

Reaction kinetics of fluidised bed gasification of Jordanian oil shales

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Abstract—Trying to achieve the optimal utilisation of oil shale resources, and the production of a more environmentally acceptable fuel, as well as a solid waste with a low sulphur content, thereby reducing acidic leachates, has led to this investigation. In this article, the influences of the bed temperature and the choice of fluidising gas on the quality and quantity of the produced fuel gas, using a continuous feed fluidised bed reactor, were investigated. The composition and calorific value of the generated gas were determined. There was a nearly linear increase in the amount of fuel gas produced as a function of temperature, reaching ~350 kg per 10³ kg of dry raw shale and the gross calorific value ranged from 15 to 23 MJ·kg⁻¹ with CO and H₂ being the major constituents. Subsequent experiments were carried out, employing a thermogravimetric analyser under similar conditions as applied to the fluidised bed reactor. Gasification of the investigated shales complied with first-order kinetics within the limits of experimental error and the activation energy and temperature at which maximum reactivity rate occurred decreased slightly as the shale particle size was reduced. © 2000 Éditions scientifiques et médicales Elsevier SAS

gasification / oil shale / gaseous fuel / kinetics / Jordan

Nomenclature

| | | |
|-------|--|--|
| E | activation energy | $\text{kJ}\cdot\text{mol}^{-1}$ |
| GCV | gross calorific value | $\text{MJ}\cdot\text{kg}^{-1}$ |
| h | heating rate | $\text{K}\cdot\text{min}^{-1}$ |
| k_0 | frequency factor | min^{-1} |
| R | gas constant = 8.314 | $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ |
| T | absolute temperature | K |
| t | time | s |
| toe | tons of oil equivalent | |
| X | amount of the oil shale decomposed during time t | % |

1. INTRODUCTION

A primary aim of oil shale gasification is to increase the calorific value per unit mass of the resulting fuel gas: this is achieved by removing unwanted constituents,

such as ash, thereby producing a gaseous fuel, which is cleaner, easier to handle and cheaper. Oil shale gasification is a relatively simple process requiring the extraction of the volatile contents of the shale through pyrolysis, followed by the partial combustion of the remaining char. This series of reactions produces a fuel gas, with CO and H₂ as the major constituents, together with small amounts of CO₂, N₂, CH₄ and H₂S.

Jordan, as an example, possesses only relatively small known reserves of traditional fossil-fuels; its indigenous crude-oil and natural-gas supplies satisfying less than 4 % of the present national annual primary fuel demand [1]. So the country is almost completely dependent on imported crude oil and refined products—see *figure 1*. Also, it has experienced temporary shortages of mineral-oil products on several occasions (e.g., during the last Gulf crises). On the other hand, oil shale is the major indigenous fossil fuel occurring in Jordan, yet it is not utilised. The identified reserves of oil shale are huge (i.e., 5·10¹⁰ tons) and sufficient to satisfy the national energy demand for hundreds of years. Thus, such a domestic resource has a potentially major role to play in reducing Jordan's dependence on imported crude oil and/or petro-

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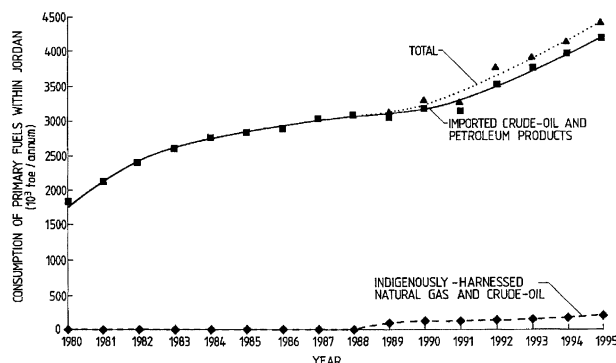


Figure 1. Jordan's dependence on imported crude oil and petroleum products.

leum products: the annual imported crude oil cost for 1998 was $\sim 4.5 \cdot 10^8$ US\$, which represented one tenth of Jordan's gross domestic product [2]. Without the exploitation of indigenous oil shale, the corresponding imports will cost $\sim (1.15 \pm 0.2) \cdot 10^9$ US\$ per annum (depending on the international unit crude-oil price) by the year 2010, when the annual rate of fuel consumption in Jordan will have approximately doubled [3].

During the last ten years, little attention has been paid to oil shale gasification, and almost all the pertinent published data are concerned with reaction kinetics of spent shale gasification. These studies were conducted on retorted shales (and not raw shales) from different origins, such as Australia [4], Sweden [5], and the Eastern [6–11] as well as the Western regions in the USA [12–15].

In the oil shale literature, several mathematical models of the retorted shale gasification, based on experience gained from coal gasification (i.e. the shrinking core models) have been presented. These were oriented towards achieving an understanding of the mass and heat transfer mechanisms as well as the influence of process variables (e.g., temperature) during gasification on the output products [7, 16].

