

Surface Retorting of Jordanian Oil Shale and Associated CO₂ Emissions

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Abstract

In this study, two oil shale samples, from two different deposits in Jordan, have been pyrolysed using a thermogravimetric analyser (TGA). The controlling parameters studied were the final pyrolysis temperature and the influence of the heating rate as well as type of purge gas employed on the process of thermal degradation of the shale sample. It is found that there are two main steps of samples' weight loss. The first one is due to conversion of organic matter to oil and gas which occurred within the temperature range of between 250 to 550 °C, while the second step represents weight loss due to carbonate decomposition releasing CO₂ and occurred at approximately higher temperature of more than 550 °C for examined samples. In directly heated systems additional quantities of CO₂ will be produced due to combustion of residual carbon in order to provide needed heat for the retorting process. Therefore, surface retorting processes aiming to produce crude shale oil from raw oil shale will release higher rates of CO₂ emissions to the environment compared with production of conventional or other synthetic fuels.

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Keywords: Oil Shale, Surface Retorting, CO₂ Emission, Jordan.

1. Introduction

The proven reserves, in the central region of the Jordan, are huge (i.e. exceeding 5×10^{10} tonnes of oil shale) with an average organic content of between 9 and 13% by weight (which would yield $\sim 5 \times 10^9$ tonnes of shale oil) [1-5]. Yet there is a dearth of information available about the pyrolysis of Jordanian oil shales, because there has been only little interest in developing such resource. The main reasons for this are that the majority of the deposits are relatively lean and located in remote regions, where, at best, only a limited industrial infrastructure exists. Equally important is the poor knowledge of their full extent and exact characteristics. Moreover, the prevailing relatively low unit-prices for crude oil on the international market have discouraged entrepreneurs from making investments to exploit these oil shale resources.

In the literature, the kinetics of the thermal decomposition of various oil shales, from different regions of the world, have been investigated and various suggestions as to the decomposition mechanisms have been reported [6-21]. Many thermogravimetric studies have been carried out under isothermal conditions (for which the rates of reaction are determined at constant temperatures), but this method involves some inaccuracies. It is more accurate to use a non-isothermal method to determine the kinetic parameters of the pyrolysis process, employing a TGA apparatus, with the sample heated at a constant rate and recording its weight change. This is mainly because of the shorter experimental times and the fewer encountered difficulties (e.g. the initial heating-up period in isothermal methods). But the principal reason for their popularity in the field of oil shale pyrolysis is that it more

closely simulates the conditions expected in commercial-scale oil shale retorting systems. Thus, such a technique for determining the reaction kinetics, such as the activation energy, has been preferred by many researchers. Hence, the kinetics of thermal degradation of a small shale particles specimen can be obtained using a TGA apparatus, which records the changes of a small shale sample with time. Consequently, this can be used to determine the characteristics of devolatilisation as well as kinetic parameters [6,12,17,19-23]. The behaviour of oil shale pyrolysis is considered to be complicated because the shale is a complex mixture of kerogen and wide range of minerals. Also, the shale oil produced by pyrolysis is the result of several physical and chemical reactions occurring simultaneously in series and parallel, while the TGA apparatus measures the overall weight loss due to these reactions. Hence, the TGA provides only general information about the overall reaction kinetics.

However, a large number of researchers have studied the influence of pyrolysis temperature and heating rate on oil shale decomposition used TGA apparatus. For example, Haddadin and Mizyed [6], Dogan and Uysal [19] and Ahmad and Williams [20] have investigated the influence of final pyrolysis temperature and reported greater weight losses, from the oil shale specimens, as the temperature was increased. Skala et al., [11], Drescher [21], Lee et al., [22], Rajeshwar [23] and Campbell et al, [24] concluded that there was a systematic shift of the region in which the maximum rate of weight loss ensues towards higher temperatures for higher heating rates. The present investigation is an experimental study using a TGA apparatus (under non-isothermal conditions) to determine the kinetics of the pyrolysis process for two Jordanian oil shales (i.e. from the Ellujjun and Sultani deposits) in relation to the heating rate, final temperature and purge gas employed. Also carbonate (CaCO₃) decomposition rates are determined at temperatures higher than desired retorting temperature.

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2. Experimental Equipment and Procedure

2.1. Shales used

Oil shale samples, from the Ellujjun and Sultani deposits, were supplied by the Natural Resources Authority (Amman, Jordan), but details of the sampling method used were not provided. The two samples of raw oil shale received were crushed, separately, by a jaw crusher and then, without further treatment, sieved in order to obtain samples of the required particle size. These oil shales have been examined in a preliminary pyrolysis study, using a fixed bed retort, reported previously [25].

