

Organic Sulfur Compounds in Coal Hydrogenation Products

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INTRODUCTION

In the Bureau of Mines Synthoil process for converting coal to low-sulfur fuel oil, a slurry of coal in recycled oil is hydrodesulfurized in a turbulent-flow, fixed-bed reactor packed with pellets of Co-Mo/SiO₂-Al₂O₃ catalyst (1,2,3).¹ At 450° C and 2,000-4,000 psi, the coal is converted to a liquid, and sulfur is eliminated as H₂S. Of the two principal forms of sulfur in coal, the pyritic sulfur is eliminated completely while 60-80 percent of the organic sulfur is eliminated. In a previous experiment to determine the role of the catalyst in hydrodesulfurization, coal slurry was hydrotreated in a reactor packed with glass pellets. At 450° C and 2,000-4,000 psi, the pyritic sulfur was eliminated completely, but only 10-20 percent of the organic sulfur was eliminated. Clearly, the catalyst's role is in the elimination of organic sulfur. To facilitate the search for effective coal hydrodesulfurization catalysts, the organic sulfur compounds formed in the hydrogenation of coal have now been identified, and qualitative information on their relative ease of decomposition by Co-Mo/SiO₂-Al₂O₃ catalyst has been obtained.

EXPERIMENTAL

Fifty g samples of coals were hydrogenated for one hour in a rotating autoclave at 450° C and 4,000 psi. No vehicle oil or catalyst was added. The products were separated into light oil, heavy oil, asphaltene, and benzene insoluble fractions by conventional methods. The oils and asphaltene were analyzed for sulfur compounds with a Dupont 21 110B high-resolution mass spectrometer.² The spectra represented the portions of the samples vaporized at 300° C and 10⁻⁶ torr. Under these conditions, 100 percent of the light oils, about 60 percent of the heavy oils, and 55 percent of the asphaltenes vaporized.

The relative ease of decomposition of the organic sulfur compounds was determined by conducting 5-pass hydrodesulfurization experiments in the continuous fixed-bed reactor of the Synthoil process(3). The feed for the first pass was a slurry of coal in high-temperature tar while the feeds for the subsequent passes were the gross liquid products (liquid products + unreacted solids) from the preceding pass. The gross liquid products from each pass were sampled and analyzed for sulfur compounds by high-resolution mass spectrometry.

RESULTS AND DISCUSSION

The analyses of the Indiana #5 coal and the Homestead mine, Kentucky, coal used in this work are given in table 1. The Indiana #5 coal contained 3.4 percent sulfur, about two-thirds of which was organic, while the Kentucky coal contained 4.6 percent sulfur, about one-third of which was organic.

¹ Underlined numbers in parentheses refer to the list of references at the end of this report.

² Reference to a specific make of equipment is done to facilitate understanding and does not imply endorsement by the Bureau of Mines.

Hydrogenation of Coal Without Catalyst

The analysis of the products from the hydrogenation of coal without catalyst is given in table 2. About 94 percent of the Indiana #5 coal and 91 percent of the Kentucky coal were converted to benzene solubles and gases. The light and heavy oils together amounted to about 50 percent of the products and the asphaltenes to about 20 percent. The high conversion of coal may be noted. Although no catalyst was added, catalysis by coal ash or a product of the reaction may be involved.

Organic Sulfur Compounds in the Products of Hydrogenation

The organic sulfur compounds corresponding to the empirical formulas derived from high-resolution mass spectrometric data for the products of coal hydrogenation are given in table 3. In the products from Indiana #5 coal, 3 sulfur compounds were found in the light oil, 9 in the heavy oil, and none in the asphaltene. The asphaltene spectrum was not sufficiently resolved to identify sulfur compounds. In the products from Kentucky coal, 2 sulfur compounds were found in the light oil, 5 in the heavy oil, and 2 in the asphaltene both of which were also present in the heavy oil. Only 4 sulfur compounds were common to the products from the two coals. The most noteworthy feature about the compounds listed in table 3 is that, with the exception of diallyl sulfide, all are thiophene derivatives. The structural formula of the compounds shown in table 4 illustrate the relationship. Although organic sulfur in coal is believed to occur in several other forms in addition to thiophene, namely thiol, thioether, disulfide, and γ -thiopyrone (4), degradation sulfur compounds from them were not detected. Clearly, they were unstable at the experimental condition and decomposed without any externally added hydrodesulfurization catalyst.