The aim of the present experimental investigation is the gasification of two oil shale samples (from different sites in the central part of Jordan) using an indirectly heated fluidised bed gasifier, and CO_2 or CO_2 and steam as the fluidising “gas”, with the ultimate goal of producing gaseous fuels with high calorific values. The compositions, yields and gross calorific values of the derived gases were determined. In addition, the two samples were gasified in a thermogravimetric analyser (TGA), under similar experimental conditions as implied on the fluidised bed reactor, in order to determine the kinetics of the studied shales, see *table I*. Such information is re-

TABLE I
Main experimental conditions employed in the present series of tests.

| | |
|---|---|
| Fluidised bed | |
| • shale type | Ellujjun |
| • sample grain size (mm) | between 0.85 and 2.36 |
| • final temperature ($^{\circ}\text{C}$) | 750–950 |
| • fluidising gas | CO_2 , or mixtures of CO_2 and H_2O with varying compositions along with N_2 |
| TGA | |
| • shale type | Ellujjun and Sultani |
| • sample grain size (mm) | less than 0.85, between 0.85 and 2.36, and between 2.36 and 3.35 |
| • heating rate ($\text{K} \cdot \text{min}^{-1}$) | 10, 13, 15 and 20 |
| • final temperature ($^{\circ}\text{C}$) | 800–1000 |
| • purge gas | CO_2 |

TABLE II
Elemental analysis of oil shale samples.

| Elemental analysis, %wt | Ellujjun | Sultani |
|-------------------------|----------|---------|
| C | 22.3 | 19.6 |
| H | 2.6 | 2.1 |
| N | 0.4 | 0.3 |
| S | 3.4 | 1.5 |
| Ash | 61.0 | 62.8 |

quired as the basis for a detailed kinetic study of the gasification process, as well as to aid in the design of an efficient oil shale utilisation systems.

2. EXPERIMENTAL

2.1. Shale used

There is no information available about the gasification of Jordanian oil shales, most probably because there has been only little interest in developing this resource, due to the prevailing low crude oil unit prices compared with those for the final energy produced from oil shale. Nevertheless, it is likely that, within next two decades this situation will be reversed.

The oil shale samples used were obtained from the Ellujjun and Sultani deposits in the central part of Jordan. Based on micro-palaeontological studies and stable carbon-isotope determinations, it is believed that these deposits were formed in the shallow marine environment, which prevailed in the Middle East about 140 million

years ago, during the Maestrichtian and Palaeocene ages. *table II* shows the elemental analysis of both samples, but more details about the samples and their elemental analyses are presented in another article [17].

2.2. The fluidised bed reactor

The $2.2 \cdot 10^{-3} \text{ m}^3$ (i.e. inner diameter is 7.5 cm with a bed height of 50 cm) stainless-steel reactor was heated externally by an electric-tubular ceramic furnace, with a single heating element and insulated by a blanket of kaowool, see *figure 2*. Because gasification reactions are endothermic and absorb large amounts of heat, a powerful furnace is necessary. Its behaviour was governed by a programmable temperature controller, which enabled the shales to be gasified at any chosen fixed-temperature.

In all of the experiments, a static bed height of 5 cm of silica particles (as the inert material) of mean individual grain size of 0.3 to 0.4 mm was used. The particles were fluidised using a 100 straight holes gas distributor plate, which is made of stainless steel and welded to the bottom of the reactor in order to avoid leakage. The plenum section (which is 20 cm in length and packed with steel balls of 1 cm diameter), served to heat up, as well ensure a more uniform distribution of, the fluidising gas. There are five (type K) thermojunctions installed in the reactor to monitor and control the temperature.

CO_2 or a mixture of CO_2 and steam with varying compositions along with N_2 , was fed to the bottom of the reactor. N_2 gas was used as an inert medium and reference gas (being fed in at a constant rate) to quantify the produced gases. For all the experiments, the total flow rate of fluidising gases was constant, i.e. at $40 \text{ l} \cdot \text{min}^{-1}$. At such a low rate, a bubbling bed was established and maintained throughout the experiments. Steam was generated by pumping water, at a predetermined and fixed rate, through the preheater and then injected at (just above) atmospheric pressure into the reactor.

Particulate matter was removed from the produced gases using a small cyclone. The amount of fines (generated by abrasion during the gasification process) collected in the catch pot was very small and nearly constant, i.e. $< 10^{-3} \text{ kg}$, regardless of the gasification temperature. The amounts of tar and other condensable matter (which formed at the cold end of the rig, close to the gas exit and caused a build-up of fine dust particles in the cyclone) were not determined in the current arrangement because this needs an additional set of condensers to be added down stream. However, based on previous experience related to the present experimental rig, it is estimated that a

nearly constant quantity of condensable matter would be less than $3 \pm 1 \%$ of the feed per run, and hence could be neglected for the purpose of this study.

