



# Recovery of shale oil condensate from different oil shales using a flow-through apparatus



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## ABSTRACT

Four oil shales from different locations and origins have been reacted in a flow-through system (425 °C, with N<sub>2</sub> or H<sub>2</sub> as sweep gases at 1 atm pressure) with a view to more closely simulating a practical process for oil shale conversion than can be achieved with a sealed autoclave system.

It was observed that there was no general correlation between the yields in the two systems, nor was there a general correlation between the amount of condensate and the amount of volatiles obtained by thermogravimetric analysis.

For all four oil shales, the condensate gave more complex gas chromatography–mass spectrometry total ion chromatograms (GC–MS TICs) than the CH<sub>2</sub>Cl<sub>2</sub>-solubles from sealed autoclave reactions. Surprisingly, the products from one of the Jordanian oil shales, Yarmouk, and an Australian Julia Creek oil shale were remarkably similar. The product from the lacustrine Colorado oil shale was much more similar to that from a lacustrine algal coal (torbanite) than to those from marine oil shales. The differences in yields and product characteristics between sealed autoclave and flow-through reactions suggest that yields and product distributions obtained from sealed autoclave reactions should be treated with caution.

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## 1. Introduction

The increase of oil prices, due to high demand, especially from developing countries, has encouraged the search for alternative energy sources. Relatively high crude oil prices make oil from oil shale an economically viable alternative to petroleum. The resources of oil shale in the world are enormous, with an estimated 2.9 trillion barrels of oil from oil shale being spread all over the world; the United States resource is always ranked as number one with more than 60% of the world reserves [1]. Jordan is a country where all petroleum materials are imported but is seventh in oil shale reserves in the world [2] so that exploitation of the oil shale resource is of economic and security interest.

Oil shale is a fine-grained sedimentary rock which takes the form of a mixture of tightly bound organic and inorganic materials that yield significant amounts of organic hydrocarbons upon pyrolysis [3,4].

Retorting is the process commercially used to extract oil from oil shale. It first breaks down the kerogen to release volatile hydrocarbons, and then further cracks the hydrocarbons into lower-molecular-weight

products. Retorting can occur in an above-ground retort (after mining the oil shale), as an ex-situ process or may be conducted underground, in-situ. In-situ processes require that the oil shale deposit be heated, to release the hydrocarbons, which are then recovered from the deposit [5,6].

The simplest method of producing and investigating the oil produced from oil shale in a laboratory is to heat the oil shale in a sealed autoclave for a known time and at a known temperature under a suitable and defined gas atmosphere and, at the end of the reaction, to collect the product and separate the oil by distillation or solvent extraction. This method has been extensively used and described in a number of recent references [7–11]. However, this method is remote from any likely commercial process, as continuous collection and condensation of the oil is the preferred option. Therefore, in order to obtain a closer approximation to a practical situation, a system in which a sample of oil shale is heated in a stream of gas followed by condensation of the resulting oil is often used. Recent examples include Na et al. [12] with western US oil shale and Al-Harashsheh et al. [13] and Nazzal [14] with the El-Lajjun oil shale. Experiments of a similar type at higher pressure were carried out using the Colorado oil shale by Le Doan et al. [15]. Another advantage of this system is that secondary reactions of the more volatile products are minimized, which may aid in understanding the reaction mechanism. It would therefore be useful to compare the two approaches and investigate the differences and similarities in the yield and composition of the products. In this study four oil shales,

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including two from Jordan, which had been previously reacted in sealed autoclaves [8,16] were reacted in flow-through experiments under conditions as similar as possible to those used for the earlier autoclave experiments.

## 2. Experimental

### 2.1. Materials

Oil shale from the El-Lajjun deposit in the Karak region was received from Jordan Energy & Mining as <2 mm particles. Oil shale from Yarmouk was supplied as bore samples by the Natural Resources Authority of Jordan. The 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, Inc., in Rio Blanco County, Colorado, U.S.A.  $H_2$  and  $N_2$  were purchased from BOC Australia Ltd (Preston, Vic, Australia). Hexane, dichloromethane ( $CH_2Cl_2$ ) and tetrahydrofuran (THF), all liquid chromatography grade, were purchased from Merck (Kilsyth, Vic, Australia).

### 2.2. Preparation and characterization of oil shales

The Colorado oil shale was washed three times with deionized  $H_2O$  to remove drilling fluid before use. The other oil shales were used without preliminary treatment. The oil shales were ground to <0.18 mm in air and the ground material stored in sealed containers under  $N_2$ . The water content of the samples was taken as the loss of weight observed when they were heated in a flow of  $N_2$  for 3 h at 105 °C. Representative samples of the shales were washed with 0.5 M HCl as described by Redlich et al. [17] 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. The acid-washed oil shale was only used for elemental analysis and solid state  $^{13}C$  NMR.

Ash yields were determined by heating the shale in air to nearly constant weight. A low ashing temperature (490 °C) was used to minimize carbonate–silica reactions and thus obtain ash yields that could be taken to represent the inorganic content of the oil shale. Several periods of heating were used until the rate of weight loss became constant; the weight was extrapolated back to zero time to allow for such carbonate–silica reaction as did take place. For the Yarmouk oil shale the ash yield was probably higher than the inorganic content, due to weight gain resulting from fixing of organic sulfur in the ash of the raw oil shale [8].

