Conf-910902--9

READINESS THROUGH RESEARCH

CONF-910902--9

TI92 002499

THE FATE OF SULFUR IN MILD GASIFICATION LIQUIDS

by

R. A. Knight
G. J. Koncar
S. P. Babu

Paper to be Presented at

1991 International Conference on Coal Science
University of Newcastle Upon Tyne
Newcastle Upon Tyne NE1 7RU

United Kingdom

September 16-20, 1991

INSTITUTE OF GAS TECHNOLOGY

3424 South State Street Chicago Illinois 60616

IGT

THE FATE OF SULFUR IN MILD GASIFICATION LIQUIDS

R.A. Knight, G.J. Koncar, and S.P. Babu

1. INTRODUCTION

Mild gasification of coal is a coal pyrolysis process of low severity compared to other types of coal conversion like gasification, direct liquefaction, or hydropyrolysis. Continuous mild gasification takes place at near-ambient pressure and at temperatures of 540° to 760°C. These conditions are designed to maximize the yield of valuable condensable co-products.

Mild gasification oils/tars can yield a variety of products, including binder pitches, chemical feedstocks, and fuel blending stocks. Although important studies on organic sulfur chemistry in coal have been published,[1,2] additional data on the distribution of sulfur in the oils/tars fractions would be useful for technology development. Also, while techniques have been proposed[3-7] to reduce the sulfur content of volatile products, the effects of such methods on sulfur distribution have not been investigated.

This investigation addresses the determination of sulfur distribution in mild gasification liquids produced from untreated coal and from coal modified in two ways to reduce sulfur in the products: *(a)* physical mixing with a sulfur scavenger (CaO), and *(b)* pretreatment with aqueous alkali followed by mixing with CaO. Coal pyrolysis in the presence of CaO has previously been investigated,[3-5] showing that CaO can be effective in reducing the sulfur content of the fuel gas, and possibly that of the product liquids. Pretreatment of coal with alkaline chemicals has also been studied,[6,7] showing reduced sulfur and other changes in the liquid products.[8] Data on sulfur distribution in the liquid products could be useful for understanding the chemistry of alkali pretreatment and CaO interaction with coal sulfur during pyrolysis.

In this work, a pyrolysis-gas chromatography (Py-GC) technique that simulates mild gasification on a milligram scale was used in conjunction with a carbon-specific flame ionization detector (FID) and a sulfur-specific flame photometric detector (FPD) to determine the sulfur distribution in oils/tars from Illinois No. 6 coal. A low-resolution packed GC column was employed to resolve oils/tars by carbon number, with ranges selected to approximate distillation fractions which might be recovered from a commercial mild gasification process. Oils/tars up to C_{18} were also collected from the pyroprobe effluent into dichloromethane for off-line study using a high-resolution GC with atomic emission detector (GC/AED) and with GC-mass spectrometry (GC/MS) to measure specific sulfur compounds.

2. DISCUSSION

2.1 Experimental Apparatus, Materials, and Procedures

The test coal, Herrin No. 6, was prepared by wet-crushing, vacuum-drying at 100°C, and dry-screening to 75 m-150 m under nitrogen. The prepared coal sample had a sulfur content of 5.18 wt%. For NaOH pretreatment, the test coal was treated with boiling 1.0*N* NaOH for three hours under a nitrogen purge. The treated coal was filtered, washed with deionized water, dried in the same manner as the untreated coal, and stored under nitrogen. The coal lost about 2.7% of its original heating value, and the sulfur content was reduced to 4.91 wt%, a 5.2% reduction. For investigation of the effects of CaO addition to untreated and NaOH-pretreated coal, a quantity of CaO powder based on a 3.5:1 Ca:S mole ratio was physically mixed with the coal. The samples of pretreated and untreated coal mixed with CaO were separately analyzed for proximate and ultimate analyses and for Ca, in order to accurately determine the CaO content of each sample.