Before starting a run, each part of the gasification system was brought to the appropriate temperature and, during preheating, only N_2 was used as the purge gas. Once steady temperatures were achieved, a pre-weighed sample (i.e. 0.05 kg of particle grain size of between 0.85 and 2.36 mm) of raw oil shale was placed in the feed bin and introduced into the reactor by a rotary feeder at a constant rate of $\sim 0.75 \text{ kg} \cdot \text{h}^{-1}$. The bottom end of the feeder was cooled, on continuous basis, by tap water in order to prevent over heating and subsequent pyrolysis (which would lead to the loss of volatile matter) of the oil shale in the feeder. The oil shale sample was kept at the final temperature until there was no further significant emission of gas. All gasification tests were conducted at atmospheric pressure and a constant fluidising velocity.

2.3. Off-gases analysis

The evolved gases from the reactor were sampled before being vented into the exhaust hood, using 20 ml plastic syringes sealed with a rubber septum in order to inhibit air infiltration into the gas sample. These samples were taken at predetermined time intervals throughout the duration of the gasification process of the oil shale and were analysed off-line by packed-column gas chromatography. The generated gas (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 constant background flow of N_2 . The concentration of CO_2 was measured separately using a silica-gel column with argon as the carrier gas and a thermal conductivity detector. The concentrations of hydrocarbon gases up to C_5 were determined with a porosil C 80-100 column with nitrogen as the carrier gas, using a flame ionisation detector. The calorific value of the fuel gas produced was calculated according to the standard method described in ASTM D3588 [18].

2.4. Thermogravimetric analysis

This analytical technique monitors the mass of the sample, which is subjected to a controlled temperature programme. It is rapid because of the small size of the

