INFLUENCE OF PARTICLE SIZE, GRADE AND PYROLYSIS TEMPERATURE ON THE OIL YIELD FROM JORDANIAN OIL SHALES

J. O. JABER*
S. D. PROBERT

School of Mechanical Engineering,
Cranfield University
Bedford MK 43 0AL, UK

P. T. WILLIAMS

Department of Fuel and Energy,
Leeds University
Leeds LS2 9JT, UK

The effect of changes in some of the experimental parameters on the oil yield has been determined in a laboratory scale reactor heated by an external electrical heater. Five categories of particle sizes of oil shale samples from two deposits in Jordan were pyrolysed by employing a fixed bed retorting system. The reactor and the oil shale sample were heated at a constant rate, and nitrogen gas was used to purge the sample, continuously, in order to remove the pyrolysis products from the reactor as well as to reduce secondary reactions. The liquid products were condensed and collected in a series of cold glass-traps and the off-gases analysed for their hydrocarbon and non-hydrocarbon species.

Subsequent experiments were carried out employing a thermogravimetric analyser using only the four smallest particle sizes under similar conditions as applied to the fixed bed retort. The activation energy was determined using the integral method. The pyrolysis of the investigated shales was found to comply with first-order kinetics within the limits of experimental error. Increasing the particle size resulted in a slight rise in the liquid oil yield, but simultaneously the total gaseous production was decreased. The highest oil yield was obtained at a temperature of 480 (±30) °C. Results obtained from this study agree with those for other grades of oil shales extracted from various deposits world-wide.

Oil Shale and Shale Oil

Oil shale is an inexact and ill-defined term since the rock does not contain oil and is not necessarily shale. Many definitions state nothing about the origin of oil shale or the amount of shale oil present in the rock. A recent definition is that "oil shale (or alum shale) is a natural, impermeable, fine-grained, laminated black or brown rock of sedimentary origin, with a

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* Corresponding author. *E-mail*: j.o.a.jaber@cranfield.ac.uk

mineral content of between 70 and 90 % (by weight), a moisture content of less than ~13 %. It is impregnated with organic matter (i.e. a solid hydrocarbon, called kerogen, typically in a concentration of between 5 and 35 % by weight) that yields oil and/or gaseous hydrocarbons when subjected to heating (in processes such as pyrolysis, destructive distillation or retorting), but is not usually commercially viable when extracted using ordinary organic solvents" [1-4].

From the point of view of energy, the most important constituent of an oil shale is its organic matter, which is composed of both bitumen and kerogen. The latter is the source of shale oil. Kerogen, which comprises the major part of the organic matter, is insoluble in organic solvents at normal pressures and temperatures. The remaining smaller part (i.e. less than 15 %) of the organic matter is mainly bitumen, which can be extracted by an organic solvent, such as benzene, toluene or chloroform [3, 5, 6].

Shale oil is crude liquid oil produced by decomposing the organic content of oil shale by retorting before it has received any additional treatment to produce a commercial product. It is dark brown, odoriferous, waxy oil that is more viscous and typically has a higher pour point than crude oil. This crude shale oil can be burnt as a boiler fuel, or further processed to convert it into commercial products.

Background

The prospects for exploiting vast naturally occurring reserves of oil shale, tar sands or biomass contribute to meeting the world's growing energy demand and receive increasing attention, particularly by the developing countries. The utilisation of such indigenous energy resources in some countries would serve to decrease the rate of dependence on imported fuels. Oil shale, natural deposits of which are widely distributed (in more than 50 countries) throughout the world with known deposits in every continent, is one of the largest undeveloped fossil-fuel resources in the world, and so could be an important source of energy for the near future [7]. Recent conservative estimates of oil shale deposits suggest that the remaining reserves (recoverable by existing technology) world-wide are about 1.3 (± 0.1) × 10^{13} tonnes [8, 9]. This could lead to the production of approximately 2.2 × 10^{13} barrels of shale oil (i.e. ~30 times the current proven reserves of crude oil). But only ~25 % of oil shale reserves are easily recoverable using present technology [10].

Oil shale has already been used as a source of liquid fuel all over the world, including Scotland, Sweden, France, South Africa, Australia, USA, and Brazil. It is still employed in China, Estonia and Russia to yield shale oil through retorting processes as well as for electric power generation by the direct combustion of oil shale.

However, the future of oil shale as an energy source still remains uncertain, because its financial viability is influenced directly by international crude-oil unit prices, as well as the security of supply. The higher the unit prices (and the tighter supplies) of crude oil (and/or

natural gas), the greater the prospects for the large-scale exploitation of oil shale (and other alternative forms of energy). However, the extent to which such an interest will become real and feasible will also depend, to a large extent, on the success of the research on developing energy-efficient, financially attractive and environmentally clean means of converting oil shale into synthetic fuels and/or electricity.

There are several variables that affect the quantity and quality of the shale oil produced as a result of oil shale processing: a thorough experimental study of the influence of all the variables would be time-consuming and not cost-effective for the present research team. However, the most important retorting conditions that may affect the yield of oil from oil shale are the type of the sweep gas, heating rate, particle size, pyrolysis temperature and pressure. In order to maximise the output and conversion efficiency at retorting optimal process conditions should be determined and applied. From previous studies it was concluded that the particle size of the oil shale employed and the pyrolysis temperature greatly influence the oil yield [11, 12], but there is a disagreement concerning the magnitude of the influence of the particle size on the shale oil yield.

Some researchers reported that higher oil yields could be achieved by using a smaller particle size – see Table 1 [13-16]. Others found that the shale oil yield rose as the particle size was increased, but greater amounts of hydrogen and methane were produced during pyrolysis as the particle size is reduced [11, 17-19]. However, another group of researchers claimed that the effect of particle size (on the oil yield), when the oil shale was pyrolysed under slow heating rates, was negligible [20-22]. It appears that the confusion has arisen because the type of oil shale and its grade have not been taken into account.

Table 1. **Conflicting Conclusions Regarding the Influence of Oil Shale Type Combined with Particle Size on the Shale Oil Yield by Pyrolysis**

Oil shale type	Shale oil yield*	Oil shale type	Shale oil yield*
Colorado, USA	(1)	Condor, Australia	(3)
Ohio, USA	(1)	Beypazari, Turkey	(3)
Kark, Pakistan	(1)	Himmetoglu, Turkey	(3)
Salt Range, Pakistan	(1)	Seyitomer, Turkey	(3)
Stuart, Australia	(1)	Maoming, China	(3)
Creek Basin, USA	(2)	Anvil Points, USA	(3)
Kentucky, USA	(2)	North Carolina, USA	(3)
Rundle, Australia	(3)		

* (1) Proportional to; (2) inversely related to; or (3) independent of the particle size.

Thermogravimetric analysis (TGA), which records the loss of weight of a sample as its temperature is raised at a uniform rate, may be used to determine the devolatilisation characteristics and the kinetic parameters for each oil shale sample tested. There is also a disagreement in the TGA results, concerning the influence of the particle size on the degradation of the oil shale as it is heated up: it corresponds to that found in pyrolysis studies. It has been reported that weight loss is proportional to the particle

grain size [23]. However, other studies have shown that the rate of the weight loss is independent of (or only slightly affected by) the particle size, but in the case of very fine particles (i.e. $< 53 \times 10^{-6}$ m maximum dimension), there is a significant decrease in the shale oil yield [24-27].

However, re-examining the data presented by Dogan and Uysal for Turkish oil shales [27] lets to suggest that there is a slight rise in the weight loss upon increasing the particle size. Retorting temperature is one of the most important parameters that affect product yield as well as its composition. Many researchers have studied the influence of this factor on the shale oil and gas yields from different shales, but there is no corresponding information available concerning Jordanian oil shales. There is a general consensus that the shale oil yield rises as the pyrolysis temperature is increased up to ~520 °C. Further increases in temperature result in the yield falling because secondary cracking of the produced vapour occurs [13, 28-31]. Consequently the gas production (consisting mainly of C_1 to C_4 hydrocarbons as well as CO, CO_2 and H_2 gases) would be increased [32-34]. Higher reactor temperatures lead to a process that is more or less far from retorting and close to gasification conditions.

In summary, organic and inorganic mineral components determine the thermal behaviour of oil shale during retorting to yield shale oil and gases. Several factors, such as the crushing and grinding techniques (which may change the carbon distribution, and hence its content in the oil shale particles), oxidation of iron pyrites (which would react with the kerogen), retorting temperature (which has a major impact on the surface secondary reactions) and particle grain size, influence the pyrolysis process.

