



Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap

Long time, low temperature pyrolysis of El-Lajjun oil shale

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ARTICLE INFO

Keywords:

Oil shale

Pyrolysis

Low-temperature

Long-time reactions

Oil characterization

High conversion

ABSTRACT

There is continuing interest in in situ production of oil from oil shale, particularly for deep deposits and for environmental reasons. Such production would involve long-time, low temperature pyrolysis. Accordingly, reactions of El-Lajjun oil shale have been carried out under N₂ for 7, 14 and 28 days at temperatures in the range 240–320 °C. The conversion plateaued at 300 °C and above at a value of about 80 wt% dmmf and was the same for 7 and 14 day pyrolysis. The total conversion decreased by 15% as the temperature decreased to 280 °C. The lower conversions at 240 and 260 °C were the same for 14 and 28 days but oil yield increased at the expense of asphaltene for the longer time. Sulfur content of the oil + asphaltene decreased with increasing reaction temperature (240–300 °C) and time (280–300 °C) from 13 wt% to a plateau of about 7 wt%. The characteristics of the oil and oil + asphaltene changed steadily with temperature up to 300 °C, but increasing the temperature further to 320 °C had little effect. The results show that high conversion to products of good characteristics can be obtained for reactions at sufficiently long times at temperatures as low as 300 °C.

1. Introduction

A significant amount of work has been carried out on attempted production of fuels from Jordanian oil shales. Reactions have been limited to short term reactions (0–10 h) in sealed autoclaves [1–6]. In addition several Jordanian shales were reacted in simple flow-through experiments giving similar yields but the flow through reactions gave much lower asphaltene/oil ratios and a much more complex mixture of products [7]. Similar techniques, in which the product is collected continuously during the run e.g. in a Fischer Assay apparatus, have been extensively applied since 2005 by various workers [8–12].

The above experiments are all relevant to ex-situ processing when the shale has been mined and then retorted above the ground. There has been significant interest in in-situ processing on Green River shales [13]. Advantages of this approach include access to shales at unmineable depths [14], potential trapping of CO₂ in the rock formation, thus preventing the release of greenhouse gases [15], lower reaction temperatures, less water use [16] and the possibility of carrying out reactions below the water table, thus minimizing the pollution of potable and agricultural water [17]. Such experiments would use reaction times up to several months [15]. Laboratory trials attempting to reproduce the long times and low temperatures to be used have been carried out for Green River oil shales [18–21]. A recent trial used similar conditions to those of this study [21] and comparisons will be

made between the results of long-time experiments for Green River and Jordanian oil shales.

Jordan possesses significant shale deposits at Azraq which are below the water table [22]. The shale is in parts deeply buried [23] and only exploratory wells have been dug [24]. It is of interest to know how the products of low-temperature, long time experiments differ from those obtained by more conventional batch autoclave and flow-through experiments. Therefore this paper describes low-temperatures, long-time experiments using El-Lajjun oil shale, for which much information is already available from higher temperature, short-time experiments.

El-Lajjun oil shale is of similar age to that from the Azraq Basin, Late Cretaceous to Mid-Eocene [25], and the average Rock-Eval hydrogen index and T_{max} values of Azraq oil shales, about 550 and 423 °C respectively [26], are similar to those for El-Lajjun oil shale, 480 and 415 °C [27]. The deposition conditions were not identical, being sub-oxic for Azraq oil shale and anoxic for El-Lajjun [23], but the similarity in location and age suggests that the two marine oil shales would show sufficient similarity that the results obtained for El-Lajjun oil shale would be useful in predicting trends for Azraq oil shale.

Pyrolysis experiments have thus been carried out on El-Lajjun oil shale using low temperatures and long reaction times. These have given promising results.

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<https://doi.org/10.1016/j.jaap.2018.01.017>

Received 11 December 2017; Received in revised form 14 January 2018; Accepted 15 January 2018
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2. Materials and methods

2.1. Materials

Oil shale from the El-Lajjun deposit in the Karak region in Jordan was supplied by Jordan Energy and Mining.

N₂ was purchased from British Oxygen Company (BOC). Liquid chromatography grade *n*-hexane (C₆H₁₄) and analytical grade dichloromethane (CH₂Cl₂) were supplied by Merck and HPLC grade tetrahydrofuran (THF) was purchased from Fischer Chemical. HCl solutions were prepared from analytical grade 32% hydrochloric acid stock solution provided by Ajax Finechem Pty Ltd.

2.2. Instrumentation and experimental method

2.2.1. Oil shale pre-reaction preparation and characterization

A representative sample of 500 g was separated by V-shaped blender and sieved through a 2.8 mm sieve. Two-thirds of the sample was retained on the sieve and the +2.8 mm fraction was ground to pass a 2.8 mm sieve to produce the final sample. Successive representative division of the sample was done in order to obtain 10 g samples for long duration reactions and sample characterization.

For ashing experiments, a representative oil shale sample was ground to < 250 μm and then ashed at 490 °C for several periods of ~5 h until the difference between successive weights was negligible. This low ashing temperature was chosen in order to minimize carbonate-silica reactions [28], thus the ash yield could be considered as an approximation to the oil shale mineral part and so could be used to convert pyrolysis product yields from a dry basis (db) to a dry mineral matter-free (dmmf) basis. A small portion of the ground sample was washed with 0.5 M HCl in order to remove carbonates and other acid soluble mineral parts so that the C, H, N and S contents of the organic fraction could be obtained by the elemental analysis of the acid-washed shale. The loss of weight on acid-washing was obtained by drying the acid-washed sample at 105 °C under N₂ until constant mass was achieved.