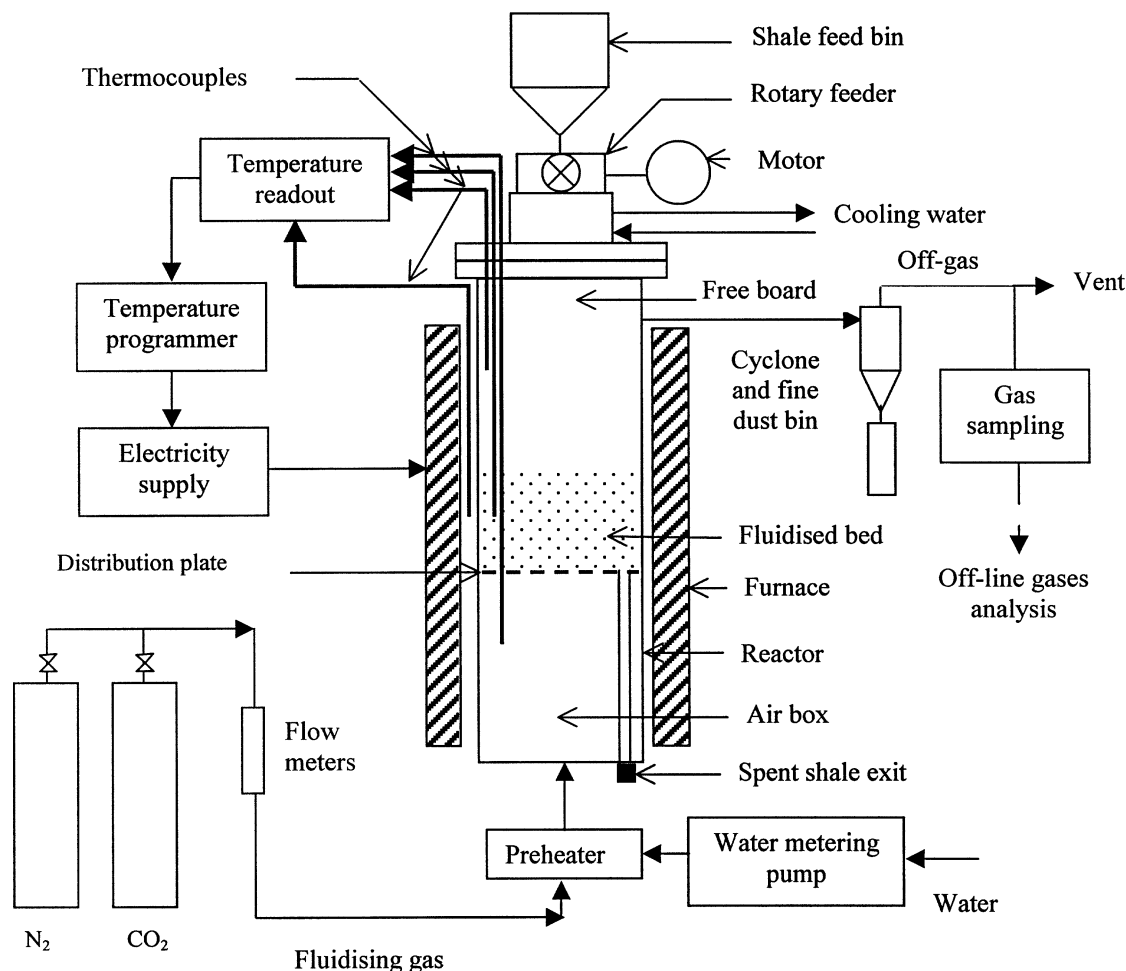


Figure 2. Schematic diagram of laboratory-scale fluidised bed reactor.

sample and the high heating rates. The non-isothermal tests of the oil shale samples were investigated using a Shimadzu Model-50 Series TG Analyser, with CO_2 (at a constant rate of $\sim 5 \cdot 10^{-5} \text{ m}^3 \cdot \text{min}^{-1}$) being employed as the purge and reactant gas. In the present investigation, TGAs were used to determine the effects of the heating rate (i.e. 10 to 20 $\text{K} \cdot \text{min}^{-1}$), particle size (i.e. smaller than 0.85, between 0.85 and 2.36, and between 2.36 and 3.35 mm) and final temperature (i.e. up to 1000 $^\circ\text{C}$) on the weight loss and reactivity of the oil shale sample. In all of the experiments, a particle sample (i.e. of between 10 and 25 mg) was placed in the alumina cell, which was then put on the sample pan hanging down inside the reaction tube, in which 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 (i.e. the continuous change in the mass of the sample is measured as well as the temperature monitoring of the furnace). Finally, and after the furnace temperature had achieved its set value, the sample was allowed to cool to room temperature.

3. RESULTS AND DISCUSSION

3.1. Kinetic analysis

Figures 3 and 4 display the weight loss (thermogravimetry, TG) profile and the derivative thermogravimetry (DTG) curves, during the gasification phase in

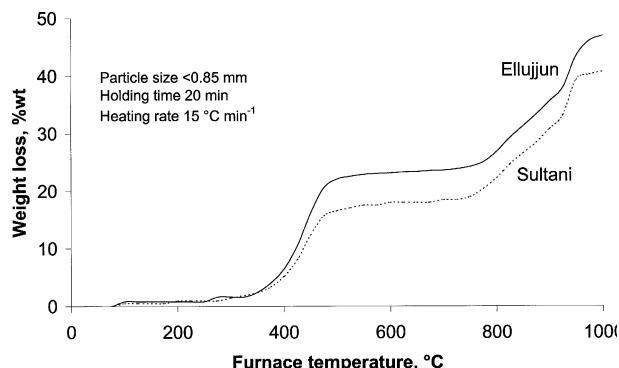


Figure 3. TG profiles for the Ellujjun and Sultani shales during TGA gasification in CO_2 .

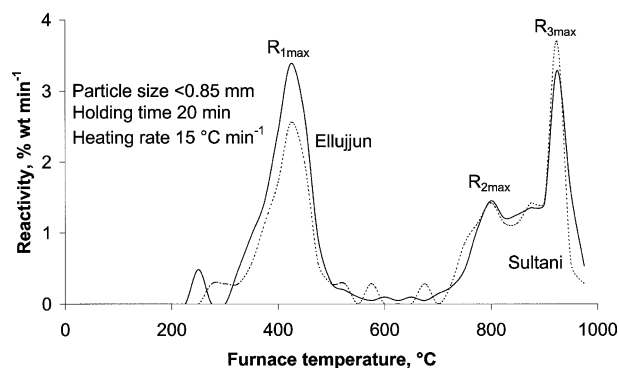


Figure 4. DTG gasification (in CO_2) profiles for the Ellujjun and Sultani shales.

CO_2 , for the Ellujjun and Sultani oil shales. It is clear that the rate of conversion of organic content is directly related to the gasification temperature: the higher the temperature, the greater the weight loss. This is because at high temperatures, the gasification reactions proceed at faster rates [19]. It is evident that the Ellujjun sample exhibits approximately 7 % higher weight loss compared with the Sultani oil shale: the latter lost (including carbonate decomposition) about 40 % of its initial weight. However, during the gasification phase alone, the Sultani specimen lost ~ 55.8 % of its total weight loss, i.e. more than the Ellujjun sample by about 5 %.

