of the product slurry is currently in progress.

Deuterated compounds were synthesized using a reagent consisting of 4% deuterium chloride in deuterated water (deuterium oxide) with 10 mg/mL added chromium metal. The amount of reagent used in each reaction was calculated to give a reaction mixture containing a 20/1 molar ratio of deuterium to aromatic hydrogen. Syntheses were performed at 200 or 300°C for 2 or 15 hours as required to yield a product with both high isotopic and chemical purity (3,4). Table 3 is a list of the compounds along with their respective chemical and isotopic purities. Dihydrophenanthrene, dihydroanthracene, and hexahydropyrene are included in the table since these compounds served as hydrogen donors in another test involving the fate of hydrogen donors under liquefaction conditions. Most of the synthesized deuterated compounds had isotopic purities that approached 95% (as determined by 10 eV low-voltage EI mass spectrometry) which is the equilibrium value expected from using a reaction mixture containing a 20/1 molar ratio of deuterium to aromatic hydrogen. It is interesting to note that the hexahydropyrene showed 12 H/D exchanges even though only four aromatic hydrogens are present on the molecule. Proton NMR analysis of the deuterated product showed that the 8 aliphatic hydrogens bonded to the carbon atoms alpha to the aromatic rings were also replaced with deuterium during the synthesis. Aliphatic hydrogens were also replaced with deuterium during the synthesis of d_6-2-methylthiophene.

CONCLUSIONS

It has been demonstrated that deuterium-labeled AO4 solvent undergoes no significant decrease in overall isotopic purity as a result of exposure to liquefaction conditions at 350°C and 1000 psia for 30 minutes. Although certain compounds such as phenol, cresols, acenaphthene, and fluorene undergo a reduction in isotopic purity under liquefaction conditions, the resulting mass spectra of the compounds are easily distinguishable from their non-deuterated counterparts. Despite a fairly low conversion, concrete evidence was found to substantiate the production of phenol and cresols during mild liquefaction of Wyodak coal. Production of tetralin was indicated but not substantiated by the data available. Analytical results from GC/MS and NMR were shown to correlate well.

REFERENCES

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TABLE 1

PROTON NMR SUMMARY

Proton Type	ppm	Normalized Proton Distribution			
		AO4	D-AO4	D-AO4 + IOM	D-AO4 + Wyodak
Aldehydic	10.0-9.0	0.3	0.1	0.0	0.1
Aromatic	9.0-5.9	73.4	18.6	29.2	24.1
Fluorenes	4.4-3.5	4.0	3.9	12.8	9.8
Acenaphthene Bridge H's	3.5-3.3	4.6	3.3	3.0	7.1
Alpha to Aromatic	3.3-1.9	11.7	29.4	23.1	25.0
Beta to Aromatic	1.9-1.5	0.4	11.4	8.1	5.0
Methylene	1.5-1.0	4.1	22.6	15.1	19.2
Methyl	1.0-0.0	1.5	10.7	8.6	9.7

TABLE 2

MASS SPECTRAL AREA COUNT DATA

A Compound	B Reaction	C Area Counts Non-labeled Compound	D Area Counts Labeled Compound	E Ratio C/D
Phenol	w/THFI	726	3959	0.24
Phenol	w/coal	3624	3863	0.94
m- & p-Cresol*	w/THFI	398	907	0.44
m- & p-Cresol*	w/coal	1146	1058	1.08
o-Cresol	w/THFI	124	399	0.31
o-Cresol	w/coal	265	387	0.68
Tetralin	w/THFI	19	80	0.24
Tetralin	w/coal	124	32	3.88
Naphthalene	w/THFI	460	47066	0.0098
Naphthalene	w/coal	59	38410	0.0015
Phenanthrene	w/THFI	2802	169659	0.017
Phenanthrene	w/coal	351	149507	0.0024
Dibenzofuran	w/THFI	722	60837	0.012
Dibenzofuran	w/coal	32	48272	0.0007

* m- and p-cresol elute as one species under the chromatographic conditions used.

Ratios in column E are area counts non-labeled aromatics to area counts labeled aromatics, in product slurries from liquefaction reactions with coal, and in product slurries from liquefaction reactions with THFI.

Area counts less than 100 are subject to substantial error and

should not be used as conclusive quantitative data. Low area counts are listed in this table solely to provide a potential indication of some of the detectable product quantities resulting from the two reactions.

