

DETERMINATION OF DIDEUTERIUM UPTAKE IN COAL PETROLEUM RESID COPROCESSING

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INTRODUCTION

Coal petroleum resid coprocessing is a novel application of direct coal liquefaction which has potential for practical applications. Several lines of argument suggest that a better understanding of the chemistry of the coprocessing reaction would lead to improvements in coprocessing technology. In order to gain insight into this problem, batch autoclave studies were carried out by using Illinois No. 6 coal with Lloydminster resid under a dideuterium atmosphere to study the deuterium incorporation in the products. Quantitative deuterium nuclear magnetic resonance methods were used to analyze the liquid products, and gas chromatography-mass spectrometry was used to analyze the gas products.

EXPERIMENTAL

Materials. The materials used were the same as those described in the accompanying article.

Coprocessing Reaction Procedure. Weighed amounts of Lloydminster resid and Illinois No. 6 in a two-to-one ratio (resid/MAF coal) and the catalyst (.02% wt) were added to an 1800 cc rocking autoclave. The autoclave was sealed and pressurized first with hydrogen sulfide and then with dihydrogen or dideuterium to give a 10 vol% hydrogen sulfide and 90 vol% dideuterium blend at 1470 psi. The autoclave was heated to 420 °C for a residence time of 2 hrs. At the reaction conditions, dideuterium was added automatically so that the desired reaction pressure (3000 psi at temperature) was maintained. After the desired time-at-temperature, the autoclave was cooled to room temperature, and then depressurized with the gas passing through a foam trap, caustic scrubbers, metering system, and then a sample was collected for analysis. To remove additional gas from the remaining reaction mixture, the material in the autoclave was stripped with dinitrogen.

This gas was also passed through the foam trap, caustic scrubber, metering system, and analyzed. Any slurry product in the foam trap was recovered with toluene and added to the toluene rinse solution. The slurry product from the autoclave was poured off. The material remaining in the autoclave was removed by rinsing the vessel with toluene until the autoclave was clean. The combined slurry product was solvent separated into four fractions according to the flow chart shown in Figure 1.

Deuterium spectra were obtained on a Varian XL 400 MHz spectrometer. One hundred to 200 scans were acquired using a 90° pulse and a 30-sec delay between pulses. Triphenylmethane-d₁ was used as a quantitative internal standard. Proton spectra were obtained similarly on the University of Chicago 500 MHz spectrometer by using tetrakis(trimethylsilyl)silane as a quantitative internal standard.

RESULTS

The autoclave reaction using a combination of Illinois No. 6 coal with Lloydminster resid mixed with a molybdenum based UOP proprietary catalyst was carried out at 420 °C for two hours under a dideuterium atmosphere at a constant pressure of 3000 psi. The results of the solvent separation of

the products are summarized in Table I. The oil, resin, asphaltene, and insoluble yields are based upon the starting amount of MAF coal and resid. As can be seen from Table I, approximately 23% of the starting material is unaccounted for. This portion represents the gas yield and the loss of a small amount of light material in the work-up procedure. The asphaltene conversion is calculated as the amount of asphaltene and unconverted coal (insolubles) in the autoclave product divided by the amount of starting MAF coal and asphaltene fraction of the starting resid. An asphaltene yield of 74% was obtained with Illinois No. 6 coal and Lloydminster resid. Coal conversion is calculated as the amount of starting MAF coal minus unconverted MAF coal (insolubles) divided by the starting amount of MAF coal. A coal conversion of 93% is obtained with Lloydminster resid and Illinois No. 6 coal. The elemental analysis of the oil, resin, asphaltene, and insoluble fractions are shown in Table II along with the fractional analyses of the starting resid. In all of the product fractions, the sulfur content significantly decreased even though hydrogen sulfide gas was present.

The deuterium incorporation into the different molecular fragments defines the paths of hydrogen transfer. In this first analysis of the results, the assignments are made according to the following chemical shift ranges. Deuterium resonances in the range of 6.3-10 ppm are assigned to aromatic deuterium atoms, while those found in the range of 4.2-0 ppm are assigned to aliphatic types. A further breakdown of the resonances in the ranges 4.2-2.0 ppm, 2.0-1.0 ppm, and 1.0-0 ppm was made by assigning resonances in those ranges to deuterium atoms alpha to aromatic rings, deuterium atoms beta to aromatic rings and in methylene and methine positions not alpha to aromatic rings, and deuterium atoms in methyl groups gamma or further from aromatic rings, respectively. Proton NMR characterization was also carried out to complement the results for deuterium. The proton NMR experiments use tetrakis(trimethylsilyl)silane as an internal standard. The NMR data from the coprocessing reaction products of Illinois No. 6 coal with Lloydminster resid are shown in Tables III and IV. In addition to the actual amount of deuterium incorporated into the products, Table III also shows the hydrogen content in each of the products. Thus, the percent deuteration of the aromatic and aliphatic regions was determined.

A relatively large amount of deuterium, 24.1 mmol g⁻¹, was incorporated into the aliphatic component of the oil. While the absolute amounts of deuterium uptake at the different structural positions vary from 2.9 mmol g⁻¹ to 24.1 mmol g⁻¹, the relative percentages of deuteration are high and not quite so varied indicating that significant exchange had taken place at all positions. These percentages are close to the initial deuterium to total hydrogen ratio of (H/H+D) = 0.25 at the start of the reaction. Some selectivity of the catalyst was observed between the solvent separated fractions with the extent of deuteration decreasing in the order asphaltene > resin > oil. In addition, aliphatic positions were slightly preferred in the asphaltene and resin fractions while the smallest amount and smallest percentage of deuterium incorporation occurred at the aromatic sites in the oil fraction.