It can also be seen that there are three peaks apparent in the DTG figure. The first one, $R_{1\text{max}}$, occurred during the devolatilization phase, at about 425°C . While, the second, $R_{2\text{max}}$, which is lower, peaked around 800°C and the third one, $R_{3\text{max}}$, occurred at approximately 925°C for both shales. The second peak can be attributed to the decomposition of carbonates (e.g., TGA tests, for pure calcium carbonate and dolomite showed that the decompositions of such materials started at approximately

$650 \pm 20^\circ\text{C}$, in a nitrogen environment) present in the shale, which is in agreement with results of the pyrolysis study for the same samples under similar experimental conditions, except that N_2 was used as the sweeper gas [17]. But there is a shift upwards of peak reaction temperature for the case of the CO_2 compared with that of the N_2 environment, which occurred at about 740°C . Also, the rate of carbonate decomposition, for both shales, was much less than that when N_2 gas was used to purge the furnace: in other words, the choice of CO_2 as a sweeping gas (rather than N_2) retards the decomposition of the carbonate contents in the shale. However, the reactivity of the shale, during the gasification phase (i.e. beyond the carbonate decomposition region), increased by approximately 10 for the Sultani as well as Ellujjun oil shales, when using CO_2 as the reactant gas compared with that for N_2 for the same samples and under identical experimental conditions. This is because CO_2 is more reactive than N_2 due to the presence of alkali metals, which are very effective in the CO_2 and/or H_2O gasifications of carbon [20], and the decomposition of carbonates is the only source for the CO_2 generated during the pyrolysis process [21, 22].

Approximately two thirds of the weight reduction during the gasification phase occurred above 850°C . Also the reactivity at 925°C is approximately 2.2 and 2.6 times more than that at 800°C for Ellujjun and Sultani shales respectively. Such results suggest that the carbon dioxide-char reaction is more likely to occur at high temperatures. But, it should be remembered that, in such cases, carbonate decomposition and more importantly the loss of the more volatile elements (such as Zn, Pb, Cd and As) would have a great influence on the degradation and final weight loss of the oil shale samples. The slight difference, in the behaviour of the two shales during gasification in a CO_2 environment, could be attributed to the fact that the Ellujjun sample is of a higher grade, i.e. contains more organic matter, than the Sultani oil shale. Equally important is that the organic part of the oil shale, called kerogen, is a macromolecular substance unevenly distributed in the shale's inorganic matrix. Also the catalytic activity of oil shale minerals, which is dependent on their concentration and dispersion in the shale, have a major role during the gasification process. There are several published studies on the catalytic behaviour of minerals in coal [23–26], but there is little information available concerning the influence of mineral materials on oil shale gasification reactivity. However, it has been proved that the inorganic, e.g., mineral impurities, content in carbon has a great influence on the reactivity of the residual carbon in the shale [12–15, 23, 27, 28]. A close look at the DTG curves shows that

TABLE III
TGA data for different particle sizes from the Sultani oil shale deposit.

| Particle size, mm | Average weight loss (%) | | | | Temperature at which maximum reactivity occurs, °C |
|-------------------|-------------------------|------------------|--------------|-------------|--|
| | Total | Devolatilization | Gasification | | |
| | | 25–600 °C | 600–900 °C | 900–1000 °C | |
| ≤0.85 | 40.8 | 44.2 | 31.4 | 24.4 | 910 |
| >0.85–≤2.36 | 39.3 | 45.3 | 29.7 | 25.0 | 933 |
| >2.36–≤3.35 | 39.1 | 43.4 | 28.3 | 28.3 | 936 |

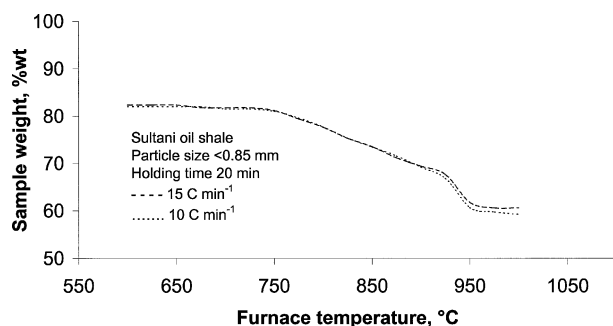


Figure 5. Weight loss profiles for different heating rates during the gasification phase.

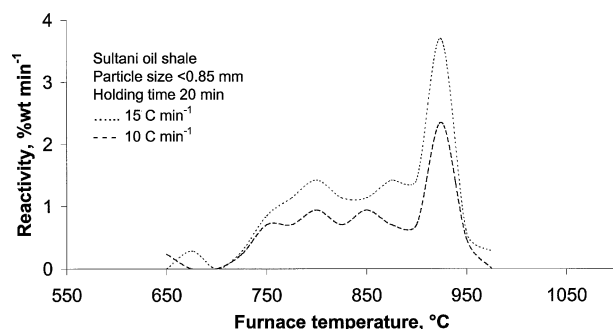


Figure 6. Shale reactivity for different heating rates during the gasification phase.

the maximum decomposition rate is almost identical for both the Ellujjun and Sultani samples. This suggests that approximately equal values occur for reactivity, defined as either the ratio of the rate of weight loss per unit of time or the rate of weight loss relative to the initial weight of the sample, for the gasification of both shales.