The present investigation was conducted in order to gain an understanding of the effectiveness of organic matter extraction from Jordanian oil shales. Two samples from different sites in the central part of Jordan have been studied and pyrolysed in a fixed-bed reactor (which closely simulates the conditions that would be found in commercial scale retorts) at a fixed heating rate and final temperature in order to measure directly the rate of oil evolution from retorting such shales. Consequently the yields of gaseous products, process water and retorted shale were determined for various ranges of oil shale particle sizes. The gases formed were analysed in order to determine their composition and yield. Four smallest sizes of oil shale samples (i.e. < 5.6 mm) were analysed in a thermogravimetric analyser to determine the product yields and kinetic parameters. Such information is needed not only as the basis for a detailed kinetic study of the pyrolysis process, but also to aid in the design of a highly efficient retorting system.

Materials and Experimental Methods

Types of Oil Shale

Oil shale is the major and most promising indigenous fossil-fuel resource for Jordan, yet not used there at present. The proven national reserves (i.e. $> 5 \times 10^{10}$ tonnes) should be sufficient to satisfy Jordan's energy requirements for several centuries [35]. However, its employment depends on the

unit cost and attractiveness of each derived product as compared with those of the more commonly used fuels, such as petroleum and natural gas. There is little information available about the retorting of Jordanian oil shales, because there has been only little interest in developing this resource, due to the prevailing low (i.e. ~13 US $ per barrel in 1998) crude oil unit prices. Hence, pre-feasibility studies suggest that the unit cost of the final energy produced (e.g. shale oil or electricity eventually generated via burning oil shale) would far exceed that obtained by using imported crude oil instead.

The representative oil shale samples (from the El-Lajjun and Sultani deposits) were provided by the Ministry of Energy and Mineral Resources, Amman, Jordan, but details about the sampling method used were not provided. These two samples were crushed as received, separately and without further treatment, by a jaw crusher, then sieved into five different sizes — see Table 2.

Table 2. **Main Experimental Conditions**

Fixed bed	
Sample grain size (mm)	< 0.85, ≥ 0.85 - < 2.36, ≥ 2.36 - < 3.35, ≥ 3.35 - < 5.6 and ≥ 5.6
Heating rate (K min^{-1})	20
Final temperature (°C)	550 and 780
Gas carrier	Nitrogen
TGA	
Sample grain size (mm)	< 0.85, ≥ 0.85 - < 2.36, ≥ 2.36 - < 3.35 and ≥ 3.35 - < 5.6
Heating rate (K min^{-1})	5, 20, 30, 40 and 50
Final temperature (°C)	400, 450, 500, 550, 600, 650, 700, 800 and 900
Gas carrier	Nitrogen (and air for one test only)

Elemental Analysis

The CHN elemental technique was used to determine the carbon, hydrogen and nitrogen content of the raw oil shale. The equipment employed for this purpose was a Perkin Elmer 240C Elemental Analyser. The sample was oxidised under static conditions in a pure oxygen environment for six minutes. The elemental analyser was calibrated initially against a known standard. Then the empty platinum boat was weighed, the oil shale sample placed in the boat and the boat re-weighed. The boat containing the sample was introduced into the elemental analyser and the automated analysis data stored. Upon completion of an analysis, the boat was removed and weighed again in order to determine the difference (i.e. the amount of the residual ash). Finally, the elemental composition of the shale was calculated using a computer package.

The Fixed-Bed Gas-Purged Pyrolysis Reactor

This laboratory system was used to pyrolyse oil shale in order to determine the liquid and gaseous products evolved during the thermal decomposition process in relation to the oil shale particle size. The 2×10^{-4} m^3 stainless-
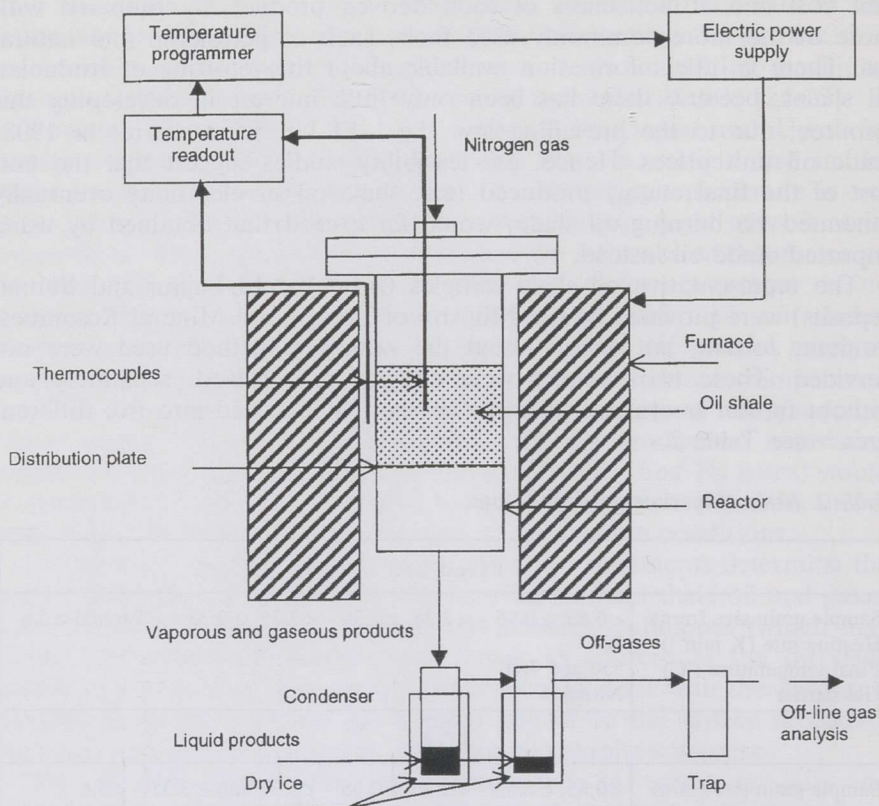
Fig. 1. The fixed bed reactor

steel reactor was heated externally by an electric-ring furnace, with nitrogen as the carrier gas at a fixed metered flow rate to sweep the evolved products from the pyrolysis zone — see Fig. 1. Thus, secondary reactions, such as thermal cracking, re-polymerisation and re-condensation, were minimised. The furnace behaviour was controlled by a programmable temperature controller, which enabled the shale sample to be heated at a fixed rate (of 20 K min^{-1}) to the final pyrolysis temperature via two steps (i.e. the heater was started and allowed to reach a temperature of about 150 °C, and held at this temperature for ~5 minutes in order to remove the water from the shale, and then continued at the same heating rate up to the desired final temperature).

The pre-weighed sample was placed in the middle of the reactor by means of a distributor plate made of stainless steel wire-mesh, which allowed vapours to pass through it under only a minute pressure drop. As the temperature rose rapidly, pyrolysis occurred and the oil vapours evolved. The oil shale sample was held at the final temperature for about an hour or until there was no further significant emission of gas.
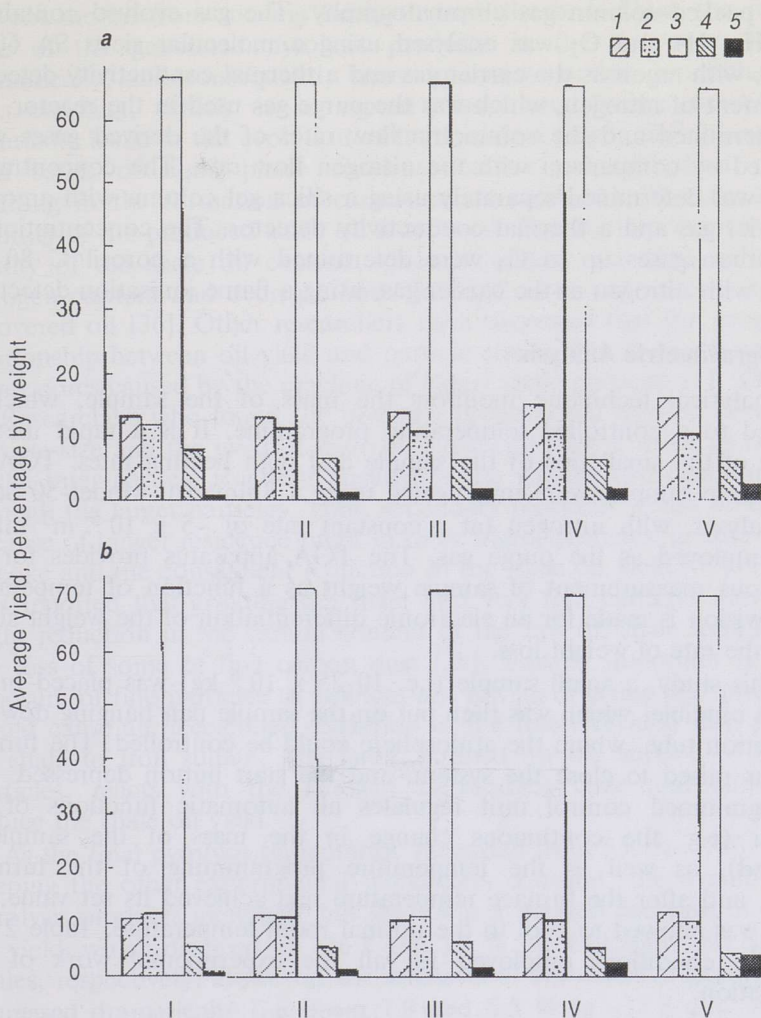
Fig. 2. Influence of the El-Lajjun (*a*) and Sultani (*b*) oil shale particle size on the product yield. Particle size: I - < 0.85; II - ≥ 0.85 -< 2.36; III - ≥ 2.36 -< 3.35; IV - ≥ 3.35 -< 5.6; V - ≥ 5.6. Yields of: *1* - oil, *2* - water, *3* - ash, *4* - gas, and *5* - losses

