

AN OVERVIEW OF MINERAL MATTER CATALYSIS OF COAL CONVERSION*

Thomas D. Padrick
Sandia National Laboratories, Albuquerque, NM 87185

INTRODUCTION

Since the 1920's, several studies have focused on the catalytic effects of inherent mineral matter on coal conversion.¹ In recent years, we have witnessed an increase in the level of coal research and the development of new coal utilization processes. In parallel with this activity, there have been reports on the effects of coal minerals on coal liquefaction, coal gasification, in-situ coal gasification, and other areas of coal utilization.²⁻⁵ This overview will deal primarily with recent results of mineral matter effects in coal liquefaction and coal gasification. The terms minerals, mineral matter, and ash will be used synonymously. An attempt will not be made to review the effects of all classes of minerals, but will only consider those minerals which have shown a large effect on coal conversion processes. A good review of the specific minerals present in a variety of coals can be found in the work of Gluskoter et al.⁶

COAL LIQUEFACTION

The Germans used coal liquefaction on a commercial scale from 1930 to the end of the second World War. They found that a catalyst could enhance liquid yields and help remove heteroatoms. The Bergius process used an iron oxide-aluminum catalyst at a 2-3% by coal weight concentration.

In recent years, it has been realized that mineral matter plays an important role in coal liquefaction,^{7,8,9} similar to the role of the added catalyst in the Bergius process. Several experimental techniques have been used to study the effects of minerals on coal liquefaction and to identify the specific catalytic phase.¹⁰ Most studies^{11,12} strongly imply that the iron sulfides are the most active species, and the other minerals appear to have little effect on enhancement of liquid yield or quality.

The specific role of pyrite (FeS_2) as a catalyst has been under investigation since pyrite was identified as the most active inherent mineral for coal liquefaction. Under liquefaction conditions, FeS_2 is transformed into a nonstoichiometric iron sulfide, Fe_{1-x}S ($0 < x < 0.125$). Thomas et al.¹³ studied the kinetics of this decomposition under coal liquefaction conditions, and concluded that the catalytic activity of FeS_2 is associated with radical initiation resulting from the pyrite-pyrrhotite transformation.

Several studies have investigated the possibility that defects in the pyrrhotite structure provide the sites for catalyst activity. A recent study¹⁴ found a linear correlation between the conversion to benzene or THF solubles and the atomic percent iron in

* This work supported by the U. S. Dept. of Energy at Sandia National Laboratories under contract no. DE-AC04-76DP00789.

the liquefaction residues. Montano *et al.*¹⁵ used *in situ* Mössbauer spectroscopy to study transformation of FeS_2 to Fe_{1-x}S . They observed a large pyrrhotite surface area at the reaction temperature (above 350°C).

Stohl and Granoff¹⁶ investigated the effects of pyrite particle sizes, pyrite defects and surface areas on coal liquefaction. They observed no effect due to surface area and concluded that the observed particle size effect was due to diffusional limitations in the transformation of pyrite to pyrrhotite.

While many studies indicate that pyrrhotites are probably involved in the liquefaction process, the exact mechanism by which pyrrhotite catalyzes the conversion of coal to oil is not clear. Based on the works of Thomas *et al.*¹³ and Derbyshire *et al.*,¹¹ one can suggest that a possible role of pyrrhotite is as a hydrogenation catalyst. However, more work is necessary on the surface properties of the pyrrhotites and the interaction with model compounds before a definite catalytic mechanism can be proposed.

COAL GASIFICATION

The gasification of coal involves two distinct stages: (1) devolatilization and (2) char gasification. Devolatilization occurs quite rapidly as the coal is heated above 400°C. During this period, the coal structure is altered, producing a less reactive solid (char), tars, condensable liquids and light gases. Nominally 40% of the coal is volatilized during this period. The less reactive char then gasifies at a much slower rate. We will discuss the effects of coal minerals on both devolatilization and char gasification.

A large volume of work has been reported on rapid devolatilization of coal (heating rates approximating process conditions).^{17,18} Recently, the effects of coal minerals on the rapid pyrolysis of a bituminous coal were reported by Franklin, *et al.*¹⁹ They found that only the calcium minerals affected the pyrolysis products. Addition of CaCO_3 reduced the tar, hydrocarbon gas and liquid yields by 20-30%. The calcium minerals also altered the oxygen release mechanism from the coal. Franklin, *et al.* attribute these effects to CaCO_3 reduction to CaO , which acts as a solid base catalyst for a keto-enol isomerization reaction that produces the observed CO and H_2O .