Heating rate, which is an important experimental parameter, was found to have little effect on the weight loss during the gasification of oil shale. There is a small decrease, of approximately 1 %, in the total weight loss when the heating rate was increased from 10 to 15 K·min⁻¹, see figure 5. As in the case with oil shale pyrolysis, the maximum reaction rate increases with the

heating rate. It was found that the reactivity rose by approximately 50 % over the studied range, i.e. the reactivity at 15 K·min⁻¹ was ~150 % higher than that at 10 K·min⁻¹, for the Sultani oil shale, see figure 6.

Table III summarises, in relation to shale particle size, the analysis of TGA data in terms of weight loss and maximum reactivity during the gasification phase. The results show a systematic higher percentage of conversion as the particle size decreased. Moreover, a higher ratio of weight loss for the smaller particles was completed below approximately 900 °C. This suggests that the rate of heat transfer is slower at lower temperatures in the bigger particles because of the longer transport paths, and hence longer gasification times are needed for the same percentage of conversion as that attained with the smaller particles [29].

Careful analysis of the observed data shows that there is a slight shift at which the maximum reactivity occurs towards higher temperatures as the particle size was increased. This can be attributed, again, to the slower rates of heat transfer within the larger particles. The reactivity values for smaller size particles are higher than those for large particles, which is due in part to the smaller particles having higher ash contents.

Because oil shale is a complex fossil fuel, when gasified, it will decompose through several simultaneous reactions. Also the TGA records only the weight loss of the sample. Therefore, the calculated gasification kinetic data will provide only general information about the overall reaction kinetics. In this investigation, assuming a first-order reaction occurred during the TGA experiments, then the following mathematical model was used in analysing the measured data in order to compute the activation energy [17]:

$$\ln[-\ln(1 - X)] = \ln\left[\frac{k_0 RT^2}{hE}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT}$$

where X is the fraction of the oil shale which has decomposed in time t , and k_0 the frequency factor, E the

TABLE IV
Influence of particle size on the apparent activation energy.

| Particle size, mm | Average activation energy, $\text{kJ}\cdot\text{mol}^{-1}$ | |
|----------------------|--|----------------|
| | Ellujun sample | Sultani sample |
| ≤ 0.85 | 151 | 149 |
| $> 0.85 - \leq 2.36$ | 163 | 158 |
| $> 2.36 - \leq 3.35$ | 177 | 203 |

activation energy, R the gas constant, h the heating rate and T the absolute temperature.

The plot of $\ln[-\ln(1 - X)]$ against $1/T$ gives almost a straight-line, with a slope of $-E/R$, which can be used to calculate the activation energy. The frequency factor k_0 can be calculated from the intercept on the $\ln[-\ln(1 - X)]$ axis. In reality, a deviation of the experimental data from this straight-line behaviour is an indication that the assumption of a first-order reaction may not be sufficiently accurate. In this study, plots were prepared for all the samples, and the activation energy was determined from the best-fit lines; the correlation factor exceeding 0.98. It is found that, for various heating rates, there are insignificant variations in the apparent activation energy. However, the activation energy increases with grain size. The average values obtained, for the Ellujun and Sultani oil shales, from this study, are summarised in *table IV*.

Such high activation energy is required for breaking the strong chemical bonds and completing the carbon dioxide-char reaction. The slight difference between the values for the two samples is due to the oil shale's dissimilar compositions, i.e. with respect to their organic and mineral contents, and difficulties involved in achieving repeatability of the experimental results, even for the same oil shale sample. It was noticed that, in the oil shale literature, there is a wide variation for the apparent values of the activation energy, i.e. between approximately 150 and 210 $\text{kJ}\cdot\text{mol}^{-1}$, which corresponds with those achieved in this investigation, depending on the type of oil shale and particle size employed, as well as the analysis technique used when determining the kinetic parameters [5, 12]. But great care should be taken in this regard, due to the influence of process parameters on the final results. Therefore, identical experimental and theoretical procedures, including sample preparation procedure, analysis method and kinetic model, should be employed. However, since oil shale has a complex heterogeneous nature, especially the kerogen, it should be remembered that it is difficult to achieve repeatability of experimental findings, even for samples from the same deposit.