The derived condensable compounds forming the liquid oil phase were trapped in a glass liner inside a cold trap, and samples of the liquid were collected during each experiment and weighed separately.

On completing each experiment, the apparatus was disassembled and each piece of retort equipment re-weighed: a mass balance of the evolved products was completed from these data.

Gas Analysis

The evolved pyrolysis gases were sampled, using a gas syringe, at intervals throughout the duration of the oil shale pyrolysis, and were analysed off-

line by packed-column gas chromatography. The gas evolved containing CO, CH_4, H_2 and O_2 was analysed using a molecular sieve SA 60-80 column, with argon as the carrier gas and a thermal conductivity detector. The content of nitrogen, which was the purge gas used in the reactor, was also determined and the volumetric flow rates of the derived gases were calculated by comparison with the nitrogen flow rate. The concentration of CO_2 was determined separately using a silica gel column with argon as the carrier gas and a thermal conductivity detector. The concentration of hydrocarbon gases up to C_4 were determined with a porosil C 80-100 column with nitrogen as the carrier gas, using a flame ionisation detector.

Thermogravimetric Analysis

This analytical technique monitors the mass of the sample, which is subjected to a controlled temperature programme. It is a rapid method because of the small size of the sample and high heating rates. TGAs of the oil shale samples were investigated using a Shimadzu Model-50 Series TG Analyser, with nitrogen (at a constant rate of $\sim 5 \times 10^{-5}$ m^3 min^{-1}) being employed as the purge gas. The TGA apparatus provides for the continuous measurement of sample weight as a function of temperature and provision is made for an electronic differentiation of the weight signal to give the rate of weight loss.

In this study, a small sample (i.e. $10-25 \times 10^{-6}$ kg) was placed in the alumina crucible, which was then put on the sample pan hanging down in the reaction tube, where the atmosphere could be controlled. The furnace tube was raised to close the system, and the start button depressed. The pre-programmed control unit regulates all automatic functions of the recorder (e.g. the continuous change in the mass of the sample is measured), as well as the temperature programming of the furnace. Finally, and after the furnace temperature had achieved its set value, the sample was allowed to cool to the normal room temperature. Table 2 lists the main conditions employed for all the experimental work of this investigation.

Results and Discussion

Oil Yield

The yields of shale oil, process water and gases, as well as the retorted shale from the pyrolysis of the El-Lajjun and Sultani oil shales are summarised in Figure 2a and b, respectively, according to the particle size. For both types of oil shale, there is an increase in the shale oil yield, whereas the gas yield and amount of ash decreased with increasing the particle size. This occurs because the small particles have a greater surface area per unit mass and that is why more oil was retained on the surface of the shale, which subsequently undergoes secondary decomposition resulting in lesser oil yields [17].

Also, smaller shale particles are packed more closely, so causing a reduction in the void volume inside the reaction zone, which would

prevent the oil from moving freely through the bed. Thus, the residence time of the generated pyrolysis products in the hot zone increased dramatically, and consequently more intense secondary reactions ensued (i.e. cracking, which is a vapour-phase bond-fission reaction that eventually leads to the evolution of hydrocarbon gases, and coking, which is a series of liquid-phase condensation or polymerisation reactions resulting in the formation of carbonaceous products). Thereby the final quantity of the produced shale oil is reduced. Equally important is the low quality of the shale oil evolved, since secondary reactions increase the nitrogen content and decrease both the H/C ratio and pour point of the recovered oil [36]. Other researchers have suggested that the proportional relationship between oil yield and particle size is due to the formation of larger pores caused by the cracking of bigger shale particles [11, 18].

Researchers who found the inversely proportional relation between the particle size and the yield of shale oil explained such a result as being due to the inter-particle reactions ensuing as the volatile hydrocarbons diffuse through the larger particles. Thus, secondary reactions would be enhanced because of longer residence times in these bigger particles, greater amounts of coke and the consequent reduction in the shale oil yield [37]. However, it is reported that grinding the shale into very fine particles may cause a slight reduction in the carbon content of the raw oil shale sample due to the loss of some of fine carbon dust [38]. Equally important is that the exposure of fine particles to ambient air, during crushing and preparation, would cause an accelerated oxidation of the finely divided iron pyrites in oil shale to iron sulfate. The latter, formed on the surface of the shale particles, reacts with the kerogen to produce coke and consequently reduce the shale oil yield.

As the final pyrolysis temperature increased from 550 to ~780 °C, while keeping the other experimental parameters constant, the overall yield of pyrolysis products increased, but there was a marked decrease in the shale oil yield, which dropped by ~16.7 and 5.6 % for El-Lajjun and Sultani oil shales, respectively. However, the amounts of combustible gases produced increased dramatically (i.e. from 7.9 and 5.5 % to ~17.8 and 17.1 % by weight for the El-Lajjun and Sultani oil shales, respectively). This is attributed to the secondary reactions occurring at high temperatures: mainly oil vapour cracking into gaseous products. Such results are in full agreement with those reported for different shales by other researchers [13, 28, 31, 39, 40].

During the pyrolysis tests, it was observed for both shales that the appearance of retorted shale resembles that of charged shale. Some of the spent shale may be broken into smaller particles during preparation or cleaning of the retorting system.

Elemental Analysis

Elemental analysis of oil shale samples, as received, in relation to the particle size has shown that there is a slight reduction in the carbon content, as well as in the ratio of carbon to hydrogen present as a result of decreasing the particle size - see Table 3.

Table 3. **Dependence of Carbon Content on Oil Shale Particle Size***

Elemental analysis (% by weight)	El-Lajjun		Sultani	
	< 0.85 mm	≥ 0.85-< 2.36 mm	< 0.85 mm	≥ 0.85-< 2.36 mm
Carbon	21.82	22.47	19.39	20.36
Hydrogen	2.23	2.25	1.83	1.90
Nitrogen	0.41	0.42	0.37	0.36
Ash	55.34	53.85	63.47	61.71

* Each of these results is the average of two or more measurements made during completely
independent tests.

This reduction in carbon content is directly responsible for the reduced shale oil yield. Equally important is the influence of secondary reactions on the increased surface area of smaller particles. In addition, the exposure of the fine-particle sample (with its high surface area) to air results in the accelerated rate of oxidation of the finely divided iron pyrites (FeS_2) present in oil shale to iron sulfate. The latter forms on the surface of oil shale particles and reacts with the kerogen to produce coke, consequently leading finally to reduced oil yield [38]. Also the role of diffusion processes during oil shale pyrolysis is significant, because larger particles tend to fissure and so develop high porosity (which develops only as products leave the matrix). Thus the liberation of the products from the shale would be enhanced, without any significant secondary reactions.

During pyrolysis of oil shale and analysis of gaseous products, a strong sulfurous odour (i.e. of rotten eggs) was present, because of the formation of sulfur compounds, mainly hydrogen sulfide (H_2S), due to the fact that Jordanian oil shales have relatively high (i.e. ~3 % by weight) sulfur content [35]. Thus, during pyrolysis H_2S gas was formed, as a result of the reaction of pyrite with organic matter [41]: it leaked out of the test rig either while gas sampling or cleaning of the system before the next test.

Gas Composition

The gases generated during pyrolysis of oil shale were sampled and analysed off-line by packed-column chromatography. They consist mainly of hydrogen, carbon monoxide, carbon dioxide, methane, ethane, ethene, propane, propene, isobutane, butane and butene − see Tables 4 and 5.