Elemental analyses for C, H, N and S for the raw oil shale and the acid-washed oil shale were carried out at the Campbell Microanalytical Laboratory, University of Otago, New Zealand.

Pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS) analysis for the acid-washed oil shale was carried out on a Chemical Data Systems (CDS) Pyroprobe 5200 connected to a GC/MS (Agilent 6850 GC and 5790 MSD). A small amount of the sample was loaded in a quartz tube with a quartz wool plug at each end and the tube inserted into the platinum heating coil of the Pyroprobe. The coil was heated under helium initially to 100 °C for 1 s, rapidly ramped to 650 °C at 10 °C/ms and kept for 15 s. The products of the flash pyrolysis process were then released through a heated transfer line (320 °C) under a helium flow to the GC/MS. An Agilent HP-5MS capillary column with a 30 m length, 0.25 mm internal diameter and 0.25 μm film thickness was used to analyze the pyrolysis products under a constant helium flow of 1.0 ml/min. The GC was operated at an inlet temperature of 320 °C. The column temperature program for all samples was: initial temperature 32 °C for 3 min; ramped firstly to 200 °C at 8 °C/min then to 305 °C at 10 °C/min and held there for 10 min.

2.2.2. Reaction procedure and work up

Long duration pyrolysis (7, 14 and 28 days) was carried out in 100 ml stainless steel autoclaves without shaking. 10 g of dried oil shale sample were charged into the autoclave and then the autoclave was evacuated, weighed and charged with 3 MPa N₂. High N₂ pressure was necessary to permit collection and analysis of gas with the system used, the actual figure of 3 MPa being chosen to be the same as in earlier work [21]. The autoclave was reweighed and this process was repeated for several days to check gas leakage. The autoclave was connected to

two heating elements, top and bottom heating elements, so that the reaction temperature would be reached quickly. Each heating element was connected to a temperature controller by a thermocouple built into the element and the reaction temperature was monitored by temperature controlling software. Temperatures in the range 240–320 °C were investigated. At the beginning of the reaction, the temperature was carefully adjusted and then monitored throughout the reaction by the software. Final reaction temperature was reached within 30–60 min. After the end of the reactions, the heating elements were switched off and were not removed until the temperature of the autoclave dropped to 100 °C. This is because a slow cooling rate will minimize gas leaks due to non-uniform autoclave cooling.

After cooling, the autoclave was connected to an Agilent 3000 Micro Gas Chromatograph. The inlet and injector temperatures were 100 °C and then the gases were introduced into four columns; MS 5A PLOT for H₂, N₂ and CH₄ (10 m × 0.32 mm, 110 °C column temperature), PLOT U for CO, CO₂, C₂ hydrocarbons, H₂S and COS (8 m × 0.32 mm, 100 °C column temperature), Alumina PLOT for C₃–C₅ hydrocarbons (10 m × 0.32 mm, 140 °C column temperature) and OV-1 for isobutane and *n*-hexane (10 m × 0.15 mm × 2.0 μm, 90 °C column temperature). After the analysis, the autoclave was vented and the total weight of the gas in the autoclave was determined assuming that the gases were ideal and that the gases detected in the analysis and N₂ were the only gases present.

The solid and liquid product workup has been described previously [3]. In brief, the sample was washed and scraped out from the autoclave liner with CH₂Cl₂ into a flask and then subjected to Lundin distillation to remove water. The water-free material was ultrasonicated for 10 min, filtered and the process was repeated twice to achieve almost complete extraction of CH₂Cl₂ soluble matter. The CH₂Cl₂ insolubles were dried at 105 °C under flowing N₂ for three hours and then weighed. After this, CH₂Cl₂ insolubles were extracted with THF using ultrasonication for 10 min and then filtered. The THF insolubles were dried at 105 °C under N₂ and weighed. A rotary evaporator was used to remove most of the THF and then the remaining filtrate (asphaltol) was dried in a vacuum oven at 55 °C to constant weight. Most of the CH₂Cl₂ in the CH₂Cl₂ soluble material was removed by rotary evaporation and the remaining CH₂Cl₂ solubles kept in the fume cupboard overnight to remove remaining traces of CH₂Cl₂. The CH₂Cl₂ soluble material was weighed and diluted by *n*-hexane (1:20 by weight). This mixture was ultrasonicated for 3 min, filtered and the solid residue of the filtration (hexane insoluble material) dried in a vacuum oven at 55 °C to obtain CH₂Cl₂ soluble, hexane insoluble material (asphaltene).

2.2.3. Product analysis

CH₂Cl₂-solubles were analysed for C, H, N, S and Cl by Campbell Microanalytical Laboratory, University of Otago, New Zealand.

The CH₂Cl₂ soluble fractions obtained after the reactions at different temperatures for different periods of time were analysed by gas chromatography-mass spectrometry (GC/MS) on a HP6890 instrument (Agilent Technologies) in splitless mode. For GC, an HP capillary column (HP-5MS 5% phenylmethylsiloxane, 30 m long, 0.25 mm internal diameter, 0.25 μm nominal film thickness) was used. The inlet temperature was 230 °C. The oven temperature was initially held at 50 °C for 2 min, raised to 200 °C at a rate of 4 °C/min and held at 200 °C for 2 min. The temperature was then raised to 300 °C at a rate of 8 °C/min and maintained at 300 °C for 3 min. For MS, the ionization potential was 70 eV, the acceleration voltage was 1.9 kV, the mass range scanned was *m/z* 45–600 and the ion source temperature was 200–250 °C.

The CH₂Cl₂ soluble fractions were dissolved in CDCl₃ and analysed by ¹H NMR using a high resolution Bruker Ultrashield 400 MHz instrument with a 90° pulse flip angle (9.5 μs delay between pulses).

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