



A comparison of the structure and reactivity of five Jordanian oil shales from different locations



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HIGHLIGHTS

- Significant differences in reactivity depending on the locality.
- Reactivity of the less reactive oil shales can be considerably enhanced by catalysts, particularly Co/Mo.
- Reaction under hydrogen gave slightly higher yields than reactions under nitrogen.
- There were significant variations in the composition of the liquid products.
- Only low yields of CO₂ were obtained under the conditions used.

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ABSTRACT

Reactions of five Jordanian oil shales, Yarmouk in the north, El-Lajjun, Sultani and Attrat Um Ghudran in the center and Ma'an in the south have been carried out at 355 °C, 390 °C and 425 °C for 1 h under N₂ or H₂. The shales showed significant differences in reactivity, with central and northern Jordanian oil shales being more reactive on a dmmf basis than those from the south. However, the dmmf product yields of southern (Ma'an) oil shale for 5 h reactions were similar to those for 1 h reactions of the other shales. The only relationship between characteristics of the oil shales and the yields of useful products was the proportion of aromatic carbon in the solid state ¹³C NMR spectra of the shales, the Ma'an shale with the lowest aromatic carbon value being the least reactive. The central Jordanian oil shales were less sensitive to the action of catalysts than those from the north and the south. H₂ generally gave higher yields of useful products than N₂. Mo-based catalysts were the most effective in all cases for both gases.

The composition of the liquid products from 390 °C reactions as reflected in the ¹H NMR spectra and gas chromatography–mass spectroscopy did not correlate with the differences in reactivity. Similarly the C, H, N and S elemental analysis data for the products did not correlate with the reactivity nor did the sulfur content of the products correlate with that of the shale. The CO₂ yields under the reaction conditions used were small.

In summary, the Jordanian oil shales show unexpected structural and reactivity differences, when it is considered that they were deposited at roughly the same time in the same region.

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1. Introduction

Jordanian oil shale was first exploited for the production of oil during the First World War [1] and there is continued interest in the recovery of liquid fuels from Jordanian oil shales [2]. Attention to date has concentrated on El-Lajjun oil shale (recently [3–7]).

Some studies on other single oil shales, Sultani [8–10] and Attrat [11,12] have appeared, and comparisons have been made between the pyrolysis of El-Lajjun and Sultani oil shale [8,9]. Most of these studies have focused on pyrolysis of the shales [10,11,13,14], including kinetics studies of El-Lajjun [4] and Attrat [11] pyrolysis. A comparison between the pyrolytic behavior of El-Lajjun and Sultani shales using TGA showed a greater reactivity for El-Lajjun shale, possibly due to its higher S content [8]. A further TGA study of these shales confirmed the greater reactivity of El-Lajjun and showed that the reactivity was not greatly influenced by particle size [15].

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Solvent extraction of El-Lajjun shale with tetralin at 230–360 °C showed no difference between reactions under N₂ or H₂ [16]. Extraction of El-Lajjun shale with a range of organic solvents in the temperature range 25–50 °C showed maximum yield of extract using a dipolar aprotic solvents such as dimethylsulphoxide [17]. Extraction of El-Lajjun shale with supercritical CO₂ and hexane as co-solvent at 450 °C and 3200 psi (22.1 MPa) gave an oil yield of about 10 wt%, significantly higher than yields obtained by extraction with conventional organic solvents e.g. CH₂Cl₂ at ambient temperature [5].

No evaluation of the effect on oil yields of adding catalysts appears to have been reported for Jordanian oil shales. Al-Harashsheh et al. [4] claimed that the demineralisation of El-Lajjun shale led to a significant increase in the Fischer Assay oil yield on a wt% basis. However, the ash yield of demineralised shale was not given, make it difficult to assess the significance of these results.

The literature indicates that no comparison of a wide range of Jordanian oil shales has been reported. All Jordanian oil shales are of Maastrichtian age, laid down in the shallow continental shelf of the Tethys Ocean. This shelf did not have a flat sea floor but consisted of a series of separate basins. The oil shales were deposited in the centers of these basins and, because the conditions varied from one basin to the next, there is a possibility of significant differences in reactivity between oil shales from different localities [18].

This paper describes the characterization and the reactivity under H₂ and N₂ of five Jordanian oil shales, Yarmouk from the north, El-Lajjun, Sultani and Attrat from the center and Ma'an from the south of the country.