Relative Ease of Decomposition of the Organic Sulfur Compounds by Co-Mo/SiO₂-Al₂O₃ Catalyst

Slurries of the Indiana #5 coal in high-temperature tar were hydrodesulfurized in multiple-pass experiments at 2,000 psi and 4,000 psi (see Experimental). Samples of the products from successive passes were analyzed for sulfur compounds. The results are presented in table 5. At 2,000 psi, the first pass product contained only 3 sulfur compounds: benzothiophene, dibenzothiophene, and naphthobenzothiophene. The second pass product also contained the three sulfur compounds but at lower concentrations. The third, fourth, and fifth pass products contained only benzothiophene and dibenzothiophene; naphthobenzothiophene was no longer detectable. At 4,000 psi, the first pass product contained a measurable concentration of dibenzothiophene and a trace of benzothiophene. The second, third, and fourth pass products contained progressively decreasing concentrations of dibenzothiophene and traces of benzothiophene. The results show that amongst the sulfur compounds formed in the hydrogenation of coal, the most difficult to decompose is dibenzothiophene followed by benzothiophene and naphthobenzothiophene. The remaining sulfur compounds of table 3 decompose readily compared to these three.

SUMMARY AND CONCLUSIONS

Bituminous coals from Indiana #5 seam and Homestead mine, Kentucky, were hydrogenated in a batch autoclave at 450° C and 4,000 psi without adding any catalyst. In one hour more than 90 percent of the coals were converted to benzene soluble liquids and gases. The liquid products contained 14 organic sulfur compounds, 13 of them thiophene derivatives. Their relative ease of decomposition was determined by repetitive hydrodesulfurization of coal slurries with Co-Mo/SiO₂-Al₂O₃ catalyst. Dibenzothiophene is most difficult to decompose, followed by benzothiophene and naphthobenzothiophene.

ACKNOWLEDGMENT

We are thankful to Walter Kawa for conducting the batch hydrogenation of coal, and to Dr. Leslie Reggel for assisting with the nomenclature of the organic sulfur compounds.

REFERENCES

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3. Akhtar, Sayeed, Sam Friedman, and Paul M. Yavorsky. Process for Hydrodesulfurization of Coal in a Turbulent-Flow, Fixed-Bed Reactor, presented at the 71st National meeting of the AIChE, Feb. 20-23, 1972, Dallas, Texas.
4. Given, P. H. and W. F. Wyss. The Chemistry of Sulfur in Coal. BCURA Monthly Bulletin, v. XXV, No. 5, May 1961, p. 166.

TABLE 1.- Analysis of coals, as received

	<u>Hvbb</u> <u>Indiana #5</u> <u>coal</u>	<u>Hvab</u> <u>Kentucky</u> <u>coal</u>
<u>Proximate Analysis, Wt Pct</u>		
Moisture	6.1	2.9
Ash	8.9	16.9
Volatile matter	38.6	36.5
Fixed carbon	46.4	43.7
<u>Ultimate Analysis, Wt Pct</u>		
Moisture	6.1	2.9
Ash	8.9	16.9
Carbon	67.0	63.4
Hydrogen	5.3	4.8
Nitrogen	1.4	1.3
Oxygen, by difference	7.9	6.1
Sulfur	3.4	4.6
as sulfate	0.37	0.13
as pyrite	0.98	3.03
as organic	2.07	1.44
<u>Calorific value, Btu/lb</u>	11,750	11,500

TABLE 2.- Analysis of the products of coal hydrogenation,
wt pct of moisture- and ash-free coal

	From Indiana #5 Coal	From Kentucky Coal
Light oils (Distillates to 105° C at 2-3 mm Hg)	17.4	13
Heavy oils (Solubles in benzene and n-pentane)	30.6	34
Asphaltenes (Soluble in benzene but in- soluble in n-pentane)	20.3	18
Organic benzene insolubles	5.8	9
Total	74.1	74
Balance (gaseous hydrocarbons, H ₂ S, NH ₃ , CO, CO ₂ , H ₂ O from make-water)	25.9	26