2.2. Experimental apparatus

Kinetic data were obtained using a Shimadzu Model-50 Series TG Analyser, with N_2 or CO_2 (supplied at a constant rate of $\sim 5 \times 10^{-5} \text{ m}^3 \text{ min}^{-1}$ at normal conditions) employed as the purge gas. The TGA apparatus permits 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, with high accuracy of $\pm 0.1\%$. In this investigation, TGAs were used to determine the effects of heating rate and final temperature on the weight loss of the oil shale sample.

Pyrolysis was carried out non-isothermally using a sample of about $15 \times 10^{-6} \text{ kg}$, 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 the 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 room temperature. All experiments were repeated in order to minimize experimental uncertainty and cross-checking

obtained results, and where significant variance was found the test a third test was conducted in order to confirm results. But it should be noted that due to the fact that oil shale is not homogeneous material, a slight difference in final results would be inevitable. Table 1 lists the main conditions employed during this experimental investigation.

Table 1. Main experimental conditions

Sample grain size (mm)	< 0.85
Heating rate ($K \text{ min}^{-1}$)	20
Final temperature ($^{\circ}C$)	400-900 (and 1000 in the case of CO_2)
Gas carrier	N_2 or CO_2

3. Results and Discussion

A typical variation of the percentage conversion with temperature (i.e. the TGA curve) is shown in Fig. 1, while Fig. 2 shows the differential weight loss (i.e. the DTG) profile for the Ellujjun and Sultani shales. The rate of weight loss, due to conversion of the organic matter, is clearly related to the pyrolysis temperature: the higher the final temperature, the greater the weight loss. This is because, at high temperatures, the pyrolysis process proceeds faster.

The DTG figure demonstrates clearly that there are three steps of the mass-loss profile. The pre-heating phase, being below $200^{\circ}C$, corresponds with the loss of the interlayer water from the clay minerals and the decomposition of nahcolite as well as the physical changes (i.e. is the softening and molecular rearrangement associated with release of gases) in the kerogen prior to its decomposition to bitumen as shown in Fig. 3 [26]. It is clear, from Fig. 3, that kerogen undergo two steps reaction: the 1st step involves some changes and conversion of light matter and in the 2nd step bitumen is decomposed into oil and gases. The loss of hydrocarbon material took place during the second stage (i.e. between 200 and $600^{\circ}C$).

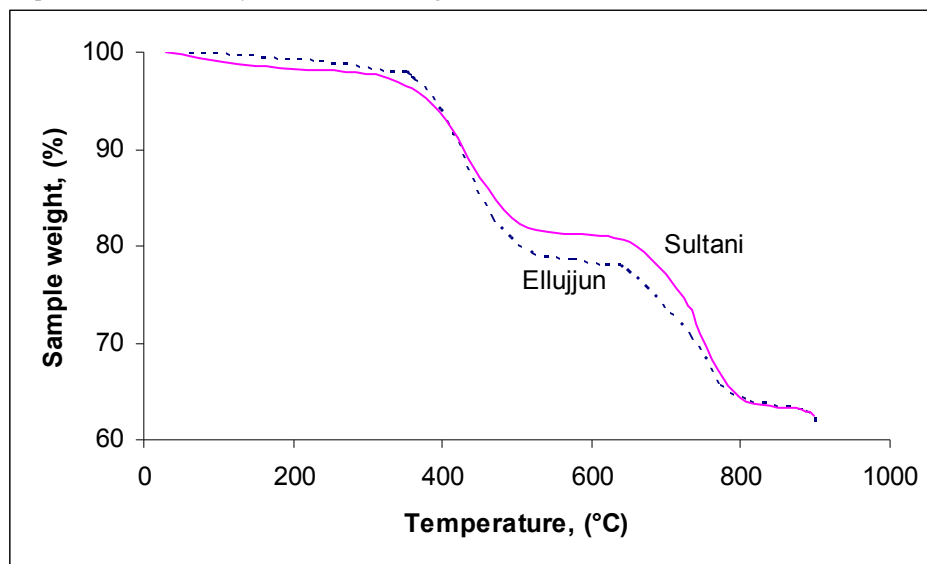


Fig. 1. TG profiles of the Ellujjun and Sultani oil shales (in N_2 , $h = 20 \text{ K min}^{-1}$)

