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The structure and reactivity of a low-sulfur lacustrine oil shale (Colorado U.S.A.) compared with those of a high-sulfur marine oil shale (Julia Creek, Queensland, Australia)

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ABSTRACT

Oil shales from two different continents (Australia and North America) of different ages (100 and 40 million years) and origins (one marine, one lacustrine) have been reacted in the range 355–425 °C under H_2 or N_2 for 1 or 5 h with or without the addition of catalyst. The shales differed in S content, and the nature of the mineral matter, but both had high atomic H/C ratios. The overall reactivity of the two shales was similar and high yields of soluble products could be obtained under relatively mild conditions with only small CO_2 yields, but the temperature dependence of reactivity and the effect of potential catalysts differed markedly. Increasing the temperature and time led to increases in conversion but of different extents. Substituting H_2 for N_2 led to a large increase to conversion for the lower-atomic-H/C ratio marine oil shale. The CH_2Cl_2 solubles from the marine oil shale showed a larger range of compounds than those from the lacustrine oil shale which resembled the CH_2Cl_2 solubles from torbanite, a coal-like material derived from lacustrine algae.

1. Introduction

There is continued interest in the production of fuels from oil shales, because of their ubiquity and the large reserves available [1,2]. Most of the work has concentrated on obtaining liquid and gaseous fuels by retorting (e.g. [1,3–6]), and this is the only technology currently in commercial use [7]. However, this leaves much of the organic matter in the residue, and interest has been expressed in more complete utilization of the organic matter by other methods, e.g. liquefaction under reducing gases [8–11]. For deeply buried shale deposits, such as the Green River oil shale in western USA, in situ extraction would be the only practicable method of obtaining the oil and is currently being evaluated [12,13].

It has been found for materials such as coal that greater insight can be gained into the effect of structure on the yields and compositions of the products by making comparisons of a range of widely distributed coals [14]. In contrast, comparisons of oil shales of different origins and ages have been relatively rarely made and restricted in the range of variables considered or limited to comparisons of kerogens [15–20]. Furthermore, reaction product comparisons were of pyrolysis products, which usually include only part of the organic matter.

For this study, two oil shales were chosen that differed markedly from each other in origin and chemical composition and would therefore be expected to exhibit different reactivities, with the hope that any conclusions would be more generally applicable. The two shales were from widely different locations, one in Australia (Julia Creek, Queensland) and one in U.S.A. (Colorado), of different origins, (marine for Julia Creek, lacustrine for Colorado) and ages (Julia Creek much older than Colorado). The Australian oil shale has never been deeply buried, in contrast to the Colorado shale. The oil shales were characterized by a variety of techniques to determine the general features of the organic and mineral components and then reacted over a range of temperatures, with the products being characterized by solvent fractionation, spectroscopic techniques and, in some cases, ultimate analysis. Comparison of the product yields and compositions for two such different oil shales were carried out to elucidate the influence of the characteristics of the original oil shales on the characteristics of the products.

2. Materials and methods

2.1. Shales

The two shales chosen for detailed study were a shale from Julia Creek, Queensland, Australia which was of marine origin, and of Albian

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age [21] (113–100 million years [22]), and has not been subjected to deep burial and high temperature at any time [23]. The American shale came from the Mahogany Layer of the Parachute Creek Member in the Green River Formation, Colorado, U.S.A. and was denoted Colorado 10H-C 1440–1445 ft. It was of lacustrine origin, and of Eocene age [24] (56.0–33.9 million years [23]).

Julia Creek oil shale was supplied as <0.25 mm particles by Extract Oil (now Global Oil Shale). The Colorado oil shale was supplied as broken fragments from Bore 10H-C drilled for Natural Soda Holdings, in Rio Blanco County, Colorado, U.S.A. The Colorado oil shale was washed three times with deionized H_2O to remove drilling fluid before use. Representative samples of both oil shales were ground to less than 0.18 mm before analysis and reaction and stored in sealed containers under N_2 until used.

2.2. Materials

H_2 and N_2 were purchased from either BOC Australia Ltd (Preston, Vic, Australia) or Air Liquide (Sunshine North, Vic., Australia). Hexane, dichloromethane (CH_2Cl_2; liquid chromatography grade) and tetrahydrofuran (THF; liquid chromatography grade) were purchased from Merck (Kilsyth, Vic., Australia). Hydrochloric acid solution (HCl; UNIVAR grade) for acid-washing the oil shale was purchased from Ajax Finechem Pty. Ltd (Taren Point, N.S.W., Australia). Copper(II) acetate, iron(II) acetate, nickel(II) acetate, cobalt(II) acetate and ammonium hexamolybdate were purchased from Sigma-Aldrich (Castle Hill, N.S.W., Australia).

2.3. Oil shale preparation and characterization

The oil shales were dried and their moisture content determined from the loss of weight on heating them for 3 h under N_2 at 105 °C. Representative samples of shales were washed with 0.5 M HCl as described by Redlich et al. [14] primarily to remove the carbonates and other acid soluble minerals and permit the organic C, N and S contents of the shales to be determined and the H content to be estimated by elemental analysis of the acid-washed shale. It has been shown that HCl of this strength will dissolve all of the carbonates in oil shales [25]. The acid-washed oil shales were also used for solid state ^{13}C NMR to improve the signal-to-noise ratio and reduce the concentration of paramagnetic materials.

