

CHANGES IN ORGANIC SULFUR COMPOUNDS IN COAL MACERALS DURING LIQUEFACTION

Randall E. Winans
Chemistry Division, Argonne National Laboratory
Argonne, IL 60439

J. T. Joseph and R. B. Fisher
Amoco Oil Company Research and Development
Naperville, IL 60566

Keywords: Coal macerals, liquefaction, sulfur types

INTRODUCTION

Environmentally sound use of coal for energy production involves effective sulfur removal from the feed coal and/or coal-derived products. Physical cleaning of coal is effective in removing substantial quantities of inorganic sulfur compounds such as pyrite. However, removal of organic sulfur by physical means has not been extremely successful. It is likely that only chemical methods will be useful in substantial removal of organic sulfur. A thorough knowledge of the chemistry of organic sulfur in coal will be valuable in attempts to remove organic sulfur from coal or its liquefaction or pyrolysis products by chemical methods. Since different coal macerals have different liquefaction reactivities, the analysis of sulfur functionalities on separated macerals is deemed to be more meaningful than studying the whole coal. Liquefaction behavior¹ and organic sulfur speciation of the macerals separated from Lewiston-Stockton coal (Argonne Premium Coal Sample bank, APCS-7) by XPS, XANES, and HRMS has been previously described². This paper describes the preliminary speciation of sulfur compounds in the asphaltene fraction of the liquefaction products from these macerals.

EXPERIMENTAL

Separation of liptinite, vitrinite, and inertinite macerals from APCS 7 coal was achieved by density gradient centrifugation methods³. The liquefaction of the macerals was performed in tubing bomb reactors under hydrogen pressure and in the presence of tetralin as a donor solvent. The details of maceral separation and liquefaction procedures have been published earlier¹. The liquefaction products were successively extracted with hexane, toluene, and tetrahydrofuran (THF). The hexane soluble fraction together with light gases was called oils+gases, hexane insoluble-toluene soluble fraction was called asphaltenes, and toluene insoluble-THF soluble fractions was called preasphaltenes. Desorption chemical ionization (DCI) and desorption electron impact (DEI) mass spectral analyses of the asphaltene and preasphaltene fractions were carried out on a three sector high resolution Kratos MS 50 Mass Spectrometer, operating at 10,000 to 40,000 resolving power². The oil fraction was not analyzed because of the presence of large quantities of tetralin and its reaction products.

RESULTS AND DISCUSSION

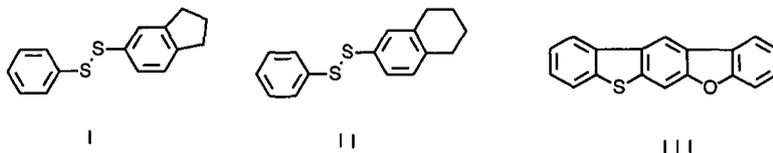
Table 1 Maceral Characteristics and Product Yields

<u>Maceral</u>	<u>% C (maf)</u>	<u>% Ash</u>	<u>Per 100 Carbons</u>				<u>Wt. % maf</u>		
			<u>H</u>	<u>N</u>	<u>S</u>	<u>O</u>	<u>Oil</u>	<u>Asphaltene</u>	<u>Preasph.</u>
Liptinite	81.7	--	110	1	0.5	8.9	20	54	13
Vitrinite	80.2	0.9	78	1.7	0.3	12	7	33	22
Inertinite	85.4	2.4	46	1.3	0.7	7.5	0	13	12

Selected information on these maceral samples and liquefaction yields are shown in Table 1. It is apparent that the sulfur content of these samples is typical of a bituminous coal, with an intermediate value. As has been seen observed in other samples, the liptinite is slightly richer in sulfur than the vitrinite. However, the difference may be much larger for the organic sulfur. The demineralization does not remove the pyrite which probably accounts for some of the 0.9% ash in the sample. The inertinite probably contains even more pyrite. Most of the sulfur in these macerals was derived from peptides in the original plant material and is not of secondary origin such as found in high sulfur coals.