The overall yield of the gases decreased as the particle size increased from < 0.85 to > 5.6 mm. The rate of gases evolved during the pyrolysis of Jordanian shale increased up to a temperature of ~500 °C, and then decreased dramatically for further temperature rises. The explanation for this is that the initial transformation of kerogen to bitumen (which is an intermediate product different from naturally occurring bitumen) produces only traces of non-condensable gases, but during the subsequent conversion of bitumen to oil, large volumes of these gases are generated. Above ~500 °C, the char underwent secondary pyrolysis which further releases hydrogen and methane. Also, secondary reactions of the oil vapours produce increased concentrations of the low molecular weight fractions, such as methane and ethane [32, 33, 42]. The presence of such

gases (i.e. hydrocarbons and hydrogen) above 500 °C indicates that significant secondary reactions occur, leading to more hydrocarbons being generated, but lower oil yields.

Table 4. **Gases Evolved from the Pyrolysis of El-Lajjun Oil Shale (Percentage by Weight of the Dry Initial Sample)**

Gas	Particle size (mm)				
	< 0.85	≥0.85-<2.36	≥2.36-<3.35	≥3.35-<5.6	≥ 5.6
Non-hydrocarbons					
Hydrogen	0.145	0.141	0.141	0.138	0.143
Carbon monoxide	0.059	0.078	0.055	0.051	0.046
Carbon dioxide	1.980	1.987	1.950	1.990	1.810
Total (1)	2.184	2.206	2.146	2.179	1.999
Hydrocarbons					
Methane	1.449	1.110	1.065	1.031	1.002
Ethane	0.755	0.709	0.658	0.588	0.571
Ethene	0.508	0.491	0.481	0.465	0.441
Propane	0.401	0.586	0.611	0.634	0.676
Propene	0.667	0.766	0.771	0.659	0.699
Isobutane	0.016	0.014	0.010	0.012	0.011
Butane	0.065	0.106	0.200	0.210	0.193
Butene	0.023	0.033	0.039	0.040	0.031
Total (2)	3.884	3.815	3.835	3.639	3.624
Total (1) + (2)	6.068	6.021	5.981	5.818	5.623
Various ratios					
Ethene/Ethane	0.673	0.693	0.731	0.791	0.772
Propene/Propane	1.663	1.307	1.262	1.039	1.034
Alkenes/Alkanes	0.446	0.510	0.507	0.470	0.477

When the final pyrolysis temperature was increased to 780 °C, while other process variables were kept constant, there was a huge increase in the concentration of individual gases released, especially of H_2, CH_4, CO and CO_2. This is due to oil cracking, which produces hydrocarbon as well as non-condensable gases (e.g. H_2, CO and CO_2). Above 500 °C, secondary pyrolysis of the shale residue releases more H_2 and CH_4 [32-34, 43]. The latter forms approximately 40 % of the total hydrocarbon gases — see Tables 4 and 5. The increase in CO concentration in the effluent gas is due to the gasification reaction between CO_2 and the residual carbon (i.e. $C + CO_2 \rightarrow 2CO$).

Most of the CO_2 emitted is attributed to the decomposition of carbonates present in the oil shale sample, but a small amount of it is contributed from the gas-water shift reaction (i.e. $CO + H_2O \leftrightarrow H_2 + CO_2$). It is also possible that CO_2 could be generated via the reaction of calcite with quartz and other silicates [40, 44, 45]. The increase in the alkenes/alkanes ratio with increased particle size (or final pyrolysis temperature) is considered to be an indication that secondary reactions are occurring faster, and thus lower yields of shale oil were obtained [46]. It was reported that ethene/ethane and propene/propane ratios have also been used as indicators of the pyrolysis conditions (i.e. lower ratios being

accompanied by increased secondary reactions) and hence oil yields were reduced [30, 47, 48].

Table 5. **Gases Evolved from the Pyrolysis of Sultani Oil Shale (Percentage by Weight of the Dry Initial Sample)**

Gas	Particle size (mm)				
	< 0.85	≥ 0.85 - < 2.36	≥ 2.36 - < 3.35	≥ 3.35 - < 5.6	≥ 5.6
Non-hydrocarbons					
Hydrogen	0.117	0.122	0.111	0.108	0.115
Carbon monoxide	0.211	0.183	0.143	0.178	0.198
Carbon dioxide	2.059	2.001	1.863	1.857	1.694
Total (1)	2.387	2.306	2.117	2.143	2.007
Hydrocarbons					
Methane	1.397	1.374	1.256	1.204	1.201
Ethane	0.590	0.531	0.457	0.466	0.427
Ethene	0.641	0.596	0.512	0.550	0.499
Propane	0	0	0.450	0.474	0.487
Propene	0.440	0.443	0.409	0.375	0.259
Isobutane	0.140	0.014	0.011	0.009	0.009
Butane	0.033	0.034	0.038	0.038	0.039
Butene	0	0	0.065	0.050	0.047
Total (2)	3.241	2.992	3.198	3.166	2.968
Total (1) + (2)	5.628	5.298	5.315	5.309	4.975
Various ratios					
Ethene/Ethane	1.087	1.122	1.119	1.180	1.168
Propene/Propane	-	-	0.907	0.791	0.532
Alkenes/Alkanes	0.246	0.249	0.445	0.445	0.372

TGA Analysis

Thermal analysis of oil shale helps in understanding as well as evaluating the retorting process mechanisms, so that the behaviour of the shale could be predicted with a high degree of certainty for a wide range of operating conditions. In this study, an attempt has been made to determine the effect of various retorting conditions, such as temperature, particle size and heating rate on the devolatilization profile of the organic matrix and the kinetic parameters of the Jordanian oil shales.

Figure 3a and b shows the weight loss thermogravimetry (TGA) and derivative weight loss thermogravimetry (DTG) curves for El-Lajjun and Sultani oil shales respectively. The rate of weight loss (i.e. due to conversion) is directly related to the retorting temperature: the higher the final temperature the higher the weight loss. This is because at low temperatures the pyrolysis process proceeds only slowly. Important features of such figures are that the total extractable kerogen content in the El-Lajjun and Sultani oil shales is ~22 and 18 %, respectively, of the total shale weight. Decomposition of carbonates commenced at a temperature > 550 °C. At temperatures much below 500 °C, decomposition was not complete, and about only 50 % conversion of the kerogen was achieved at ~425 (±10) °C.
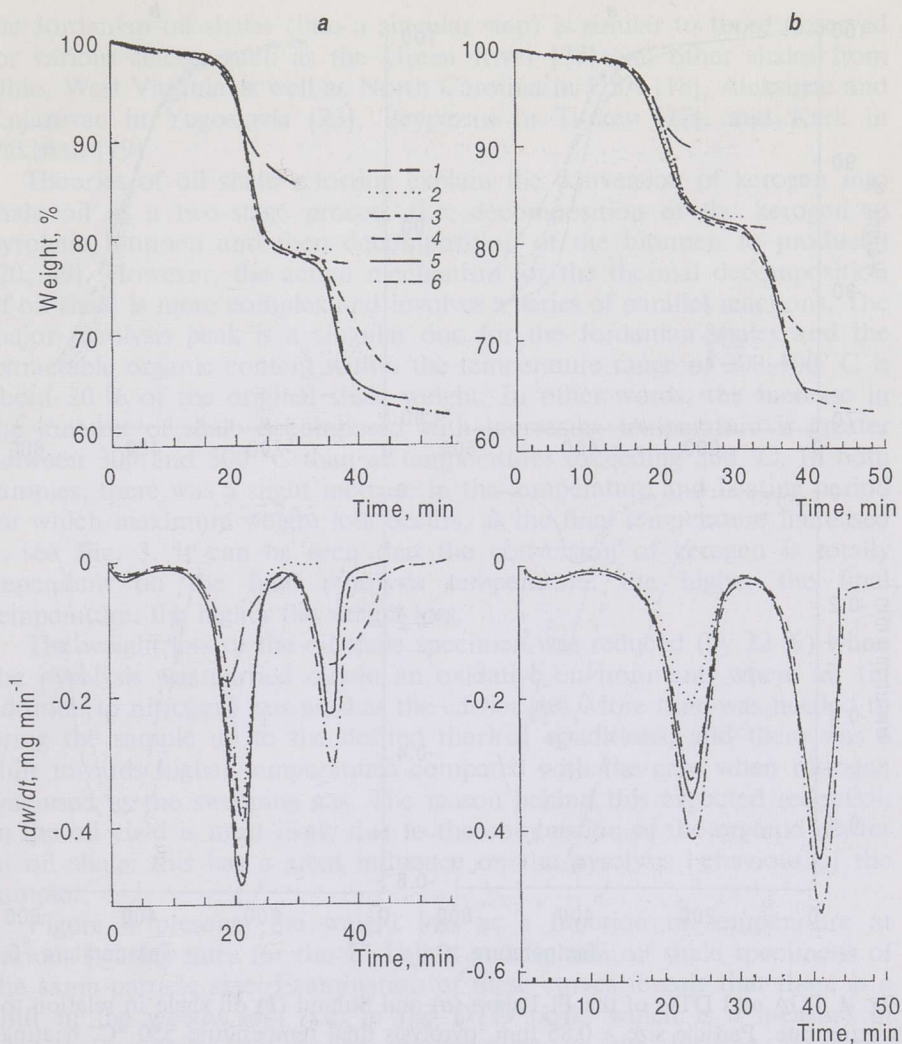
Fig. 3. TGA and DTG of the El-Lajjun (*a*) and Sultani (*b*) oil shales in relation to pyrolysis temperature. Particle size < 0.85 mm, heating rate 20 K min⁻¹, pyrolysis temperature, °C: *1* − 400, *2* − 500, *3* − 600, *4* − 700, *5* − 800, *6* - 900