Py-GC experiments employed a Chemical Data Systems Model 120 Pyroprobe fitted to a Perkin-Elmer Sigma 1B GC with a Supelco Petrocol-B column. A stream splitter was used for simultaneous FID and FPD analyses of the volatile products. The reaction/carrier gas was helium, and temperature programming was used to optimize peak resolution from C_7 to C_{48}. Approximately 1 mg of coal was retained between two quartz-wool plugs in a quartz tube. The tube was inserted into a snug-fitting platinum coil in the pyroprobe, which was then placed in the 288°C GC injection port for five minutes to purge air and desorb moisture from the coal. The coil was then rapidly heated (500°C/s) by capacitor discharge to a final sample temperature of 650°C, which was held for 20 seconds.

The GC/AED and GC/MS instruments used for off-line sulfur determination in the C_7-C_{18} volatile products were, respectively, a Hewlett-Packard Model 5921A and a Finnigan 4510. The coal was pyrolyzed in the pyroprobe as usual, but the effluent stream, instead of entering the GC column, was collected in dichloromethane. Samples of the solution were analyzed separately in the GC/AED and GC/MS instruments. A relative quantitation of sulfur species in the oils/tars was obtained by normalizing peak areas to a basis of equal coal sample mass.

2.2 Sulfur Distribution in Mild Gasification Liquids

The relative FID and FPD peak areas from the Py-GC were used to correlate the fractional yields based on carbon and sulfur. The overall yield (30.0 wt% of dry coal) and sulfur content (3.11 wt%) of mild gasification oils/tars from this coal had previously been determined using a free-fall reactor.[9] By combining these data, an estimate of the yield and sulfur content of each carbon-number fraction was formulated. The mass percentage of the original coal sulfur found in each fraction can also be calculated. Table 1 shows these estimates for the three samples of interest, based on the mean of three replicate experiments with each sample. In the Py-GC experiments, the sulfur content of mild gasification liquids decreased with increasing carbon number in all three cases, with the light oils from the untreated coal having more than twice the sulfur level of the corresponding whole liquid (C_7-C_{48}). The data also show that CaO addition did not significantly change the oils/tars yield or fractional yields, but did bring about a 24% reduction in the sulfur content of the overall liquid, primarily in the C_7-C_{12} fraction, for which the sulfur reduction was 40%. NaOH pretreatment, on the other hand, resulted in a 31% loss of oils/tars yield without any net reduction of sulfur in the total liquid product, although the sulfur content of the light oils fraction was significantly reduced.

Table 1. Yields and Sulfur Distribution in Mild Gasification Oils/tars
(Illinois No. 6 coal, 650°C, 0.15 MPa)

	Untreated Coal			Untreated Coal/CaO			NaOH-Treated Coal/CaO		
	Yield wt% of coal	Sulfur content wt%	Wt% of coal sulfur	Yield wt% of coal	Sulfur content wt%	Wt% of coal sulfur	Yield wt% of coal	Sulfur content wt%	Wt% of coal sulfur
C_7-C_{12}	3.4	6.4	4.2	3.5	4.0	2.7	3.5	2.7	1.9
C_{13}-C_{18}	8.8	2.5	4.2	8.7	2.0	3.4	6.8	2.0	2.8
C_{19}-C_{24}	8.1	2.9	4.5	8.4	2.4	2.2	5.3	2.6	2.8
C_{25}-C_{48}	9.7	2.7	5.0	10.9	2.2	4.5	5.2	2.4	2.7
Total	30.0	3.1*	18.0	31.5	2.4*	14.4	20.8	2.4*	10.3

* This quantity is the overall sulfur content, not a sum.

Off-line GC/AED and GC/MS analyses showed that 90-95% of the sulfur in the light oils from the untreated coal with or without CaO was in the form of thiophene and alkylthiophenes. For the coal/CaO sample, GC/AED and GC/MS confirmed a reduction in sulfur content of mild gasification liquids, with the reduction being moderately selective towards less-substituted thiophenes.