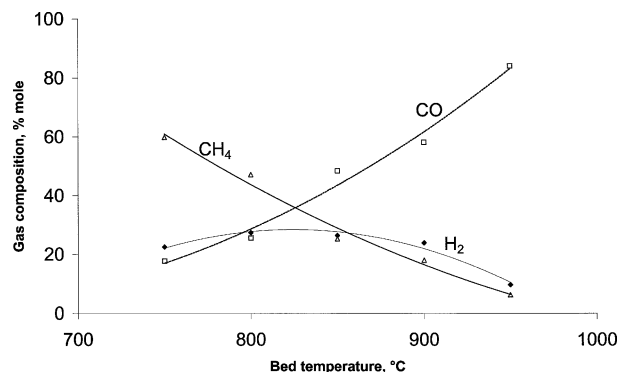


Figure 7. Composition of produced fuel gas with respect to bed temperature.

3.2. Fluidised bed gasifier

As soon as the oil shale particles are poured on to the top of the surface of the hot bubbling bed of inert material, they mix rapidly and are entrained by the circulating vortices. Consequently, their temperature soon becomes that of the fluidising bed. During this short period, devolatilization and flash pyrolysis of organic matter occur and the resulting char is distributed throughout the bed. In the present investigation, an attempt was made to study the influence of key parameters, such as gasification temperature and the nature of the fluidising gas, on the quality and quantity of the gaseous fuel produced from the fluidised bed gasifier.

Figure 7 shows the product gas compositions, when a mixture of 50 % CO_2 and 50 % N_2 were used to fluidise the bed, as a function of final temperature for the Ellujun oil shale. The concentrations of various constituents in the produced fuel gas were calculated on the basis of free CO_2 and N_2 in order to facilitate the comparison of the fuel gas generated by using different types of fluidising gases. The main resulting carbon containing gases are CO as well as the hydrocarbon gases, namely methane, and to a lesser extent ethene and propene, represented here as CH_4 . Visual inspection of the colour of the exit hose, close to the exit hood, showed that tar and other condensable matter were formed and caused a build-up of fine dust particles on its interior surface. Also no significant change in the sizes of the particles occurred during the gasification process. But it was observed that the spent shale is much softer, i.e. it can be more easily ground or crushed, than the raw shale. This is because, during gasification process, the oil shale particles tend to fissure and so develop an increased porosity, as the gaseous products leave the matrix, and hence the spent shale is more friable.

The H_2 content of the produced fuel gas rose by approximately 50 % as the final gasification temperature was increased by 100 K, i.e. from 750 to 850 °C, then decreased sharply during the next 100 K increment (i.e. from 850 to 950 °C). Also, the hydrocarbon gas, i.e. CH_4 , content dropped from approximately 42 to about 5 % on a molar basis, over the same temperature range. This is most probably due to the lack of hydrogen, because the only source of hydrogen is from the oil shale itself, i.e. from the water released in the bed from the shale's moisture content and interlayer water, for completing the reactions leading to the production of hydrocarbon gases and hydrogen sulphide. More important is that, at high temperatures, the water–gas shift reaction consumes H_2 and produces CO, but on the overall basis, there is a net production of hydrogen. The rate of CO evolution increased with temperature: the yield of generated fuel gas increased from 0.135 to about 0.33 kg, on the basis of free N_2 and CO_2 , per kg of raw shale. Such an increase in the mass yield suggests that CO_2 is converted to CO through the Boudouard reaction, which occurs more intensively at higher temperatures. Actually there was a marked increase in the CO/CO_2 ratio, and a drop in the concentration of CO_2 , as the temperature increased; this again being strong evidence that a reduction in CO_2 by conversion to CO, through the Boudouard reaction, was ensuing. Also CO is produced by the steam–carbon and water–gas shift reactions; the latter being faster than the other gasification reactions occurring. These findings corroborate the conclusions of corresponding studies for gasifying retorted oil shale [5, 6, 9, 21, 30, 31].

The yield and composition of gaseous products from the oil shale gasification process depend also on the reactant gas composition. So by changing the ratio of steam to CO_2 , before being introduced into the reactor, the steam–carbon and water shift reactions can be controlled at the desired gasification temperature to provide the required gas composition. The effect of introducing steam on the mass yield was studied only at a temperature of 800 °C. It was found, in the present investigation, that introducing steam at a temperature of approximately 350 °C into the reactor increased the mass yield of produced gas to reach ~0.4 kg, on the basis of free N_2 and CO_2 , per kg of dry shale. Such an increase suggests that steam is becoming part of the produced gases, i.e. the concentration of individual gases increased including hydrocarbon gases. It is reported that the steam–carbon reaction is faster by about 3 times compared with carbon dioxide–carbon reaction [12, 31]. The results of elemental analysis of spent shale ensued from the gasifier showed that nearly 94 % of the initial carbon content in the shale was converted to final products and about 70 % of the total sulphur in