TABLE 3

ISOTOPIC AND CHEMICAL PURITIES OF DEUTERATED COMPOUNDS

Compound	Isotopic Purity (%)	Chemical Purity (%)
d8-dihydrophenanthrene	96.6	81.5
d12-hexahydropyrene	97.0	86.3
d_7-dihydroanthracene	97.2	89.0
d10-phenanthrene	95.3	101.0
d10-pyrene	95.0	98.8
d10-biphenyl	94.9	98.5
d7-naphthol	89.7	97.7
d5-phenol	96.0	95.9
d4-o-cresol	91.0	97.5
d3-3-ethyl-5-methylphenol	94.1	96.1
d4-4n-propylphenol	96.5	53.1
d3-3-methylcatechol	97.0	91.4
d8-dibenzofuran	95.4	100.0
d9-phenanthridine	79.5	100.0
d7-quinoline	64.7	102.0
d_5-pyridine	99.0	100.0
d8-carbazole	94.7	105.0
d8-dibenzothiophene	95.3	100.0
d6-2-methylthiophene	94.8	82.3

Chemical purity values are + or - 5%.

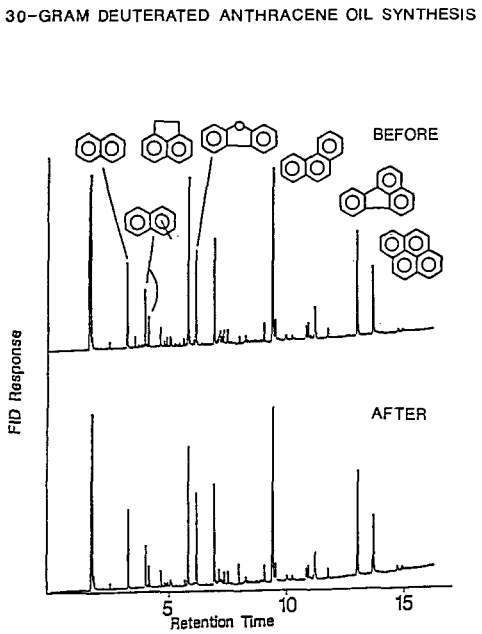

Figure 1. Gas chromatogram of AO4 before (top) and after (bottom) deuteration.

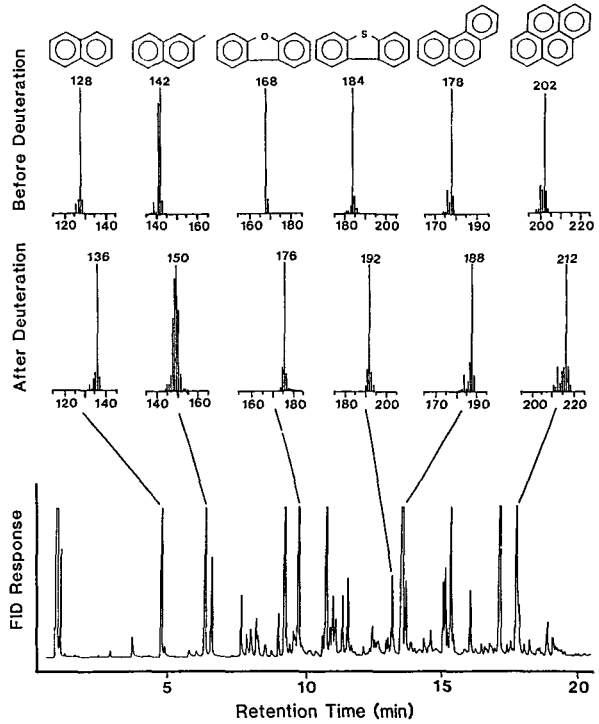

Figure 2. Mass spectra of components of AO4 before (top) and after (bottom) deuteration.