It can be seen also from the DTG figures that there are three stages of the mass-loss profile. The first, occurring below a temperature of 200 °C, corresponds with the loss of water (i.e. hydration and interstitial water in minerals). The real decomposition of the organic matter took place during the second stage (i.e. between 200 and 550 °C). The third one, which was observed at higher temperatures (> 550 °C) is related to the dissociation of the carbonate mineral component of the oil shale specimen (which is an endothermic reaction). This explains the reduction in the efficiency of the retorting process when it is carried out at high temperatures, because carbonate minerals would require some energy (e.g. ~1.16 and 1.62 MJ kg⁻¹ for dolomite and calcite, respectively) in order to become dissociated.
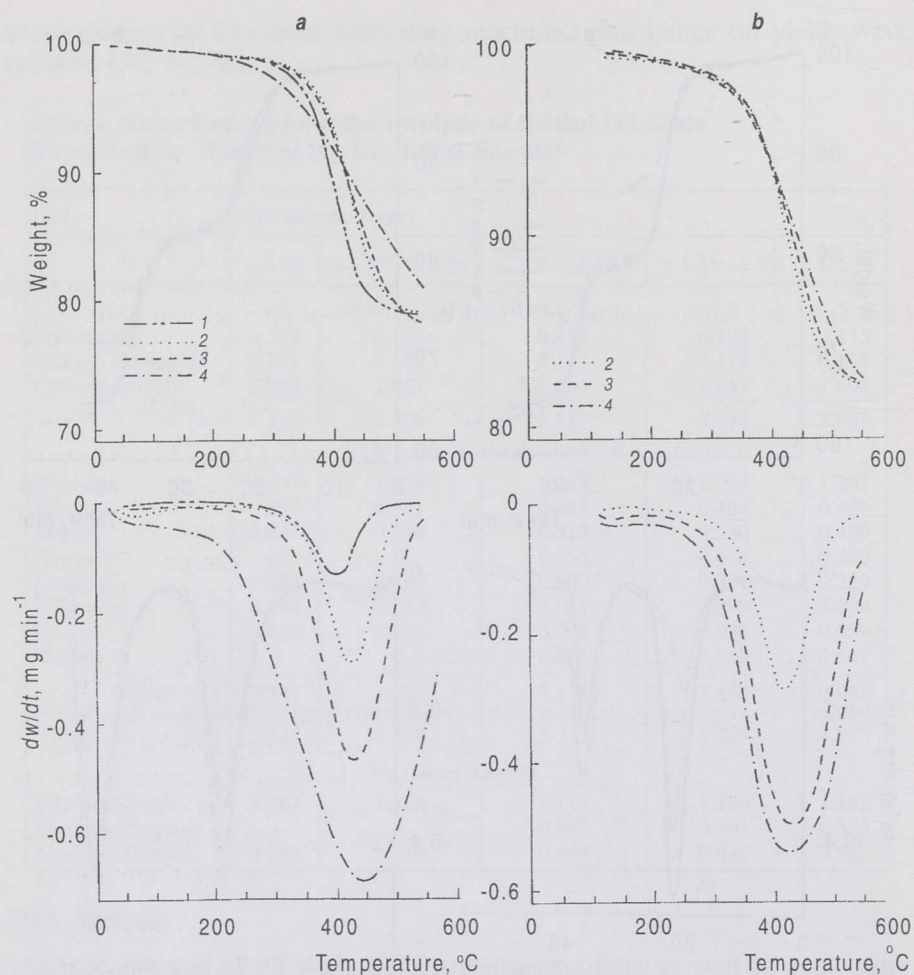
Fig. 4. TGA and DTG of the El-Lajjun (*a*) and Sultani (*b*) oil shale in relation to heating rate. Particle size < 0.85 mm, pyrolysis final temperature 550 °C, heating rate, K min^{-1}: *1* − 5, *2* − 20, *3* − 30, *4* − 50

But the continued loss from the sample weight, as the temperature was increased beyond ~600 °C, could be attributed to the possibility of continued pyrolysis, as well as the presence of CO_2 (which evolved from the carbonate decomposition) and which reacts with the residual char forming carbon monoxide (i.e. $C + CO_2 \rightarrow 2CO$). From the fixed-bed pyrolysis tests, it was observed that water starts emerging from the oil shale sample within the temperature range 120-160 °C, and the devolatilization in oil shale occurs at temperatures as low as 250 °C and up to ~500 °C. However, TGA experiments showed that oil shale does not completely devolatilize until temperatures of about 520 °C are reached.

Because oil shales originate from different geological environments, it is not surprising that they behave differently when subjected to similar pyrolysis conditions. However, the thermal decomposition behaviour of

the Jordanian oil shales (into a singular step) is similar to those observed for various shales, such as the Green River [37] and other shales from Ohio, West Virginia as well as North Carolina in USA [18], Aleksinac and Knjazevac in Yugoslavia [23], Beypazari in Turkey [27], and Kark in Pakistan [19].

Theories of oil shale retorting explain the conversion of kerogen into shale oil as a two-stage process (i.e. decomposition of the kerogen to pyrolytic bitumen and then decomposition of the bitumen to products) [20, 49]. However, the actual mechanism for the thermal decomposition of oil shale is more complex and involves a series of parallel reactions. The major pyrolysis peak is a singular one for the Jordanian shales and the extractable organic content within the temperature range of 300-500 °C is about 20 % of the original shale weight. In other words, the increase in the amount of shale decomposed with increasing temperature is greater between 300 and 500 °C than at temperatures exceeding 500 °C. In both samples, there was a slight increase in the temperature and heating period for which maximum weight loss occurs, as the final temperature increased − see Fig. 3. It can be seen that the conversion of kerogen is totally dependent on the final pyrolysis temperature: the higher the final temperature, the higher the weight loss.

The weight loss of the oil shale specimen was reduced (by 22 %) when the pyrolysis was carried out in an oxidative environment, where air (in addition to nitrogen) was used as the carrier gas. More time was needed to bring the sample up to the desired thermal conditions, and there was a shift towards higher temperatures compared with the case when nitrogen was used as the sweeping gas. The reason behind this expected reduction in the oil yield is most likely due to the combustion of the organic matter in oil shale: this has a great influence on the pyrolysis behaviour of the sample.

Figure 4 presents the weight loss as a function of temperature at various heating rates for the El-Lajjun and Sultani oil shale specimens of the same particle size. Examination of these curves reveals that there is a shift in the weight loss (i.e. in the DTG peak, which is a measure of relative reactivity) to higher temperatures as the heating rate was increased. This is due to variations in the rate of heat transfer with changes in the heating rate, and the short exposure time to a particular temperature at higher heating rates, as well as the effect of kinetics of decomposition [50, 51]. In this study, the thermocouple measured the temperature of the furnace close to the sample boat. Thus, it is deemed that the observed shift towards higher temperature is likely to be due to changes in the kinetics of the thermal decomposition. Of course, the influence of mass and heat transfer cannot be ruled out.

Almost a complete decomposition of the kerogen occurred at lower heating rates, while at high heating rates (e.g. 50 °C min^{-1}), complete decomposition would occur at a higher pyrolysis temperature of ~600 °C instead of the temperature 550 °C. This difference is because of the longer exposure time to a particular temperature at lower heating rates.