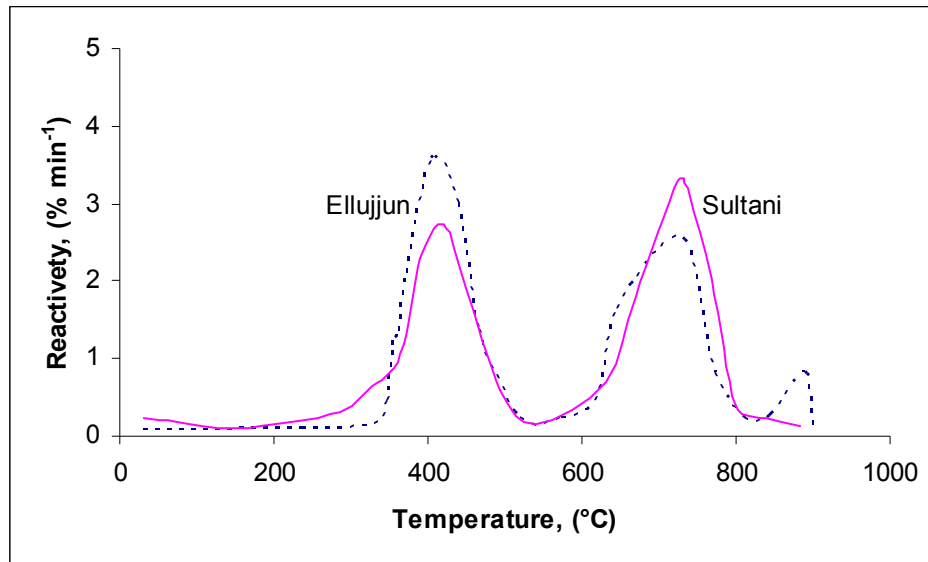


Fig. 2. DTG of the Ellujjun and Sultani oil shales

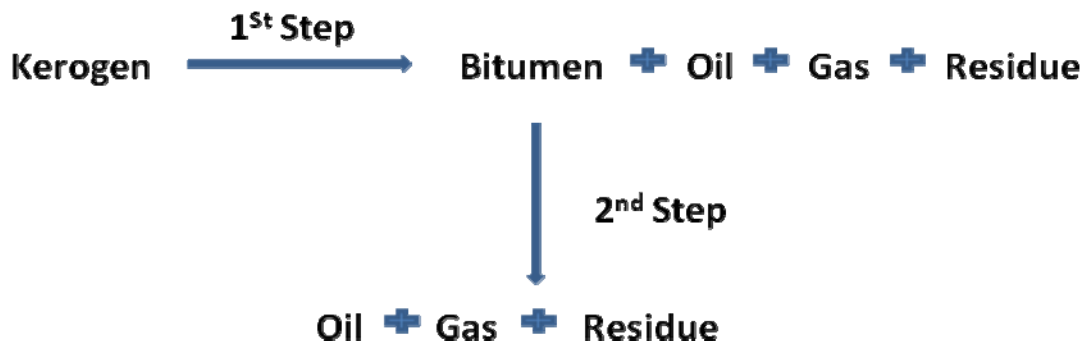


Fig. 3. Mechanism of thermal decomposition of oil shale particles

It is evident that the major pyrolysis peak is a singular one and the extractable organic contents, within the temperature range of 200 to 500 °C, are approximately 21 and 17% of the original sample weight for the Ellujjun and Sultani shales, respectively. Previously, it had been observed, from fixed-bed pyrolysis tests, that water starts emerging from the oil shale sample within the temperature range of 120 to 160 °C, and the devolatilization in the oil shale started at temperatures as low as 250 °C and continued up to approximately 500 °C [4,25]. The third stage, which occurred at higher temperatures exceeding 600 °C, is due to the decomposition of the carbonate (i.e. calcite and dolomite). The sample's continued loss of weight, as the temperature was increased above 600 °C, could be attributed to the possibility of continued pyrolysis, as well as the presence of CO₂ (which evolved as a result of carbonate decomposition) and which reacts with the residual char, through the Boudouard reaction, so forming carbon monoxide.

The two shales exhibit qualitatively the same patterns of thermal degradation when the pyrolysis temperature was raised over the studied range. But it is evident, within experimental error, that during the pyrolysis phase alone, the Ellujjun sample exhibits approximately a 30% higher weight loss compared with the Sultani oil shale: the latter lost about 17% of its initial weight when N₂ was used to purge the furnace and 18% in the case when CO₂ was employed as the sweeping gas. In general, within experimental error, a

slightly greater weight loss occurred from the shale sample as a result of using CO₂ instead of N₂ to purge the TGA system. This is because CO₂ is more reactive than N₂ due to the presence of alkali metals, which are very effective in the CO₂ and/or H₂O reactions with carbon [27-29]. The increase in the amount of shale decomposed with increasing temperature is greater between 200 and 550 °C than for temperatures exceeding 550 °C. This is due to the fact that the optimal temperature for maximizing oil shale retorting is around 550 °C.

