Thermochimica Acta, 84 (1985) 371–375
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

A DTA STUDY OF SOME OXIDATION CHARACTERISTICS OF COLORADO OIL SHALE

I.C. LEE, M.D. LEE * and H.Y. SOHN

*Department of Fuels Engineering, University of Utah, Salt Lake City, Utah 84112-1183 (U.S.A.) and * Department of Chemical Technology, Seoul National University, Seoul 151 (Korea)*

(Received 23 July 1984)

In combustion retorting processes most of the heat necessary for producing oil by the thermal decomposition of kerogen is obtained by burning the carbonaceous residue produced when kerogen is decomposed. The success of the combustion retorting process depends partly on achieving a uniform ignition over the entire cross-section of the oil shale bed to initiate such a process. Thus, the oxidation characteristics of oil shale are important. To describe the ignition process, it was desirable to study the oxidation behavior of oil shale.

Oil shale is sensitive to the presence of oxygen during heating. Two exotherms are generated by oil shale heated in atmospheres containing oxygen [1,2]. The first exothermic peak can be assigned to the combustion of light hydrocarbon fractions from the shale organic matter and the second exotherm arises from the oxidation of char [1,2].

In this study the thermal behavior of the oil shale was studied as a function of shale grade, gas composition, and particle size.

EXPERIMENTAL

The oil shale used in this work originated from the Anvil Points mine site, located in the Colorado Piceance Creek Basin of the Green River formation. The oil yield of the shale sample was determined by the Modified Fisher Assay method [3].

The samples had Modified Fisher Assay values of 0.04, 0.08, 0.13 and 0.19 $l\ kg^{-1}$. Each of these samples was crushed in a jaw crusher. The oil shale was classified, using Tylor standard screens, into four size fractions: $-1.7+0.85$ mm ($-10+20$ mesh); $-0.825+0.425$ mm ($-20+35$ mesh); $-0.425+0.250$ mm ($-35+60$ mesh); and $-0.250+0.150$ mm ($-60+100$ mesh).

A Rigaku PTC-10A unit was used in this experiment. All thermal curves presented in this work were obtained using a heating rate of 20 K min^{-1} and

0040-6031/85/$03.30

an air flow of 250 cm^3 min^{-1}. A Pt/Pt–13%Rh thermocouple was used to measure the temperature.

RESULTS AND DISCUSSION

When oil shale is heated in an inert atmosphere, its DTA behavior shows that the reactions are endothermic. On the other hand, when oil shale is heated in air, its DTA behavior shows that the reactions are exothermic. Two exotherms are due to the combustion of organic matter in two separate phases as discussed above.

The effect of grade

DTA plots for different grades of oil shale are shown in Fig. 1. As the oil shale grade increases, the organic carbon content of the oil shale increases [4]. Thus, as the oil shale grade increases, the exothermic peaks become stronger due to the fact that the higher grade oil shale contains more organic carbon.

The effect of oxygen partial pressure

The effect of oxygen concentration on DTA peaks is shown in Figs. 2 and 3. Figure 2 represents cases in which the air was diluted with nitrogen, and

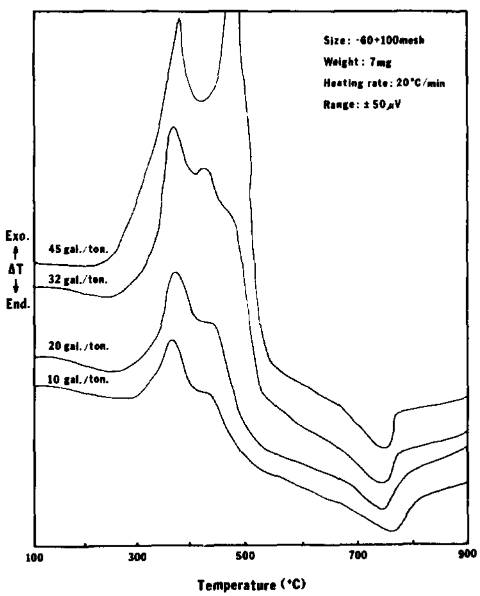


Fig. 1. Effect of grade on the DTA peaks obtained under air.

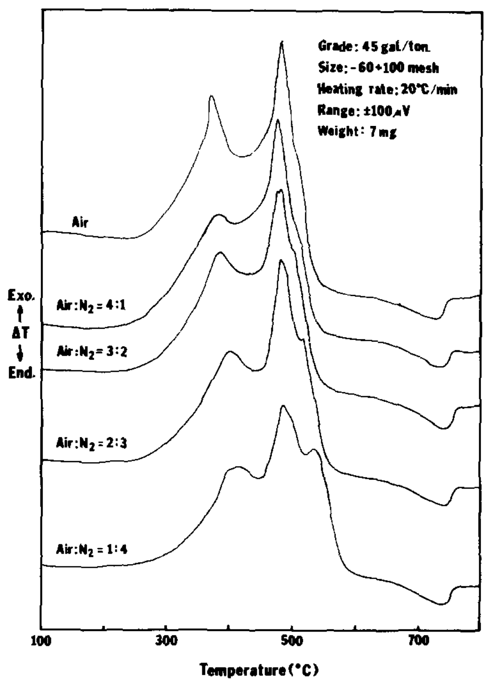
Fig. 3 represents cases in which the air was diluted with carbon dioxide.