2. Experimental

2.1. Materials

Oil shale from the El-Lajjun deposit in the Karak region was received from Jordan Energy & Mining Ltd., a company investigating commercial development of the El-Lajjun deposit, as <2 mm particles. Oil shales from Sultani, Attrat, Ma'an and Yarmouk were supplied as bore samples by the Natural Resources Authority of Jordan. H₂ and N₂ were purchased from BOC Australia Ltd. (Preston, Vic, Australia). Hexane and dichloromethane (CH₂Cl₂; liquid chromatography grade) and tetrahydrofuran (THF; empura grade) were purchased from Merck (Kilsyth, Vic, Australia). The soluble salts used to treat the oil shales with potentially catalytically active metals, 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).

2.2. Oil shale pre-reaction preparation and characterization

The oil shales were ground to <180 μm in air and the ground material stored in sealed containers under N₂ until used. The water content of the samples was taken as the loss of weight observed when they were heated in a flow of N₂ for 3 h at 105 °C. Representative samples of shales were washed with 0.5 M HCl as described by Redlich et al. [19] to remove the carbonate minerals, so that the C, H, N and S contents of the organic fraction of the shales could be obtained by elemental analysis of the acid-washed shale. A second wash with 0.5 M HCl or substituting 1.0 M for 0.5 M HCl had no significant effect on the removal of cations from the oil shales. The removal of carbonate by acid washing is demonstrated by the analytical results in Table 1, which showed significant decreases in C content on acid washing. The acid washed oil shale was only used for elemental analysis and solid state ¹³C NMR.

Representative samples of oil shales were impregnated with Cu, Fe, Ni, Co and Mo (0.5 mol/kg 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. Cu, Fe, Ni and Co were added as the divalent acetates and Mo as ammonium hexamolybdate. Solution(s) containing the required amount of metal(s) were added to the oil shale in a flask and the mixture stirred under diaphragm pump vacuum (~0.1 kPa) until the oil shale was well wetted. Stirring was continued for 6–12 h with the flask sealed under N₂, and then N₂ was passed through the flask till all the liquid water had evaporated. The ammonia from ammonium molybdate was lost during treatment, as evidenced by the dry weight of the treated oil shale. The treated oil shales were stored in sealed containers closed under N₂ until used; they were only dried immediately before charging into the reaction autoclave.

Ash yields were determined by heating in air to nearly constant weight. A low ashing temperature (490 °C) was used to minimize carbonate–silica reactions [20] and thus obtain ash yields that could be taken to represent the inorganic content of the oil shale. For Yarmouk oil shale the ash yield was probably higher than the inorganic content, due to weight gain resulting from fixing of sulfur in the ash of the raw oil shale.

Elemental analyses for C, H, N, S and Fe for raw and acid-washed oil shales were carried out by two established commercial laboratories, HRL Technology Ltd (El-Lajjun and Sultani-not Fe) and the Campbell Microanalytical Laboratory, University of Otago, N.Z. (Attrat, Ma'an, Yarmouk and Fe for Sultani). 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 O analysis (by difference) was calculated on 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 errors caused by the presence of pyritic S would be expected to be small, because XRD indicated only a small pyrite content. It is likely 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, except for Attrat oil shale. In that case an accidental loss occurred during acid-washing and the loss of weight on acid washing was calculated from the ash yields.

Representative samples (10 g) of the raw oil shales were ultrasonically extracted with CH₂Cl₂ for 10 min at ambient temperature, filtered, more CH₂Cl₂ added to the filter cake and the process repeated. The CH₂Cl₂-soluble and insoluble fractions were each further processed by the procedure used to work up the CH₂Cl₂-solubles and insolubles from the autoclave reactions (see Section 2.3).

The solid state ¹³C NMR spectra for acid-washed oil shales were determined using a Bruker 400(¹H)/100(¹³C) MHz spectrometer with cross polarization-magic angle spinning (CP/MAS). The acquisition time was 1000 min with 20,000 scans averaged and a repetition time of 3.0 s, sample spinning rate 30 kHz. Thermogravimetric analysis (TGA) was carried out on the raw oil shale using a Setaram 24 Thermogravimetric Analyser. The sample (~20 mg) in a flow of N₂ was held at 20 °C for 10 min, heated to 120 °C at 10 °C/min, held at 120 °C for 30 min, then heated to 950 °C in a flow of N₂ at 10 °C/min, then held at 950 °C for 50 min in air. X-Ray diffraction (XRD) spectra were obtained for the raw oil shales using a Philips PW1140 diffractometer with a monochromatic Cu Kα source radiation (λ = 1.5406 Å) operated at 40 kV and 30 mA, scanned over the 2θ range from 0°–100° at 1°/min rate and 0.02° intervals. The chemical composition of the raw oil shales

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