CONCLUSIONS

Analysis of the deuterium NMR results clearly shows that the level of deuterium atom incorporation was significant at all positions. All components of the system are undergoing hydrogen transfer chemistry, and there are plentiful opportunities for fragmentation and addition reactions. The deuterium contents of the reaction products, (D/H+D), are only moderately different than the values expected for complete equilibration. The modest differences that do exist are compatible with the view that the weaker carbon-hydrogen bonds such as the alpha aliphatic group undergo reaction selectively even in the presence of the effective catalyst. The high deuterium incorporation at the other sites such as the methyl and methylene groups in paraffinic components, when coupled with the fact that the catalyst is essential for high conversions, suggests that the modest selectivity that is observed arises more from the differences in the way in which the organic molecules bind to the catalyst than to inherent differences in their thermal chemistry.

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Table I. Solvent Separation of Coprocessed Lloydminster Resid and Illinois No. 6 Coal with Dideuterium

Sample	Wt % MAF
Oil	62.32
Resin	3.91
Asphaltene	8.50
Insoluble	2.40
Coal Conversion	92.78
Asphaltene Conversion	74.08

Table II. Analysis of Original Resid Components and Solvent Separated Product

	Starting Material	Products
<u>Oil fraction</u>		
Wt.% MAF	73.50	62.32
Carbon, wt.%	82.86	84.88
Hydrogen, wt.%	10.82	13.67
Sulfur, wt.%	4.30	1.24
<u>Resin fraction</u>		
Wt.% MAF	10.41	3.91
Carbon, wt.%	82.68	86.16
Hydrogen, wt.%	8.76	8.66
Sulfur, wt %	7.44	1.73
<u>Asphaltene fraction</u>		
Wt.% MAF	16.09	8.50
Carbon, wt.%	82.82	87.70
Hydrogen, wt.%	8.51	7.09
Sulfur, wt.%	7.85	1.68
<u>Insoluble fractions</u>		
Wt.% MAF	-	2.40
Carbon, wt.%	-	24.03
Hydrogen, wt.%	-	1.71
Sulfur, wt.%	-	6.51

Table III. Hydrogen and Deuterium Content of Solvent Separated Coprocessing Products

	Hydrogen (mmol g ⁻¹)		Deuterium (mmol g ⁻¹)		% Deuteration	
	Aromatic (6.3-10 ppm)	Aliphatic (4.2-5 ppm)	Aromatic (6.3-10 ppm)	Aliphatic (4.2-0 ppm)	Aromatic (6.3-10 ppm)	Aliphatic (4.2-0 ppm)
Oil	14.5	86.8	2.9	24.1	16.7	21.7
Resin	16.7	45.6	5.3	14.6	24.1	24.3
Asphaltene	14.5	31.7	5.0	11.9	25.6	27.3

Table IV. Aliphatic Deuterium Content in Solvent Separated Coprocessing Products

Solvent separated fraction	Alpha-D 2.0-4.2 ppm (mmol g ⁻¹)	Beta-D 1.0-2.0 ppm (mmol g ⁻¹)	Gamma-D 0.0-1.0 ppm (mmol g ⁻¹)	% Alpha deuteration
Oil	6.2	15.6	2.3	31.6
Resin	7.5	6.0	1.1	29.1
Asphaltene	5.9	4.8	1.2	29.4

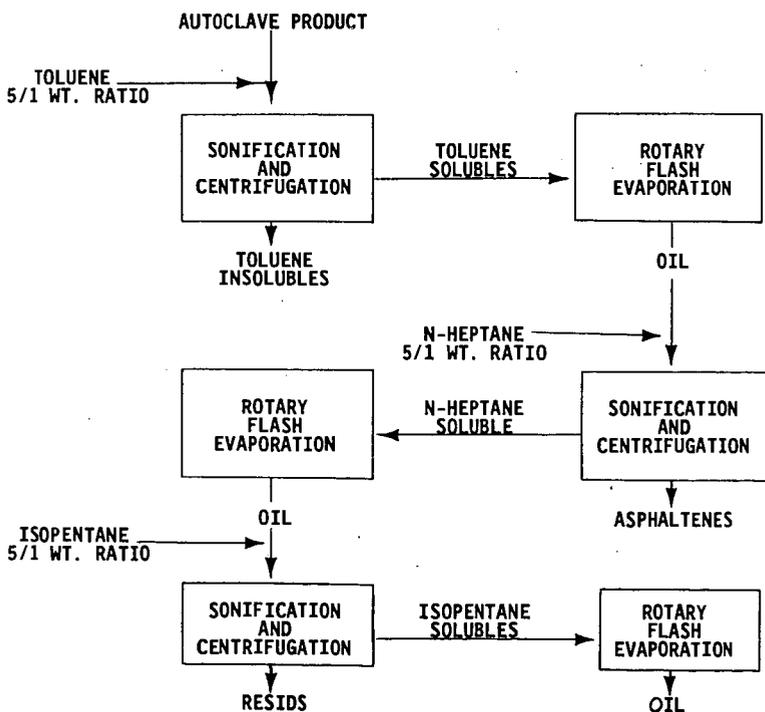


Figure 1. Solvent Separation of Coprocessing Product