During pyrolysis, coal sulfur, both organic and inorganic, undergoes changes in chemical environment. Attar and Dupuis[1] concluded that the organic sulfur in Illinois No. 6 coal contains about 73% thiophenic sulfur, with the remainder primarily in alicyclic or aromatic sulfides which are less thermally stable. Calkins[2] indicated that aliphatic sulfides decompose at 600-800°C, aromatic sulfides are stable to about 900°C, and thiophenic structures are stable to at least 950°C. Consequently, a significant part of the thiophene/alkylthiophene content of the pyrolysis liquids may be a product of secondary reactions of other volatile sulfur compounds, including H_2S, with hydrocarbons, rather than from fragmentation of thiophenic structures in the coal matrix.

3. CONCLUSIONS

The sulfur content of liquids from mild gasification of Herrin No. 6 coal tends to be highest in the lowest-boiling fractions. At least 95% of the sulfur in the light and middle oils is in the form of thiophene and C_1- to C_3-substituted thiophenes. The abundance of these species increases with the level of alkyl substitution.

The addition of 20-25 wt% of CaO to this coal significantly reduces the sulfur content of mild gasification oils/tars, particularly in the light oil (C_7-C_{12}) fraction, without adversely affecting yield. Addition of CaO to coal results in reduction of thiophenes in the pyrolysis products, with some selectivity towards the less-substituted members of the series. NaOH pretreatment of the coal results in a further sulfur reduction, without any loss of yield, in the light oils fraction, but the yields of higher-MW products decrease, while the sulfur content actually increases.

These observations seem to favor a view that at least part of the sulfur in the mild gasification liquids originate from secondary reaction of gaseous hydrocarbons with H_2S, which in turn results from the decomposition of the more reactive organic sulfur components as well as pyrites. In the absence of the CaO sorbent, this sulfur may be reincorporated into the liquids in stable thiophenes and alkylthiophenes. This conclusion is supported by the observed sulfur reduction in the pyrolysis liquids produced in the presence of CaO. The role of inorganic sulfur in donating sulfur to the organic pyrolysis liquids in this way may also be significant, and can explain the further reduction in light oils sulfur by NaOH pretreatment of the coal, whereby pyritic sulfur is decreased by conversion to water-soluble Na_2S which is removed in the washing of the treated coal.

4. ACKNOWLEDGEMENT

This work has been sponsored by the Illinois Department of Energy and Natural Resources through its Coal Development Board and Center for Research on Sulfur in Coal (CRSC), and the CRSC Coal Industry Committee. The CRSC Project Monitor was Dr. D. D. Banerjee.

5. REFERENCES

1 Attar, A., and Dupuis, F., *ACS Div. of Fuel Chem. Prepr.*, 1978, **23:2**, 44-53

2 Calkins, W.H., *ACS Div. of Fuel Chem. Prepr.*, 1985, **30:4**, 450-465

3 Sudbury, J. D., and Zielke, C.W., 1984, U.S. Patent No. US 4,439,304

4 Khan, M. R., *Fuel Sci. Technol. Int.*, 1987, **5**, 185

5 Sundaram, M. S., *ACS Div. of Fuel Chem. Prepr.*, 1989, **34(1)**, 1-8

6 Chang, C. Y., Guin, J.A., Tarrer, A.R., and Lee, M.H., *J. Chin. Inst. Chem. Eng.*, 1982, **13**, 113

7 Saranchuk, V. I., Tamko, V.A., Plotnikova, L.A., Lapshin, S.A., and Vdovichenko, A.N., *Khim. Tverd. Topl.*, 1987, **3**, 83

8 Salbut, P. D., Bimer, J., and Berlozecki, S., *Koks, Smola, Gaz*, 1985, **30**, 218

9 Knight, R.A., Koncar, G.J., and Babu, S.P., Final Technical Report to CRSC, Carterville, Illinois, 1990, Subgrant 89-04

END

DATE FILMED

01/03/92