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THE GEOLOGY, GEOCHEMISTRY, AND PYROLYSIS KINETICS OF SEVERAL KEY WORLD OIL SHALES

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INTRODUCTION

International oil shales vary widely in age and geological genesis and thus there are great differences in their behavior under pyrolyzing conditions. Our purpose is to understand and quantify how these differences in world oil shales may influence their future recoverability.

Emphasis is on a comparative study of several key international oil shales. Information is presented on the geology, organic and inorganic chemistry, and pyrolysis kinetics. To study and compare the thermal decomposition behavior of the oil shales, a series of nonisothermal gravimetric tests was performed. The thermal data were analyzed using several different kinetic models (Coats-Redfern, Nuttall-Chen, and Anthony-Howard). Results are presented for oil shales from Australia (Rundle), Brazil (Irati), China (Fushun and Maoming), USA (Green River Formation), Israel, Morocco, Sweden (Naerke), and Yugoslavia.

SUMMARY

This study addresses the measurement, analysis, and comparison of pyrolysis kinetics and other characteristic parameters for several key international oil shales. Geologic and chemical information about each of the oil shale samples is presented to illustrate the widely varying nature of oil shale.

A summary of the kinetic models and data analysis methods is presented below along with the more significant kinetic results.

I. The weight loss data were first treated using the two parameter models (Coats-Redfern and Nuttall-Chen). The calculated activation energies were physically very low, thus leading to the evaluation of more sophisticated treatment methods and kinetic models.

II. Next, the TGA data were treated using the models mentioned in 'I', but the temperature range was divided into two regions (i.e., a region above and below 375°). This approach gave a better fit to the single heating rate data, but was not satisfactory for correlating the full multiple heating rate data.

III. The three parameter model, by Anthony and Howard, was best for correlating the full range of nonisothermal data. This is the first time that the Anthony-Howard model has been used to treat nonisothermal oil shale pyrolysis data. The calculated activation energies were physically more reasonable and the overall fit to the data was improved as compared to the two parameter models. This model gave satisfactory results for the full range of heating rates tested. Of course, a different set of model parameters was required for each sample.

IV. The Moroccan shale exhibited the highest kinetic rate constant.

V. Colorado oil shale showed the highest activation energy.

VI. The pyrolysis results clearly show that oil shales differ greatly in their thermal decomposition behavior and that some process modifications or new reactor designs may be needed to optimally treat a specific oil shale. Since oil shales are from widely different physical locations and were formed at greatly different geological times, it is not surprising that the pyrolysis kinetics and other properties vary widely.

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