In the oil shale literature, most of the studies proved that the weight loss as indicated by the TG curves decreases with decreasing particle size

[19, 23, 52]. In the present study, it was found that there is a significant influence of the particle size on the extent and rate of decomposition, and on the temperature at which the maximum weight loss occurs: it rises with increasing particle grain size − see Fig. 5.
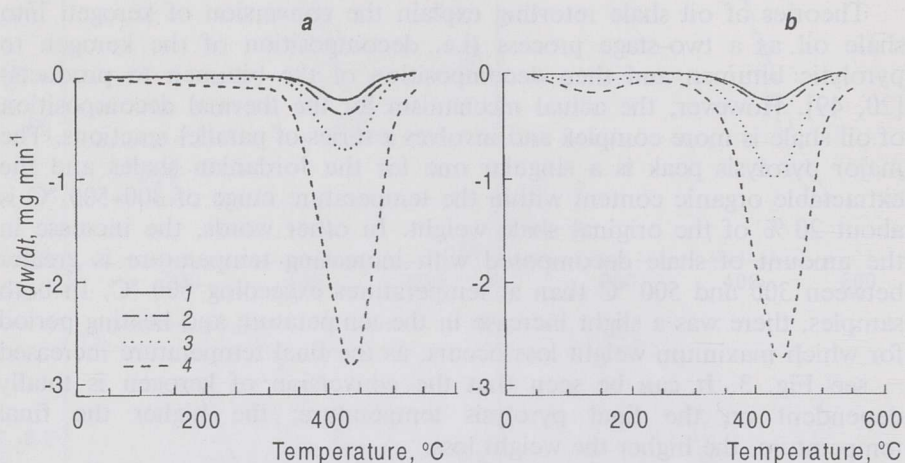

Fig. 5. DTG curves for various particle sizes: 1 - < 0.85; 2 - ≥ 0.85 -< 2.36; 3 - ≥ 2.36 -< 3.35; 4 - ≥ 3.35 -< 5.6. *a* - El-Lajjun, *b* - Sultani oil shale; pyrolysis final temperature 550 °C, heating rate 20 K $^{-1}$

Such an effect may be attributed to the change in the composition of the raw shale due to the grinding process (i.e. smaller particle would contain a higher ratio of ash in relation to organic matter because of the loss of some of fine carbon dust) as well as the variations in the heat and mass transfer properties within the sample.

There is a difference between the El-Lajjun and Sultani oil shales, in terms of the weight loss, which is lower for the Sultani shale. This is in agreement with the result obtained from the fixed-bed reactor experiments, which showed that the shale oil yield was higher for the El-Lajjun oil shale. Such a result is to be expected because the El-Lajjun shale is of a higher grade. For the El-Lajjun oil shale specimens, the weight loss peak occurred at longer time as well as at a higher temperature, under identical experimental conditions compared with those for the Sultani oil shale sample. This could be related to the grade of the oil shale, because the lower thermal conductivity associated with the richer shale would result in a longer heating period relative to those for the leaner grades [14, 49, 53]. This indicates clearly that more time should be allowed for pyrolysing the El-Lajjun oil shale for most of the organic matter to be extracted.

Activation Energy

The use of non-isothermal methods to determine kinetic parameters of the oil shale pyrolysis process by employing TGA, based on heating the

sample at a constant heating rate and recording the weight change, is more practical than those obtained using isothermal methods. This is mainly because of the shorter experiment time and the fewer difficulties (as a result of the initial heat-up period) compared with the isothermal methods. Thus, such a technique has been preferred by many researchers in determining reaction kinetics, such as the activation energy [27, 54, 55]. Because oil shale is a complex mixture of kerogen and many inorganic minerals, when pyrolysed, it will decompose through several different reactions. Therefore, and since the TGA records weight loss, it will provide only general information about the overall reaction kinetics.

There are various ways to determine the activation energy and other kinetic parameters for thermal degradation of an oil shale sample, such as the method of maximum rate, as well as the integral and differential methods [21, 39, 56-59]. The mathematical procedure used in the analysis of TGA data for determining the activation energy in the present study (based on the integral method) assumes that the mass loss occurs during the TGA experiments according to the first-order reaction kinetics. The rate of decomposition is then given by the following formula:

$$\frac{dX}{dt} = k(1-X) \tag{1}$$

where X is the fraction of oil shale decomposed in time t;
   k is the rate constant, given by the Arrhenius expression:

$$k = k_o \exp(-E/RT) \tag{2}$$

where k_o is the frequency factor;
   E — activation energy;
   R — gas constant;
   T — absolute temperature.

For non-isothermal kinetic parameters, with a constant heating rate ($h = \frac{dT}{dt}$) during the TGA experiment, the integration of Equation (1), assuming the first-order reaction, results in the following equation:

$$\ln[-\ln(1-X)] = \ln\left[\frac{k_o R T^2}{h E}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT} \tag{3}$$

The plot of $\ln[-\ln(1-X)]$ against $\frac{1}{T}$ gives a straight line with a slope of $-\frac{E}{R}$, which can be used to calculate the activation energy. In reality, deviation of the experimental data from the straight-line trend is an indication that the assumption of first-order reaction may not be accurate enough. In this study, plots of Equation (3) were prepared for all the samples, and the activation energy was determined from the best-fit lines. The frequency factor (i.e. k_o) can be calculated from the intercept.

The important feature in this analysis is that the El-Lajjun and Sultani oil shales have one kinetic expression over the temperature range covered

while heating the sample. This simply means that the rates of the decomposition reactions for both shales change beyond some critical temperature (i.e. a plot of Equation (3) gives two straight lines over the studied range). The average value of the critical temperature was ~315 (±10) °C for both shales. Similar observations of the existence of two temperature regions (between 300 and 400 °C) have been reported for different shales [19, 27, 37, 57, 60]. This temperature range overlaps with the current results. In the first step heat is absorbed to soften the kerogen, accompanied by a small weight change (i.e. during this stage, physical factors control the softening process). During the second step, destructive distillation (i.e. chemical conversion into products) accompanied by cracking at higher temperatures occurs.

Table 6. **Activation Energy Values for Different Particle Sizes**

Particle size (mm)	Activation energy (kJ mol^{-1})	
	El-Lajjun oil shale	Sultani oil shale
< 0.85	54.7	61.7
≥ 0.85 -< 2.36	71.7	64.3
≥ 2.36 -< 3.35	86.2	77.2

The average values of activation energy, obtained from this study, for the main stage of decomposition (during which almost all of the conversion occurs) for both the El-Lajjun and Sultani shales are shown in Table 6. There is a slight increase in the activation energy with increasing particle size. This might be caused by the reduced effects of diffusion processes during the pyrolysis of oil shale [19, 23, 37]. One may therefore suggest that the diffusion process becomes less important for the larger particle sizes as would be expected because of the increased porosity and surface area for the larger particles.

Such a low value of the activation energy is slightly greater than that (i.e. the evaporation energy of ~40 kJ mol^{-1}) of bituminous materials from Colorado shale [54]. This suggests that chemical factors would predominantly control the conversion process of kerogen into oil and gas. Such a finding agrees with the serial reaction model, which assumes that kerogen is first converted to bitumen and then to shale oil and gas [20, 32, 60]. However, oil generation may occur at the beginning of the pyrolysis process. So the thermal degradation mechanism, which may be appropriate for the investigated shales is that kerogen is initially converted to bitumen, oil, gas and residue, and in the second stage, the bitumen is converted to oil, gas and residue.

In the oil shale literature, there is a wide variation for the apparent values of the activation energy (i.e. between ~20 and 217 kJ mol^{-1}), depending on the type of oil shale, pyrolysis method employed, and analysis technique used when determining the kinetic parameters [27, 49, 59]. Many studies give activation energy ratings close to those calculated

in this investigation [19, 54, 56, 61, 62]. However, great care should be taken in this regard, due to the influence of process parameters, such as heating rate and particle size, on the final results. Therefore, the same experimental technique, including sample preparation procedure, analysis method and kinetic model should be employed. In addition, oil shale has a complex heterogeneous nature, especially the kerogen: hence, it is difficult to achieve repeatability of experimental findings, even for the same sample.

Sensitivity and Error Analysis

As in all experimental laboratory-scale research rigs, there are certain limitations and sources of errors that would affect the overall mass balance and the results obtained. The most important points observed during the present experiments, which may influence the investigation results, are the following:

- The sampling method, which has been employed to obtain the required oil shale samples from the two deposits, was not under the control of the authors. Thus, the question of representative sampling and sample heterogeneity could be important and may affect findings obtained by this study.

- The small size of available equipment allows to process only small-sized particles (e.g. the average weight of each sample used in the TGA tests was $< 50 \times 10^{-6}$ kg). Hence the optimal particle size was not deter-mined due to the system limitations. In addition, for the same reason, the testing apparatus allowed only the particles of two smallest sizes to be analysed elementally.