A direct comparison of DTA peaks between the cases in which the air was diluted with nitrogen and with carbon dioxide is shown in Fig. 4. This figure shows that the exothermic peaks are affected by the oxygen concentration but not by which gas the air is diluted with. The only difference is the carbonate decomposition temperature. Because CO_2 is present in the sweeping gas, the production of CO_2 gas from the decomposition of carbonaceous minerals is restrained. The carbonate decomposition temperature is therefore higher in CO_2 than in N_2.

Figures 2 and 3 show that the first exothermic peak temperature increases as the oxygen concentration decreases. Regardless of whether the air was diluted with nitrogen or carbon dioxide, the exothermic peak area is the same at the same oxygen partial pressure.

The effect of particle size

DTA results with different particle sizes are shown in Fig. 5. The first exothermic peak height decreases as the particle size increases. Since the



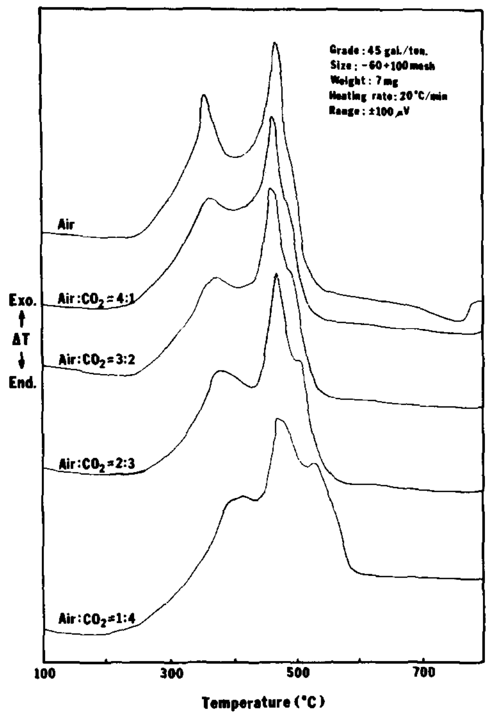


Fig. 2. Effect of oxygen partial pressure on the DTA peaks (air diluted with N_2).

Fig. 3. Effect of oxygen partial pressure on the DTA peaks (air diluted with CO_2).

specific surface area increases as the particle size decreases, more surface reactions are possible in smaller particles. Therefore, smaller particles are more readily ignited.

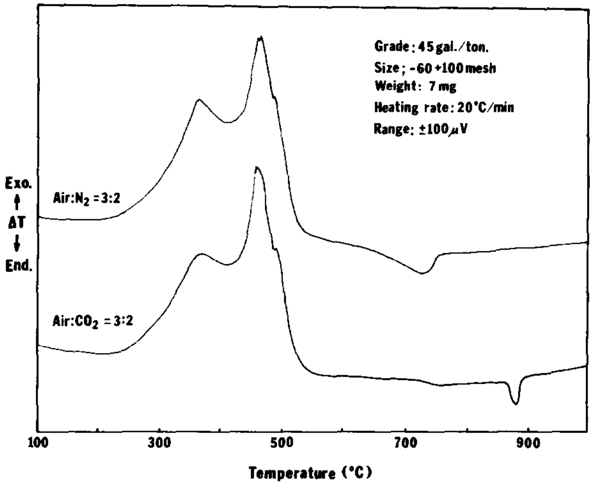


Fig. 4. Effect of dilution species on the DTA peaks.

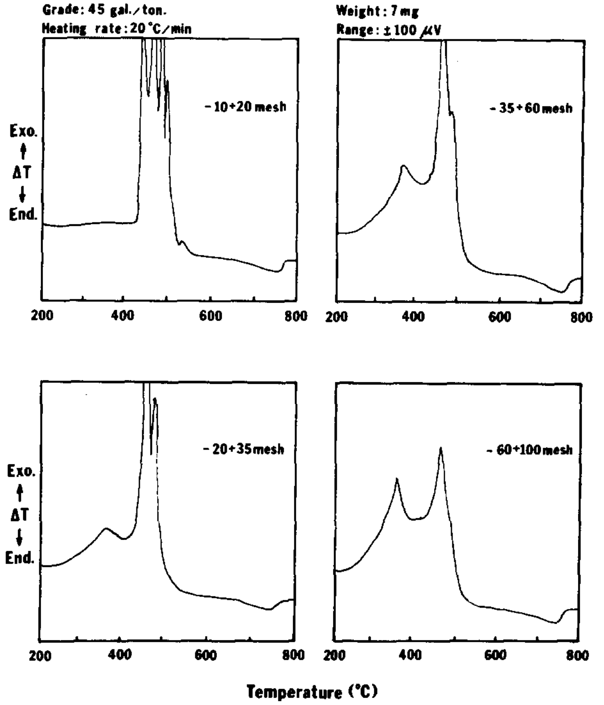


Fig. 5. Effect of particle size on the DTA peaks.

ACKNOWLEDGMENTS

This work was supported in part by a Chevron Oil Company research grant and a Camille and Henry Dreyfus Foundation Teacher–Scholar Award to H.Y.S.

REFERENCES

1 K. Rajeshwar, R. Nottenburg and J. DuBow, J. Mater. Sci., 14 (1979) 2025.
2 J.W. Smith and D.T. Johnson, Am. Chem. Soc., Div. Fuel Chem., Prepr., 21 (1976) 25.
3 N. Stout, G. Koskinas and S. Santor, in O.P. Strausz and E.M. Lown (Eds.), Proc. Symp. on Oil Shale and Oil Sand Chemistry, Verlag Chemie, New York, 1978, p. 285.
4 K.E. Stanfield, I.C. Frost, W.S. McAuley and H.N. Smith, U.S. Bur. Mines, Rep. Invest., (1961) 5725.