Walker and co-workers at the Pennsylvania State University have investigated the reactivity of a variety of coals during gasification in air, CO_2 , H_2 and steam.²⁰⁻²³ Hippo and Walker²¹ found a linear correlation between reactivity and CaO content in the ash. They also observed an increase in reactivity with MgO , up to about 1%. They found no correlation between reactivity and iron content or total K or Na content. In their studies on hydrogen and steam gasification, the Penn State group used coals demineralized by acid washing to study mineral matter effects. While changes were observed in these studies, it was difficult to attribute these changes to catalytic effects or physical effects.

Mahajan *et al.*²⁴ observed that the presence of pyrite in coal had a beneficial catalytic effect on hydrogenation at 570°C. They suggested that the catalytic activity was due to pyrrhotite formation. Hüttinger and Krauss²⁵ reached a similar conclusion concerning the catalytic activity of pyrite, and concluded that

above 850°C, iron enhanced the methane formation if the H₂ pressure was sufficiently high.

Padrick *et al.*²⁶ observed enhancement of the hydrogasification rate of a Pittsburgh Seam coal at 1000°C when various iron-containing minerals were mixed with the coal. They investigated the chemical effect of the minerals by measuring H₂/D₂ exchange rates, and also determined the physical effect of the mineral addition on the resultant surface areas and pore volumes of the chars. While the correlation of 1000°C hydrogasification rates with measured parameters was somewhat better including the chemical effects of the minerals, it was concluded that the gasification rates for the various sources of reduced iron were primarily due to the physical interaction of the minerals with the coal.

REFERENCES

1. Marson, C. B. and Cobb, J. W., *Gas J.* 171, 39 (1925).
2. Davidson, R. M., "Mineral Effects in Coal Conversion," Rept. No. ICTIS/TR22, IEA Coal Research, London, January 1983.
3. Otto, K., Bortosiewicz, L., and Shelef, M., *Fuel* 58, 85 (1979).
4. Fisher, J., Young, J. E., Johnson, J. E., and Jonke, A. A., Report ANL 77-7 (1977).
5. Plogman, H. and Kuhn, L., Proceedings of the International Conference on Coal Science, Düsseldorf, Germany, September 7-9 (1981).
6. Gluskoter, H. J., Shimp, N. F. and Ruch, R. R., in "Chemistry of Coal Utilization. 2nd Supplementary Volume," John Wiley and Sons, New York, NY, pp. 369-424 (1981).
7. Granoff, B. and Traeger, R. K., *Coal Process. Technol.* 15, (1979).
8. Mukherjee, D. K. and Chowdhury, P. A., *Fuel* 55, 4 (1976).
9. Gray, David, *Fuel* 57, 213 (1978).
10. Gray, J. and Shah, Y. T. in "Reaction Engineering in Direct Liquefaction," Adison Wesley Pub. Co., New York, NY (1981).
11. Derbyshire, F. J., Varghese, P. and Whitehurst, D. D., Preprints, Amer. Chem. Soc., Div. Fuel Chem. 26, No. 1, 84 (1981).
12. Whitehurst, D. D., Mitchell, F. U. and Farcasiu, M., in "Coal Liquefaction. The Chemistry and Technology of Thermal Processes," Academic Press, New York, NY, pp. 163-177 (1980).
13. Thomas, M. G., Padrick, T. D., Stohl, F. V. and Stephens, H. P., *Fuel* 61, 761 (1982).
14. Montano, P. A. and Granoff, B., *Fuel* 59, 214 (1980).

15. Montano, P. A., Bommanavar, A. S., and Shah, V., Fuel 60, 703 (1981).
16. Stohl, F. V. and Granoff, B., 90th Annual Meeting of the AIChE, Houston, TX (1981).
17. Anthony, D. B. and Howard, J. B., AIChE J. 22, 625 (1976).
18. Stangby, P. C. and Sears, P. L., Fuel 60, 131 (1980).
19. Franklin, H. D., Peters, W. A. and Howard, J. B., Preprints, Amer. Chem. Soc., Div. Fuel Chem. 26, No. 2, 121 (1981).
20. Jenkins, R. G., Nandi, S. P. and Walker, P. L. Jr., Fuel 52, 288 (1973).
21. Hippo, E. J. and Walker, P. L. Jr., Fuel 54, 245 (1975).
22. Tomita, A., Mahajan, O. P. and Walker, P. L. Jr., Fuel 56, 137 (1977).
23. Linares-Solano, A., Mahajan, O. P. and Walker, P. L. Jr., Fuel 58, 327 (1979).
24. Mahajan, O. P., Tomita, A., Nelson, J. R. and Walker, P. L. Jr., Fuel 56, 33 (1977).
25. Hüttinger, K. J. and Krauss, W., Fuel 60, 93 (1981).
26. Padrick, T. D., Rice, J. K. and Massis, T. M., Preprints, Amer. Chem. Soc., Div. Fuel Chem. 27, No. 3, 300 (1982).