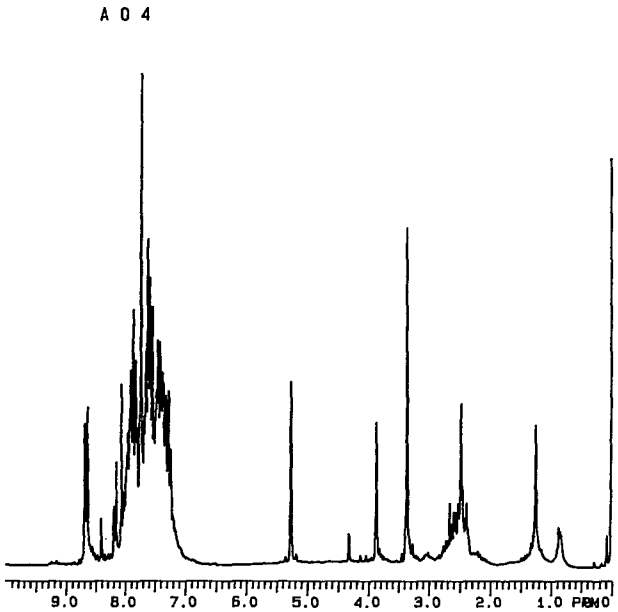

Figure 3a. Proton NMR spectrum of non-deuterated AO4.

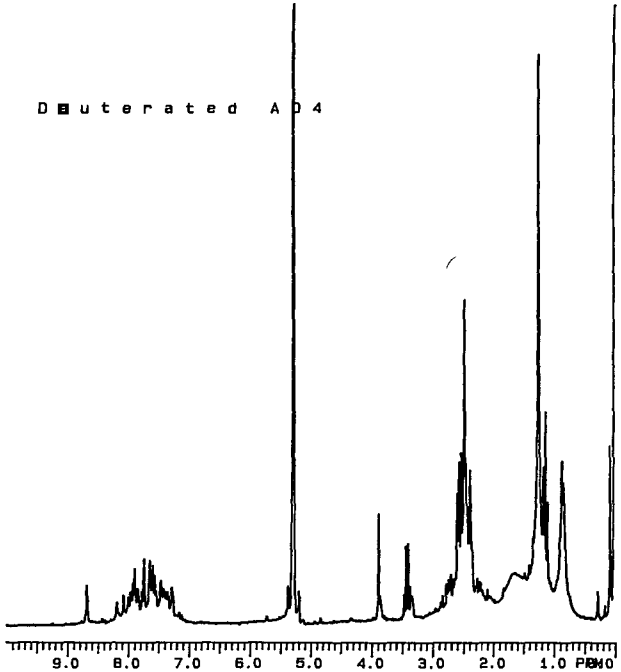

Figure 3b. Proton NMR spectrum of deuterated AO4.

Before (left) and after (right) liquefaction.

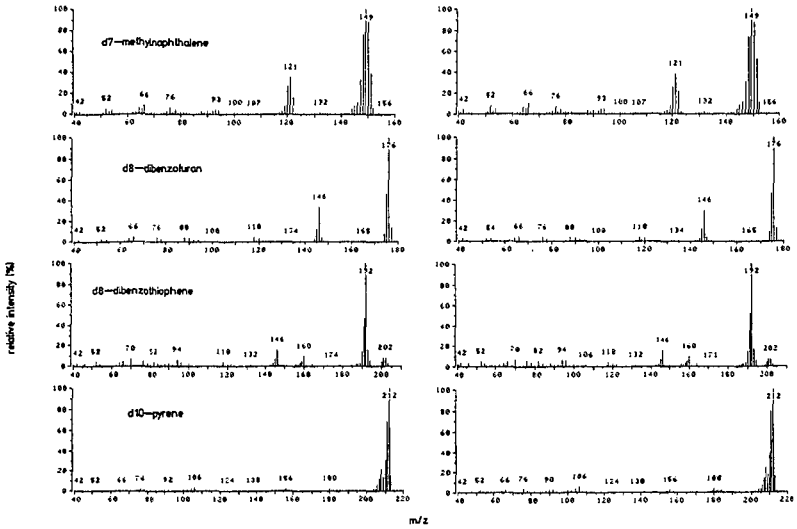

Figure 4. Mass spectra of 4 components of deuterated AO4 before (left) and after (right) exposure to liquefaction conditions with THFI, H_2S, CO, and water.