The distribution of sulfur compounds determined by DEIHMS for the unreacted macerals is shown in Figure 1. Although only a fraction of the organic sulfur compounds are volatilized by pyrolysis, in a comparison with two direct techniques the ratio of aliphatic to aromatic sulfur compounds agree within experimental error². This result suggests that the species observed are representative of the whole maceral. The average size of the molecules is observed by DEIHMS is 300-350 which, based on the heteroatom content, would suggest that an average molecule will have more than one heteroatom. This is statistically more significant for the less abundant heteroatom such as sulfur. The results shown in Figure 1 match this hypothesis. It is interesting to note the relatively large abundance of compounds containing both nitrogen and sulfur. This may be related to the hypothesized origin of sulfur compounds from peptides which are rich in nitrogen. Also, the abundant yield of the combination with oxygen would result from this type of input of organic materials. Overall, the abundance of aromatic sulfur species increases in the order liptinite < vitrinite < inertinite which also follows inversely the liquefaction reactivity.

The sulfur results for HRMS of the asphaltene fractions are shown in Figure 2. Several general trends can be noted. Aliphatic sulfur compounds are in very low abundance while larger polycyclic aromatic sulfur compounds are in significant abundance. What is striking is the dominance of molecules containing two sulfur atoms. These species are similar across all three maceral groups as is demonstrated in Figure 3. Because of this similarity, we feel that they are the result of secondary reactions possibly between H₂S and the solvent tetralin. Possible disulfide structures for the hydrogen deficiency of 9 is shown below(I and II). These species are currently being investigated using tandem MS which will provide structural information. Another commonality between the three macerals is found for S+O for a hydrogen deficiency of 14. A likely possible structure is the combination of a thiophene and furan(III).



If the results for the asphaltene is adjusted for the yields, one can directly compare products with the starting material. This has been done for the liptinite and the results are shown in Figure 4. For the single sulfur compounds the aliphatics are gone and large polycyclic aromatics were formed. However, the overall abundance decreased. The total yields of two sulfur compounds were very similar but there was a different mix of molecules with the same general trend observed for the single sulfur. The S+O species shifted to more polycyclic aromatics in the products. Compounds with both N and S must be very reactive under these liquefaction conditions since they are gone in the products.

SUMMARY

Several general trends were observed in the reactivity patterns of sulfur compounds in macerals. Sulfur is reduced in the asphaltene fraction compared to the initial maceral. Aliphatics are removed and polycyclic aromatic compounds are both stable and probably formed under these conditions. Molecules containing two sulfur atoms are formed. The preasphaltenes are now being analyzed by DEIHMS.

ACKNOWLEDGEMENT

This work was performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy, under contract number W-31-109-ENG-38.

REFERENCES

1. Joseph, J. T.; Fisher, R. B.; Masin, C. A.; Dyrkacz, G. R.; Bloomquist, C. A.; Winans, R. E. *Energy Fuels*, **1991**, *5*(5), 724-729.
2. Winans, R. E.; Melnikov, P. E.; Dyrkacz, G. R.; Bloomquist, C.A.; Gorbaty, M. L.; George, G. N. *Am. Chem. Soc., Div. Fuel Chem. Prepr.*, **1993**, *38*(2), 375-378.
3. Dyrkacz, G. R.; Bloomquist, C. A., *Am. Chem. Soc., Fuel Chem. Prepr.*, **1988**, *33*(3), 128-135.