Thermogravimetric analysis (TGA) was carried out on the raw oil shales as described by Amer et al. [7] (see Supporting information). The solid state  $^{13}C$  NMR spectra for acid-washed oil shales were determined as described by Amer et al. [7] (see Supporting information).

### 2.3. Flow-through reaction procedure and product workup

A representative sample of ~10 g of oil shale dried at 105 °C for 3 h in a flow of  $N_2$  was charged into a stainless steel cage, which was placed in a 70 ml Inconel autoclave modified with an outlet in the bottom for admitting the sweep gas. The stainless steel cage was fitted with a fritted top and bottom, so that the gas could flow freely through the cage and be distributed throughout the volume of the sample. The autoclave was then sealed and connected to the gas flow system as shown in Fig. 1. Gas was supplied from two lines fitted with valves so that a choice of gas mixture could be made. The gas flowed through flow controllers capable of giving flow rates in the range 10–500 ml/min into the bottom of the autoclave. At the top of the autoclave was a line heated by a heating jacket whose temperature was controlled to be about 10–15 °C above that of the autoclave. The sweep gas and the volatile product passed through this line into a condenser which was immersed in a mixture of water and ice. The condenser was constructed with inlet and outlet tubes designed so as to inhibit loss of condensate into the

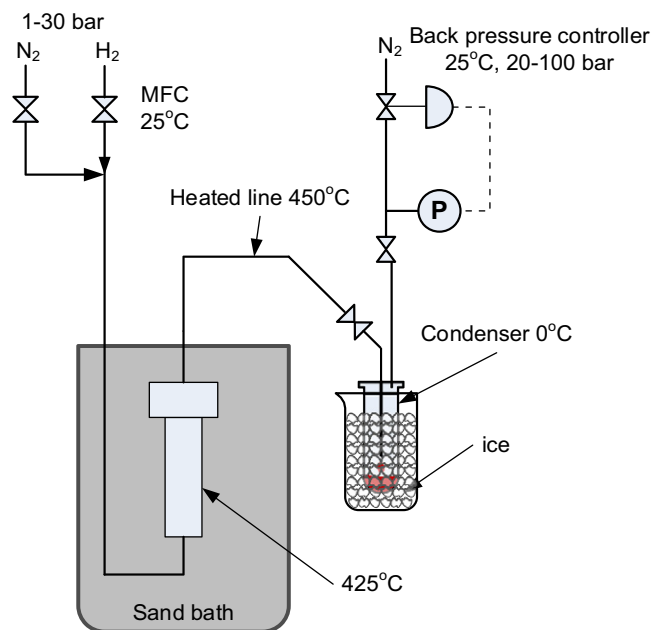


Fig. 1. Flow-through apparatus schematic.

sweep gas in the outlet tube. The sweep gas passed through a back pressure regulator with a pressure range of 2–10 MPa and was exhausted to the atmosphere. The flow controllers and back pressure regulator were spark proof to allow the use of flammable gas mixtures and the electrical supply to the units was led through Zener diodes to prevent spark propagation along the electrical lines.

Before reaction, the autoclave was positioned above the heated sand bath and the sweep gas passed through the autoclave at 500 ml/min, equivalent to a space velocity of 24  $min^{-1}$  under standard conditions and a contact time of 2.3 s, until the sand bath had reached the required temperature. The heater for the heating jacket was switched on and the jacket rapidly reached the final temperature. The autoclave was lowered into the sand bath and reached the set temperature in 10 min, then the sand bath was held at temperature for the required time. For optimum condensate yield (see Section 3.2) the sweep gas flow rate was reduced to 350 ml/min when the autoclave temperature reached 100 °C, then to 200 ml/min when the autoclave temperature reached 200 °C, then to 100 ml/min when the autoclave temperature reached 300 °C, and finally to 50 ml/min, equivalent to a space velocity of 6  $min^{-1}$  and contact time of 23 s, when the autoclave temperature reached 400 °C. This flow rate was maintained throughout the reaction. After the required time at temperature had elapsed, the autoclave was lifted out of the sand bath. The ice level around the condenser was kept topped up during the reaction and until the temperature of the autoclave had fallen to 200 °C. The flow of sweep gas and heating of the jacket were also continued until the autoclave temperature fell to 200 °C. When the autoclave was cool the condenser was removed and weighed and the product in the autoclave scraped out and washed out with  $CH_2Cl_2$ . The solid and liquid product workup was as described in detail by Amer et al. [7]. The oil (hexane-solubles)+ $H_2O$ +gas yield (OWG), including the condensate yield, was determined by difference. Weighing uncertainties and the range of results for replicated runs indicated an uncertainty in the yields of  $CH_2Cl_2$ -solubles+ $H_2O$ +gas of about  $\pm 0.3$  wt.% db, and in OWG, asphaltol (THF soluble,  $CH_2Cl_2$  insoluble) and asphaltene ( $CH_2Cl_2$  soluble, hexane insoluble) yields of  $\pm 0.5$  wt.% db.

### 2.4. Condensate analysis

Selected condensate samples were analyzed for C, H, N, S and Cl by Campbell Microanalytical Laboratory (Otago, New Zealand). The

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