- There is a basic difference in the sample composition, especially for small particle sizes as a result of the crushing and sieving processes, which will affect the decomposition behaviour of the tested oil shale. Also oxidation of fine particles during preparation and handling, due to the exposure to ambient air, may affect the quantity and quality of the final products.

- Very fine shale and spent ash particles could be lost during the preparation or cleaning of the reactor.

- The initial heating-up period (i.e. which is partly dictated by the thermal inertia of the fixed-bed reactor) of the oil shale sample and the required residence time would affect the pyrolysis products. In TGA experiments, the small amount of kerogen compared with the total mass of the oil shale sample (which is in itself minute), as well as complications caused by simultaneously occurring mineral decomposition reactions and noises in the experimental system due to particle cracking and condensation, may affect the final results. Moreover, the use of a single sample piece is practical, but any heterogeneity or non-uniformity in the distribution of organic matter will manifest itself as variations in the measured parameter (e.g. the weight loss).

- Approximation used in the integral method for determining the values of the activation energy (which is generally accepted in terms of its accuracy) may affect the final results.

- Sample geometry (which was not taken into account) is another important variable in TGA experiments that might contribute to uncertainties in the results obtained. Also, sample storage and drying prior to a TG run would contribute to alterations, deviations and loss of findings representability.

- The analysis of hydrocarbon gases was possible only up to butene(C_4H_8), the identification of other gases was not possible by available technique. Fortunately the results of the off-line packed-column gas chromatography can rely on the precision, or repeatability of measuring device rather than its accuracy, as values were compared with each other, and were not needed to be correct in absolute terms.

- The calculation of the concentrations of the individual gaseous products generated during the pyrolysis process was based on determining the number of moles per minute evolved, using the trapezium rule. Such a procedure involves an approximation; hence, the final results could be affected.

- For the fixed-bed reactor, the condensation system was not particularly efficient, because some of the produced shale oil was condensed on the water trap and rubber tube between the condenser and the trap. Thus, a portion of shale oil was lost during the experiments.

- Changing the particle size and keeping other conditions constant could influence the heat and mass transfer processes, but not the kinetics of oil shale decomposition.

In order to reduce the margin of error and so produce more reliable data, some of the key tests were repeated for all experiments. Finally, it should be clear that this study was carried out in a fixed-bed reactor and using a non-isothermal TGA that has its own limitations. Because of the small scale of the experiments, it would be difficult to extrapolate quantitatively the results obtained as to what will happen in a commercial retort. However, the presently identified trends could serve as guidelines or indicators, but a more detailed research concerning the properties and behaviours of Jordanian oil shales is needed in order to determine the set of optimal retorting conditions, for a full-size system in order to maximise the oil yield from shale.

Conclusions

The pyrolysis of Jordanian oil shales was accomplished successfully in a laboratory-scale retort, which was capable of pyrolysing ~50 g of the sample. All the experiments were performed non-isothermally using a constant heating-rate. Such a fixed-bed reactor fulfilled the requirements for determining the yields of oil, gas, water and solid residue, as well as collecting the produced shale oil for further analysis.

Elemental analysis of raw oil shales, as well as pyrolysis tests implied that the El-Lajjun shale yields more oil than the Sultani shale. This was confirmed by examining the total weight loss in the TGA experiments. However, the principal conclusion of this study confirmed, within the limits of experimental error, that particle size has a great effect on the oil shale degradation during retorting. It was found for the oil shale samples (from two deposits in Jordan) pyrolysed by employing a fixed-bed retort that shale oil yield was an almost linear function (while gaseous products were inversely proportional) of the particle grain size. It is also possible that the oil yield would increase for particles larger than those studied in the present apparatus.

However, larger particles could not be investigated by using the employed fixed-bed reactor. TGAs of the studied two shales, in relation to particle size, are in full agreement with the results obtained from the fixed-bed reactor. Because the particle size is directly related to mass transfer conditions, it can be said that the shale oil yield is strongly dependent upon particle mass transfer conditions. Thus, the correct mass and heat transfer conditions should be provided around the shale particles, so that the oil yield can be maximised.

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REFERENCES

1. *Gavin, M. J.* Oil Shale: a Historical, Technical and Economic Study / Bureau of Mines, U.S. Department of the Interior. - Washington, DC, USA, 1922.

2. *Yen, T. F.* Oil shales of the United States // Science and Technology of Oil Shale (ed. T. F. Yen) / Newcastle University, Ann Arbor Science Publishers. Ann Arbor, Michigan, USA, 1976.

3. *Probstein, R. F., Hicks, R. E.* Synthetic Fuels. International Student Edition, McGraw-Hill Chemical Engineering Series. - New York, USA, 1982.

4. *Matheson, S. G, Sorb, L. A.* Proposals for the reporting of oil shale resources in Queensland, Australia // Fuel. 1990. Vol. 69. P. 1076-1080.

5. *Blanco, C.G., Prado, J.G., Guillen, M.D., Borrego, A.G.* Preliminary results of extraction experiments in an oil shale // Organic Geochemistry. 1992. Vol. 18, No. 3. P. 313-316.

6. *Ballice, L., Yuksel, M., Saglam M., Schulz, H.* Evolution of volatile products from oil shales by temperature-programmed pyrolysis // Fuel. 1996. Vol. 75. P. 453-458.

7. *Russell, P. L.* Oil Shales of the World, Their Origin, Occurrence and Exploitation. - Pergamon Press, Oxford, UK, 1990.

8. *Holopainen, H.* Experience of oil shale combustion in Ahlstrom Pyroflow CFB-Boiler // Oil Shale. 1991. Vol. 8, No. 3. P. 194-209.

9. *Pets, L., Vaganov, P., Rongsheng Z.* A Comparative study of remobilization of trace elements during combustion of oil shale and coal at power plants // Oil Shale. 1995. Vol. 12, No. 2. P. 129-138.

10. *Fainberg, V., Hetsrni, G.* Oil shale as an energy source // Energy Sources. 1996. Vol. 18. P. 95-105.

11. *Lee, S.* Oil Shale Technology. - CRC Press Inc., Boca Raton, Florida, USA, 1991.

12. *Dung, N. V.* Factors affecting product yields and oil quality during retorting of Stuart oil shale with recycled shale: A screening study // Fuel. 1995. Vol. 74. P. 623-627.

13. *Wallman, P. H., Tamm, P. W., Spars, B. G.* Oil shale retorting kinetics // Oil Shale, Tar Sands and Related Materials (ed. H. C. Stauffer). ACS Symposium Series 163, American Chemical Society, Washington, DC, USA, 1981.

14. *Guffey, F. D., McLendon, T. R.* Evaluation of oil yield losses during the retorting of oil shale at low void fractions: Part 1. The Effects of particle size and resource grade // Liquid Fuels Technology. 1984. Vol. 2, No. 4. P. 439-461.

15. *Rubel, A. M., Davis, E.* The effect of shale particle size on the products from the bench scale fixed bed pyrolysis of Kentucky Sunbury shale // Eastern Oil Shale Symposium, Kentucky Energy Cabinet, Lexington, Kentucky, USA, 1985.

16. *Roberts, M. J., Rue, D. M., Lau, F. S.* Pressurised fluidised-bed hydroretorting of six eastern shales in batch and continuous laboratory-scale reactors // Fuel. 1991. Vol. 71. P. 335-341.

17. *Bartke, J. C., Duvall, J. J.* Effects of particle size on retorting oil shale in a controlled-state retort. // Proceedings of the Ans. Topical MTG, Energy and Minerals Resources Recovery, April 1977. P. 516-527.

18. *Lee, S., Polasky M. E., Joshi, R.* Pyrolysis kinetics of various eastern shales in nitrogen and carbon dioxide atmospheres // Eastern Oil Shale Symposium, 13-16 November 1983, University of Kentucky, Kentucky, USA.

19. *Ahmad, N., Williams, P. T.* Influence of particle grain size on the yield and composition of products from the pyrolysis of oil shales // Journal of Analytical and Applied Pyrolysis. 1998. Vol. 46. P. 31-49.

20. *Campbell, J. H., Koskinas, G. H., Coburn, T. T., Stout, N. D.* Dynamics of oil generation and degradation during retorting of oil shale blocks and powders // Proceedings of the Tenth Oil Shale Symposium, Colorado School of Mines, Golden, Colorado, USA, 1977.

21. *Campbell, J. H., Koskinas, G. H., Stout, N. D.* Oil shale retorting: effects of particle size and heating rate on oil evolution and intraparticle oil degradation // In Situ. 1978. Vol. 2, No. 1. P. 1-47.