TABLE 3.- Organic sulfur compounds in the products of coal hydrogenation

	<u>Michigan No. 6</u>			Kentucky Coal		
	<u>m/e</u>	<u>Mol. Form.</u>	<u>Identification</u> ¹	<u>m/e</u>	<u>Mol. Form.</u>	<u>Identification</u> ¹
Light oil	134	C ₈ H ₆ S	Benzothiophene	98	C ₅ H ₆ S	Methylthiophene
	148	C ₉ H ₈ S	Methylbenzothiophene	114	C ₆ H ₁₀ S	Diallylsulfide
	162	C ₁₀ H ₁₀ S	Dimethylbenzothiophene			
Heavy oil	98	C ₅ H ₆ S	Methylthiophene	208	C ₁₄ H ₈ S	Benzo[def]dibenzothiophene
	138	C ₈ H ₁₀ S	Tetrahydrobenzothiophene	234	C ₁₆ H ₁₀ S	Naphthobenzothiophene
	174	C ₁₁ H ₁₀ S	Benzylthiophene	248	C ₁₇ H ₁₂ S	Methylnaphthobenzothiophene
	184	C ₁₂ H ₈ S	Dibenzothiophene	284	C ₂₀ H ₁₂ S	Dinaphthothiophene
	198	C ₁₃ H ₁₀ S	Methyldibenzothiophene	298	C ₂₁ H ₁₄ S	Methyldinaphthothiophene
	208	C ₁₄ H ₈ S	Benzo[def]dibenzo- thiophene			
	234	C ₁₆ H ₁₀ S	Naphthobenzothiophene			
	248	C ₁₇ H ₁₂ S	Methylnaphthobenzothiophene			
	284	C ₂₀ H ₁₂ S	Dinaphthothiophene			
Asphaltenes	<u>Spectrum not well resolved</u>			234	C ₁₆ H ₁₀ S	Naphthobenzothiophene
				284	C ₂₀ H ₁₂ S	Dinaphthothiophene

¹ Based upon molecular formula determined by high-resolution mass spectrometry. Other isomeric forms possible in some instances.

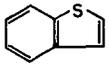
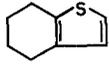
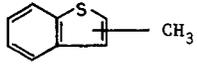
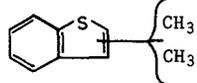
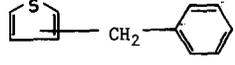
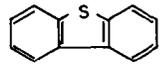
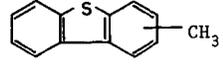
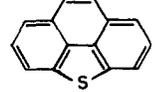
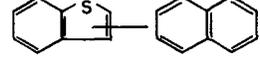
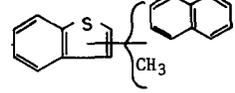
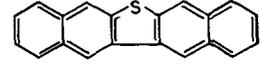
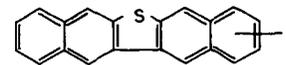
98	C_5H_6S		Methylthiophene
134	C_8H_6S		Benzothiophene
138	$C_8H_{10}S$		Tetrahydrobenzothiophene
148	C_9H_8S		Methylbenzothiophene
162	$C_{10}H_{10}S$		Dimethylbenzothiophene
174	$C_{11}H_{10}S$		Benzylthiophene
184	$C_{12}H_8S$		Dibenzothiophene
198	$C_{13}H_{10}S$		Methyl dibenzothiophene
208	$C_{14}H_8S$		Benzo[def]dibenzothiophene
234	$C_{16}H_{10}S$		Naphthobenzothiophene
248	$C_{17}H_{12}S$		Methyl naphthobenzothiophene
284	$C_{20}H_{12}S$		Dinaphthothiophene
298	$C_{21}H_{14}S$		Methyl dinaphthothiophene

TABLE 4.- Structural formulas of the organic sulfur compounds

TABLE 5.- Sulfur compounds in the products from
multi-pass hydrogenation of Indiana #5
coal with Co-Mo/SiO₂-Al₂O₃ catalyst

A. Operating pressure: 2,000 psi

<u>Compound</u>	<u>Concentration, as percent of ionization</u>				
	<u>I Pass</u>	<u>II Pass</u>	<u>III Pass</u>	<u>IV Pass</u>	<u>V Pass</u>
Benzothiophene	0.26	0.15	0.13	0.12	0.04
Dibenzothiophene	1.67	0.70	0.70	0.49	0.27
Naphthobenzothiophene	0.09	0.02	None	None	None

B. Operating pressure: 4,000 psi

<u>Compound</u>	<u>Concentration, as percent of ionization</u>			
	<u>I Pass</u>	<u>II Pass</u>	<u>III Pass</u>	<u>IV Pass</u> ¹
Benzothiophene	trace	trace	trace	trace
Dibenzothiophene	0.30	0.17	0.08	0.07

¹ Only 4 passes were conducted at 4,000 psi.