The singular step thermal decomposition behavior of Jordanian oil shales is similar to those observed for various shales, such as those from Colorado [30], Ohio, West Virginia and North Carolina [22] all in the USA, Aleksinac and Knjazevac in Yugoslavia [17], Beypazari in Turkey [19], Kark, Dharangi and Malgeen in Pakistan [20] and Attarat in Jordan [4]. The conclusions derived from this study concerning the Ellujjun oil shale are in full agreement with those reported by other researchers [6]. Whatever the shape of the decomposition profile (i.e. single or double stage), oil shale pyrolysis studies indicate that the conversion of kerogen into shale oil is a two-stage process. In the first, decomposition of the kerogen to pyrolytic bitumen occurred and then, in the second, decomposition of the bitumen to products ensued [15,19,24]. However, the mechanism for the thermal decomposition of oil shale is complex and involves a series of parallel reactions.

4. Predicted GHG Emissions from Retorting Unit

Major gas emissions from oil shale processing plants are particulates, nitrogen oxides, sulfur oxides and carbon dioxide: the relative amounts emitted increase as the thermal efficiency decreases. Much concern has been expressed recently over the "excessive greenhouse effect", where the increased concentrations of CO₂ in the atmosphere resulting from the burning of fossil fuels are leading to global increases in air temperature and long-term climatic changes. The burning of hydrocarbon fuels with the high hydrogen/carbon ratios (i.e. as with natural gas) would reduce CO₂ emissions per unit of heat (or other form of energy) produced. However, this is not the case with synthetic fuels, where the total amount of CO₂ generated must include that portion released during their manufacture – see Table 2 [31]. So, in shale oil production or oil shale direct combustion, there are additional releases of CO₂ due to the decomposition of the carbonates that are present in the raw shale. Thermal decomposition occurs at high rates at $\geq 500^{\circ}\text{C}$: therefore it is

not expected to be significant for the indirectly-heated retorting process. However, it is an important source in the directly-heated retorts as well as in some in-situ retorting methods, because the temperature in the combustion zone would then be in the range of 700 to 1100 °C. This would generate more quantities of such emissions due to the combustion of residual carbon remained in the retorted shale. Although CO₂ is potentially a pollutant of global concern, its emission is not controlled by the present air quality and pollution standards which are imposed on air emissions in most countries. As for the oil shale combustion process, a relatively-high temperature (i.e. on average $\sim 800 (\pm 50)^{\circ}\text{C}$ in the case of fluidized-bed combustors and about $1300 (\pm 100)^{\circ}\text{C}$ for pulverized oil shale combustion) are necessary in order to ensure complete oxidation of the CO and various HC species. Consequently, decomposition of the carbonate content occurs, but only a small percentage (i.e. $\leq 10\%$ of the total) of this decomposition is desirable for the capture of the sulfur oxides (i.e. mainly SO₂).

Table 2. CO₂ produced in the synthetic fuels' manufacturing processes and burning of fuel (mol CO₂ per MJ of product)

Fuel	Manufacture	Combustion	Total
C	-	2.54	2.54
CH ₂	1.36	1.61	2.97
CH ₄	2.17	1.25	3.42
CH ₃ OH	1.92	1.57	3.49

It is hard to estimate with certainty the rates of CO₂ that would be produced by any proposed oil shale project, unless technology and capacity are known. However, it is predicted that, if one quarter only of the carbonate content of the raw shale is decomposed, this would be responsible for emitting approximately 20-25% more CO₂ than from the combustion process alone. Such an endothermic decomposition reaction would consume approximately 5-8% of the total heat released during the combustion process [32]. This is unfavorable from the flue-gas emissions point-of-view, but simultaneously the decomposed carbonates will produce a pozzolanic ash, which is desirable for improving the characteristics of the spent shale in order for it to be used later as a raw material in the construction and cement industries or for safe disposal. Also from the environmental side, increasing rates of CO₂ emission is not favorable due to its contribution to climate change and global warming effects.

5. Conclusion

For both oil shale samples tested, the conversion of kerogen is totally dependent on the final pyrolysis temperature: the higher the final temperature, the greater the weight loss from each sample. Using CO₂ instead of N₂ to purge the TGA system led to a slight increase in the weight loss from the oil shale sample. The principal conclusion of this study is that both of Ellujun and Sultani oil shale samples' behaviour can be described as a singular reaction phase over the studied temperature range. The second stage, which occurred at higher temperatures exceeding 600 °C, is due to the decomposition of the carbonate. In real oil shale projects, it is expected that GHG emissions would be higher due to many reasons, e.g. mining activities, combustion of residual carbon and transportation of raw oil shale and finished products.

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