22. *Suuberg, E. M., Sherman, J., Lilly, W. D.* Product evolution during rapid pyrolysis of Green River formation oil shale // Fuel. 1987. Vol. 66. P. 1176-1184.

23. *Skala, D., Sokic, M., Kopsch, H.* Oil shale pyrolysis: A new approch to the kinetic investigation of different kerogen type samples // Thermochimica Acta. 1988. Vol. 134. P. 353-358.

24. *Allred, V. D.* Oil shale retorting phenomenology // Oil Shale Processing Technology (ed. V. D. Allred). The Centre for Professional Advancement, New Jersey, USA, 1982.

25. *Drescher, E. A., Bassil, C. A., Rolinski, E. J.* The kinetics of the thermal decomposition of Green River oil shale by thermogravimetric analysis // Alternative Energy Sources V. Part D (ed. T. N. Veziroglu). Elsevier Science Publishers, Amsterdam, Netherland, 1983.

26. *Li, S., Qian, J.* Study of the pyrolysis of Maoming oil shale lumps // Fuel. 1991. Vol. 70. P. 1371-1375.

27. *Dogan, O. M., Uysel, B. Z.* Non-isothermal pyrolysis kinetics of three Turkish oil shales // Fuel. 1996. Vol. 75. P. 1424-1428.

28. *Jiying, C., Changshan, L.* Factors affecting the results of fischer assay of oil shale // Proceedings of International Oil Shale and Shale Oil Conference, 1988, Beijing, China.

29. *Reasoner, J. W., Naples, K. V., Margalis, M. J* Analytical pyrolysis of Eastern oil shale // Proceeding of 1982 Eastern Oil Shale Symposium, Lexington, Kentucky, USA.

30. *Williams, P. T., Nazzal, J. M.* Polycyclic Aromatic compounds in oils derived from the fluidised bed pyrolysis of oil shale // Journal of Analytical and Applied Pyrolysis. 1995. Vol. 35. P. 181-197.

31. *Williams, P. T., Nazzal, J. M.* Polycyclic Aromatic compounds in shale oils: Influence of process conditions // Journal of Environmental Technology. 1998. Vol. 19. P. 775-787.

32. *Campbell, J. H., Koskinas, G. J., Gallegos, G., Gregg, M.* Gas evolution during oil shale pyrolysis: Non-isothermal rate measurements // Fuel. 1980. Vol. 59. P. 718-726.

33. *Campbell, J. H., Gallegos, G., Gregg, M.* Gas evolution during oil shale pyrolysis: Kinetic and stoichiometric analysis // Fuel. 1980. Vol. 59. P. 727-732.

34. *Huss, E. B., Burnham, A. K.* Gas evolution during pyrolysis of various Colorado oil shales // Fuel. 1982. Vol. 61 P. 1188-1196.

35. *Jaber, J. O., Probert, S. D.* Exploitation of Jordanian oil shales // Applied Energy. 1997. Vol. 58, No. 2-3. P. 161-175.

36. *Burnham, A. K.* Chemistry of shale oil cracking // Oil Shale, Tar Sands and Related Materials (ed. H. C. Stauffer). ACS Symposium Series 163, American Chemical Society, Washington, DC, USA, 1981.

37. *Weitkamp, A. W., Gutberlet, L. C.* Application of a microretort to problems in shale pyrolysis // Industrial and Engineering Chemistry, Process Design and Development. 1970. Vol. 9, No. 3. P. 386-395.

38. *Hanna, J., Lamont, W. E.* Effect of sulphur and particle size on Fischer assay oil yields from oil shale. // Eastern Oil Shale Symposium, Kentucky Energy Cabinet, Lexington, Kentucky, USA, 1987.

39. *Campbell, J. H., Kosinas, G. H., Stout, N. D.* Kinetics of oil generation from Colorado oil shale // Fuel. 1978. Vol. 57. P. 372-376.

40. *Burnham, A. K.* Studies of oil-shale reaction chemistry at LLL // Institute of Gas Technology Symposium on Synthetic Fuels from Oil Shale, 3-6 December 1979, Atlanta, Georgia, USA.

41. *Burnham, A. K., Bey, N. K., Koskinas, G. J.* Hydrogen sulphide evolution from Colorado oil shale // Oil Shale, Tar Sands and Related Materials (ed. H. C. Stauffer). ACS Symposium Series 163, American Chemical Society, Washington, DC, USA, 1981.

42. *Ekstrom, A., Fookes, C. J. R., Loeh, H. J., Randall, C. H., Rovere, C., Ellis, J., Crisp, P. T.* Chemical and pyrolysis characteristics of two types of oil shale from the Condor deposit in Queensland, Australia // Fuel. 1987. Vol. 66. P. 1133-1138.

43. *Rubel, A. M., Audeh, C. A.* Comparison of product yields obtained from the New Albany shale by different rapid heating retorting procedures // Eastern Oil Shale Symposium, University of Kentucky, Lexington, Kentucky, USA, 1984.

44. *Burnham, A. K.* Reaction kinetics between CO_2 and oil shale residual carbon. I. Effect of heating rate on reactivity // Fuel. 1979. Vol. 58. P. 285-291.

45. *Burnham, A. K.* Reaction kinetics between CO_2 and oil shale residual carbon. II. Partial pressure and catalytic-mineral effects // Fuel. 1979. Vol. 58. P. 713-718.

46. *Coburn, T. T., Bozak, R. E., Clarkson, J. E., Campbell, J. H.* Correlation of shale oil 1-alkene/*n*-alkane ratios with process yield // Analytical Chemistry. 1978. Vol. 50, No. 7. P. 958-962.

47. *Burnham, A. K., Clarkson, J. E.* Determination of process yield for oil shale retorting using oil analysis by capillary column chromatography // Proceedings of the 13th Oil Shale Symposium, Colorado School of Mines, Golden, Colorado, USA, 1980.

48. *Raley, J. H.* Monitoring Oil shale retorts by off-gas alkene/alkane ratios // Fuel. 1980. Vol. 59. P. 419-424.

49. *Williams, P. F. V.* Thermogravimetry and decomposition kinetics of British Kimmeridge clay oil shale // Fuel. 1985. Vol. 64. P. 540-545.

50. *Rajeshwar, K.* Thermal analysis of coals, oil shales and oil sands // Thermochimica Acta. 1983. Vol. 63. P. 97-112.

51. *Thakur, D., Nuttall, H. E.* Kinetics of pyrolysis of Moroccan oil shale by thermogravimetry // Industrial Engineering and Chemical Res. 1987. Vol. 26. P. 1351-1356.

52. *Galan, M. A., Smith, J. M.* Pyrolysis of oil shale: Experimental study of transport effects // AIChE Journal. 1983. Vol. 29, No. 4. P. 604-610.

53. *Rajeshwar, K., Nottenburg, R., Dubow, J.* Thermophysical Properties of oil shales // Journal of Materials Science. 1979. Vol. 14. P. 2025-2052.

54. *Allred, V. D.* Kinetics of oil shale pyrolysis // Chemical Engineering Progress. 1966. Vol. 62, No. 8. P. 55-60.

55. *Williams, P. T., Besler, S.* The pyrolysis of rice husks in a thermogravimetric analyser and static batch reactor // Fuel. 1993. Vol. 72. P. 151-159.

56. *Skala, D., Kopsch, H., Sokic, M., Neumann H. J., Jovanovic, J.* Thermogravimetrically and differential scanning calorimetrically derived kinetics of oil shale pyrolysis // Fuel. 1987. Vol. 66. P. 1185-1191.

57. *Haddadin, R. A., Tawarah, K. M.* DTA derived kinetics of Jordan oil shale // Fuel. 1980. Vol. 59. P. 539-543.

58. *Burnham, A. K., Huss, E. B., Singleton, M. F.* Pyrolysis kinetics of Green River oil shale from the Saline Zone // Fuel. 1983. Vol. 62. P. 1199-1204.

59. *Ekstrom, A., Callaghan, G.* The pyrolysis kinetics of some Australian oil shales // Fuel. 1987. Vol. 66. P. 331-337.

60. *Haddadin, R. A., Mizyed, F. A.* Thermogravimetric analysis kinetics of Jordan oil shale // Industrial Engineering Chemistry, Process, Design and Development. 1974. Vol. 13, No. 4. P. 332-336.
61. *Haddadin, R. A.* Kinetics of tetralin Extraction of Jordan oil shale // Fuel. 1980. Vol. 59. P. 535-538.
62. *Skala, D, Kopsch, H., Sokic, M., Neumann, H. J., Jovanovic, J. A.*, Kinetics and modelling of oil shale pyrolysis // Fuel. 1990. Vol. 69. P. 490-496.