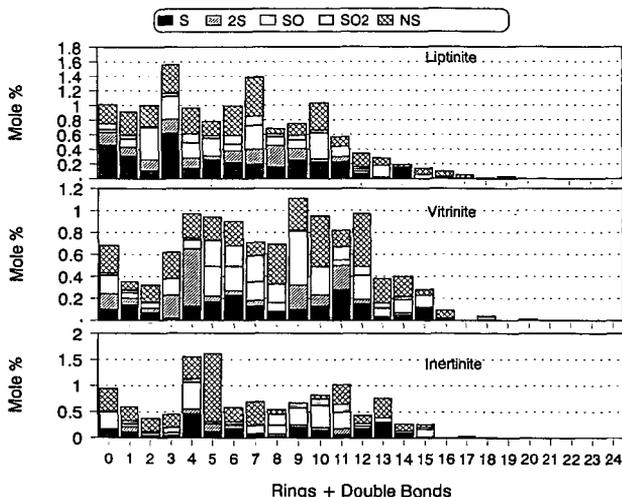


Figure 1. Distribution of sulfur containing molecules from DEIHRMS of the unreacted macerals.

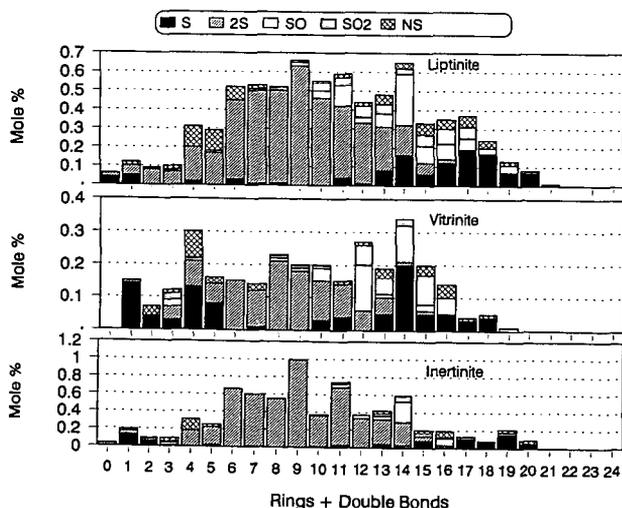


Figure 2. Distribution of sulfur containing molecules from HRMS analysis of the asphaltene products of the liquefaction of the macerals.

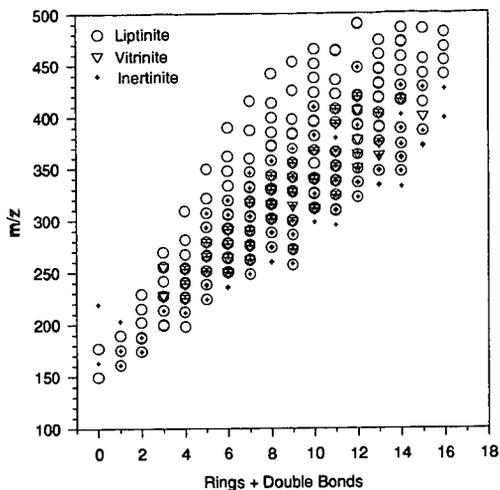


Figure 3. Occurrence of molecules which contain two sulfur atoms in the asphaltene products.

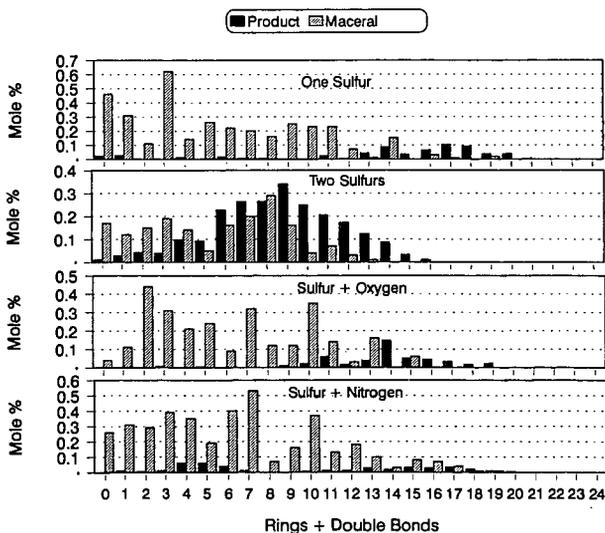


Figure 4. Comparison of sulfur types from the whole maceral and from the asphaltene product of the liptinite. Raw product data were multiplied by 0.54, which is the yield for asphaltene.