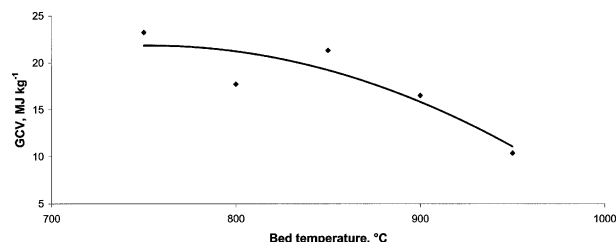


Figure 8. Effect of gasification temperature on the calorific value of generated gaseous fuel.

the shale was converted to sulphurous compounds. During the gasification process and analysis measurements of the produced gases, a sulphurous odour was noted in the exit gas. This is attributed to the formation of sulphur compounds (i.e. mainly H_2S) as a result of both the thermal and chemical decomposition of the high, i.e. 3 % by weight, sulphur content of the oil shale [1, 9]. The measurement of the H_2S formed was not possible during these experiments. But the removal of the sulphur from the shale as H_2S would make the spent shale more environmentally acceptable and allow for elemental sulphur by-product recovery, e.g., via the Claus reaction.

The gasification temperature has an important effect on the calorific value of the produced fuel gas: the higher the temperature, the lower the calorific value, which decreased more than linearly over the studied range, see *figure 8*. This could be explained as a result of the large reduction in the hydrocarbon species, which have high heating potentials of approximately 3 times that for CO or H_2 , content in the evolved gases. Such heating values for the produced fuel gas are relatively high, i.e. between 15 and 25 $MJ\cdot kg^{-1}$, due to the fact that the required heat was supplied by an external source, i.e. the reactor being externally heated by an electrical furnace, and it was calculated on a CO_2 and N_2 free basis. However, in a commercial gasifier and based on the limited published information in this field, it is predicted that the calorific value of the produced fuel gas would be lower, i.e. between 5 and 15 $MJ\cdot kg^{-1}$ depending on the type of gasifier employed and the reactant gases used, than that anticipated in this study. It has been reported that gasifying oil shale, from the Eastern regions in the USA as well as from Sweden, in a direct combustion fluidised bed gasifier produced a fuel gas with an average calorific value in the range of 7–10 $MJ\cdot m^{-3}$ on the basis of N_2 free gas [5,6]. Such a gaseous fuel could be used to energize a simple gas turbine combined cycle system with no additional problems. It is reported that burning this fuel gas, with such a relatively low calorific value, in a heavy-duty gas turbine or a simple plant combined cycle system is capable of achieving plant heating rates of about

9.6 and 7.1 MJ·kWh⁻¹, respectively [32]. Additionally, the high efficiencies of the combined cycle system can mitigate the conversion losses incurred in gasifying the oil shale, and so still deliver a high overall efficiency as well as provide economically the superior environmental performance required. The latter is achieved because pollutant reductions are accomplished before combustion ensues: the mass of gas then to be cleaned is much less, so facilitating achieving a high clean-up efficiency. Also, it is important to note that the higher the ratio of H₂ content in the produced fuel gas compared with that of natural gas would provide the possibility of reducing NO_x as well as CO₂ emissions when this gaseous fuel is burnt in a gas turbine to generate electricity. But the use of a fuel gas with low calorific value, i.e. approximately $8 \pm 1 \text{ MJ}\cdot\text{m}^{-3}$, incurs some problems and requires special considerations, with respect to the fuel supply and management systems and the combustor's design to cope with the increased fuel flow as well as turbomachinery of the engine to accommodate the increase in the mass flow rate across the turbine's expander.

4. CONCLUSION

The realisation of the forthcoming severe decline in the availability of liquid and gaseous fossil fuels during the next century has generated new interest in the utilisation of the relatively abundant resources of oil shale world-wide. However, the immediate exploitation of oil shale is inhibited because of the present low unit prices of crude oil and natural gas. This experimental study was undertaken to determine gasification potential of Jordanian oil shale, and this is the first reported experimental investigation concerning these particular grades of oil shale. The results of the TGA and fluidised bed gasification tests have shown that Jordanian shales can be converted successfully to a synthesis combustible gas. The gasification of Jordanian oil shale, using a continuous fluidised bed, generated a relatively high quality combustible gas dominated by H₂ and CO. The effectiveness of the conversion of the shale's organic content into a gaseous fuel is dependent on the bed temperature, i.e. it increased with temperature, as well as the fluidising gas. Experiments made with pure CO₂ and N₂ as the reactant and fluidising gas respectively, resulted in CO as the only significant combustible component in the effluent gas. This, of course, is because the only source of H₂ is from the raw shale itself. But as expected, using steam, as a reactant fluid, is more effective than CO₂ in producing H₂ and the hydrocarbon species during the gasification process.

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