Ash yields were determined by heating in air at 490 °C to almost constant weight. A low ashing temperature was used to minimize carbonate–silica reactions [26] so that the ash yield could be used to calculate the results on a dry mineral-matter-free (dmmf) basis, and thus permit valid comparisons between the different oil shales.

Elemental analyses for C, H, N, S and Fe of raw and acid-washed oil shales were carried out by the Campbell Microanalytical Laboratory, University of Otago, N.Z. The values of organic C, H, N and O contents and estimates of inorganic C and of the different forms of S were calculated from the elemental analyses, the ash yields and the loss of weight on acid washing. The organic H and N content so determined may be high because of the presence of water of constitution and hydroxide in acid-insoluble minerals and N-containing minerals, so that an estimate of the error from this was made using the XRD and EDX analyses described below. The O analysis (by difference) also required the assumptions that none of the S was fixed by the ash of acid-washed oil shale and that all the S in the acid-washed oil shale was organic. The first assumption is reasonable in view of the probable loss of most of the Ca, Mg, etc. in acid-washing. The second assumption is not unjustified because XRD indicated only a small pyrite content in all the oil shales. The uncertainty in the O content could be relatively high, because it had to take into account the uncertainty in the amount of water of constitution of clay minerals as well as uncertainties in the C, H, N, and S analyses. The high inorganic content of the oil shales exacerbated the problem. It is at least possible that much of the acid-insoluble Fe was not pyritic but a constituent of the clays or other minerals. The loss of weight on acid-washing could be obtained by direct weighing or from the ash yields of the raw and acid-washed oil shales. The former was considered preferable as being less affected by systematic errors arising when inorganics are converted to ash, but in general the difference between the two determinations was small.

Solid state ^{13}C NMR and thermogravimetric analysis (TGA) were carried out as described by Amer et al. [27]. X-ray diffraction (XRD) spectra were obtained for the raw oil shales using a Philips PW1140 diffractometer with a monochromatic Cu Kα radiation source ($\lambda = 1.5406$ Å) operated at 40 kV and 30 mA, scanned over the 2θ range from 0° to 100° at 1°/min rate and 0.02° intervals. The chemical composition of the raw oil shales was obtained using a JEOL 2100F scanning transmission electron microscope (STEM) equipped with a Bruker 50 mm JEOL X-flash Si (Li) electron-dispersive X-ray detector (EDX).

Representative samples (10 g) of the raw oil shales were ultrasonically extracted with CH_2Cl_2 for 10 min at ambient temperature, filtered, more CH_2Cl_2 added to the filter cake and the process repeated. The CH_2Cl_2-soluble and insoluble fractions were each further processed by the procedure used to work up the CH_2Cl_2-solubles and insolubles from the autoclave reactions (see Section 2.4).

Representative samples of oil shales were impregnated with Cu, Fe, Ni, Co and Mo (0.5 mol/kg dry basis (db) oil shale), and Ni/Mo and Co/Mo (0.195 mol/kg db of Ni or Co and 0.5 mol/kg db of Mo) from suitable aqueous solutions, as described by Amer et al. [27]. This method of impregnation gives excellent dispersion of the catalyst, which is deposited as very fine particles. In materials such as coal, this mode of addition gives high conversion [28,29]. Cu, Fe, Ni and Co were added as the divalent acetates and Mo as ammonium hexamolybdate.

2.4. Reaction procedure and product workup

A representative sample including ~2.1 g of oil shale was dried at 105 °C for 3 h in a flow of N_2 and charged into a stainless steel liner, which was then inserted into a 27 ml stainless steel autoclave. The autoclave was sealed, evacuated, weighed and charged with 3 MPa (cold) of N_2 and weighed again to determine the weight of the gas charge and hence the free space in the autoclave. Before H_2 reactions, the autoclave free space was determined as above, then the autoclave was evacuated, charged with H_2 (3 MPa, cold) and weighed again. N_2 was used to determine the free space because it is denser and a more accurate value of free space could be obtained than with H_2. The high pressure of gas was used to give a sufficiently high pressure to enable transfer of the gas to the gas chromatograph after reaction for analysis.

The reaction procedure and product workup have been described in detail by Amer et al. [27,30]. Asphaltene was defined as the fraction soluble in CH_2Cl_2 and insoluble in hexane and asphaltol as the fraction soluble in THF and insoluble in CH_2Cl_2. The oil + H_2O yield was determined by difference. Direct weighing of the CH_2Cl_2 solubles after removing the CH_2Cl_2 would give inaccurate results because it is very difficult to ensure that all the CH_2Cl_2 is evaporated off in a rotary evaporator without also evaporating off the low boiling constituents of the oil shale product. Furthermore, experiments in a flow through system in which the volatile product including the H_2O was collected indicated that the H_2O yield was small (unpublished work) so that the oil + H_2O yield approximated the oil yield within the limits of error.

Based on weighing uncertainties and the spread of results for replicated runs, the uncertainty in CH_2Cl_2 solubles and gas was about ±1.5 wt.% db (6–7 wt.% dmmf), and in oil + H_2O and asphaltene yields about ±2 wt.% db (8–10 wt.% dmmf). The uncertainty in the yields of individual gases, taking into account weighing and calibration uncertainties, was about 15% of the result, but the spread of results for replicated runs indicated higher uncertainties.

2.5. Product analysis

The CH_2Cl_2-solubles from 390 °C and some 425 °C runs were analyzed by gas-chromatography–mass spectrometry (GC–MS) on a