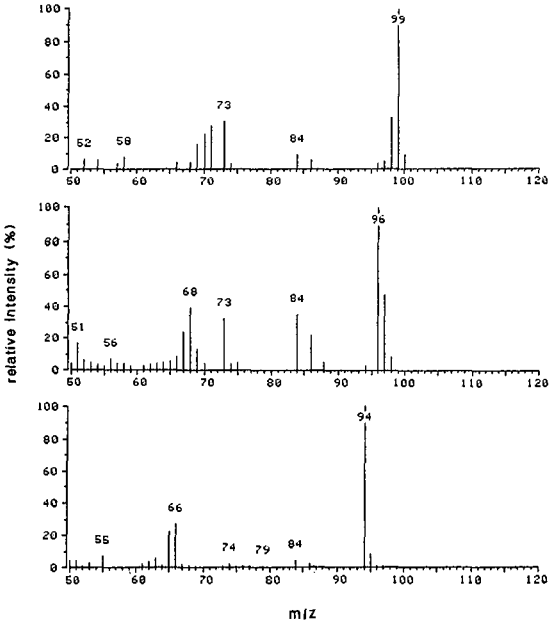

Figure 5. Mass spectra of d_5-phenol as it appears in deuterated AO4 prior to stability testing (top spectra), d_2-phenol as it appears following stability testing (middle spectra), and phenol as it appears in non-deuterated AO4 (bottom spectra).

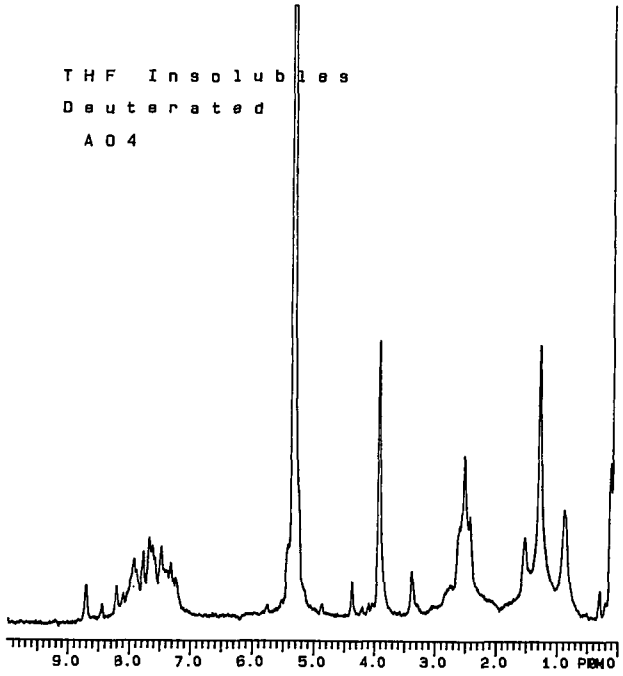

Figure 6. Proton NMR spectrum of methylene chloride solubles obtained from the reaction of deuterated AO4 and THF-insolubles.

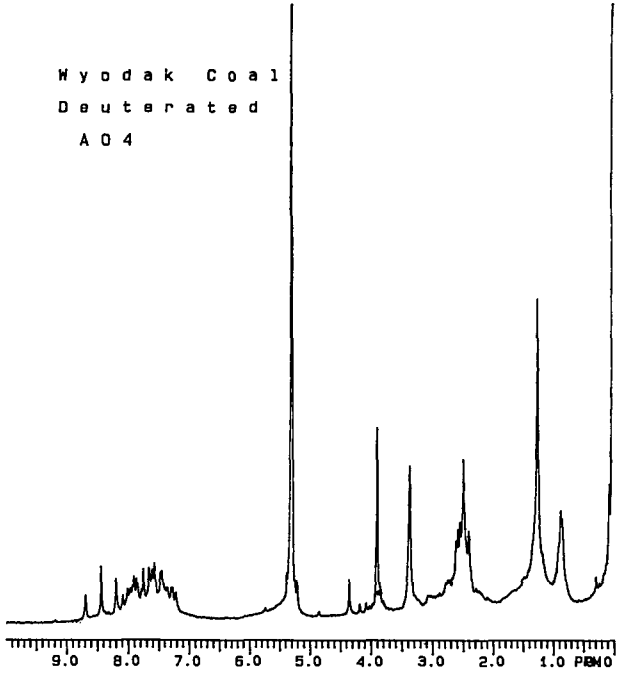

Figure 7. Proton NMR spectrum of methylene chloride solubles obtained from the reaction of deuterated AO4 and Wyodak coal.