

OIL SHALE PYROLYSIS IN FIXED-BED RETORT WITH DIFFERENT HEATING RATES

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Production of oil at pyrolysis of Ellajun oil shale was investigated at different heating rates (0.2–2.8; 2.2–5.0 and 7.0–13.0 °C min⁻¹ in a fixed-bed retort. Total weight loss and oil yield were calculated for the temperature range 610–873 K. Total weight loss of oil shale sample increased from 12.5% to 18% with increasing the heating rate from 0.2 to 13 °C min⁻¹, whereas shale oil yield (calculated based on Fisher Assay for Ellajun sample) decreased from 80% to 40%. Sulfur content of produced liquid hydrocarbons decreased from 7.4 wt.% to 6.5 wt.% with increasing heating rate and pyrolysis temperature. Density of the produced shale oil increased from 0.947 to 0.982 g cm⁻³ with increasing heating rate indicating the formation of heavier compounds. The rate of shale oil accumulation was monitored by digital mass scales. Higher heating rates resulted in higher rates of accumulation. The rate of oil and water collection passed through a maximum for different heating rates at different pyrolysis temperatures.

Introduction

Heterogeneity of oil shale in composition and origin makes it an interesting material to study [1]. Reaction temperature, fluid of generated hydrocarbons leaving the reaction zone [2–4], rate of heat input [5–8], particle size [9], mineral content [10] are among the most important factors that dictate the behavior of oil shale decomposition during pyrolysis. The most important of them is the heating rate that exerts a significant influence on the reactions and products of the pyrolysis process.

Several authors [3, 5, 11–13] have studied the effect of heating rate on the rate of weight loss of oil shale during pyrolysis using TGA and/or DGA.

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The main objective of this research work was to determine the rate of oil formation and water mass loss under the influence of different heating rates in an equipment other than TGA, DGA or DSC. In addition, the heating rate effect on oil yield, shale oil density and sulfur content of shale oil as function of pyrolysis temperature were investigated.

Experimental

Oil shale samples investigated in this work were obtained from Ellajun area located in the southern region of Jordan. The original oil shale samples were ground in a ball mill and sieved to particle size 0.5–2.1 mm. The size selection was based on diffusional influence and mass transfer studies. All samples were dried in oven at $110\text{ }^{\circ}\text{C} \pm 3$ for a period of 10–12 hours.

All experiments were conducted in a stainless-steel fixed-bed retort. Five hundred grams of oil shale sample were electrically heated in an 800-cm^3 cylindrical retort. Reactor and furnace temperatures were controlled to obtain the desired retorting temperature. Type K thermocouple was inserted from the top side of the retort to the middle point of the oil shale sample for monitoring purpose, while the other thermocouple was situated between the external body of the retort and the inner side of the ceramic cylinder for controlling the retort temperature. Sweep gas was introduced from the top of the retort in an 8-mm pipe for preheating while passing downward to the bottom of the retort and then was allowed to disperse to sweep the generated products toward the retort topside outlet. Oven temperature was controlled and monitored by digital temperature controller indicated as oven T.C. in Fig. 1 below.

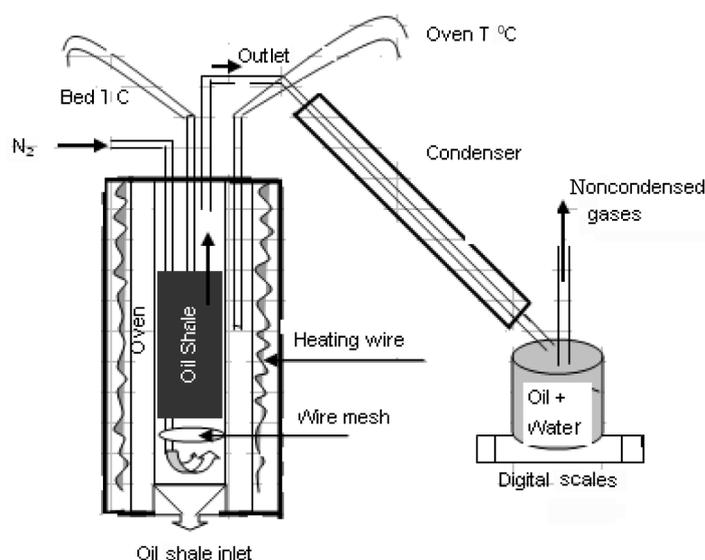


Fig. 1. Diagram of experimental setup.

The generated hydrocarbons were swept from the reaction zone by gaseous nitrogen. The circulating coolant was maintained at 2 ± 2 °C to condense liquid hydrocarbons and water carried by nitrogen gas. Condensable hydrocarbons and water were collected while the non-condensable light organics and other non-condensable gases were vented into the atmosphere. The weight of the condensed liquid shale oil and water was recorded continuously as a function of time and retort temperature as the digital scales indicate the increase of the accumulated weight on its digital panel. Finally oil and water were separated from each other for oil yield calculation. At the end of each run, the retort was emptied and the spent shale weighed for the total weight loss measurement.

Results and discussion

Oil shale retorting has been gaining momentum in recent years to develop an efficient retorting technology for utilizing the abundant oil shale reserves scattered all over the globe. The desired technology should be available and ready in case crude oil prices exceed the breakeven point of the oil shale processing cost. In order to develop the desired technology, numerous research works are needed to assist in maturation of such technology.

Among several parameters that play a vital role in the reaction of carbon-containing material (kerogen) during oil shale pyrolysis is the rate of heat input to the system. Several investigators [3, 5] have studied the heating rate effect on the kinetics of Ellajun oil shale pyrolysis. Ellajun deposits are characterized elsewhere [9]. The impact of the heat supply on the rate of oil generation and kerogen decomposition is evident from its impact on the composition of the products. Most of researchers investigating the effect of heating rate and determining the kinetics of oil shale pyrolysis have employed TGA and/or DGA data. In TGA and/or DGA runs, a maximum of 50-milligram sample is used to measure the weight loss of a sample as the function of time and temperature at a constant heating rate. No studies on liquid accumulation, sulfur and density measurement have been conducted so far.

Oil and water collection rate measurement

The rate of weight loss determined by the rate of accumulation of shale oil and water was measured as the function of both time and pyrolysis temperature. All runs were conducted to the final temperature 873 K. Figure 2 shows the effect of increasing pyrolysis temperature on the rate of liquids' accumulation for different heating rates. Heating rate in the range $0.2\text{--}2.8$ °C min⁻¹ is considered low, while intermediate one covers the range $2.2\text{--}5.0$ °C min⁻¹ and high heating rate is $7.0\text{--}13$ °C min⁻¹. As it can be seen from the figure, low heating rate e.g. $0.2\text{--}1.8$ °C min⁻¹ produced low liquids'

accumulation rate passing through a maximum value at a temperature close to 643 K. In the low heating rate range, the percentage of liquids' formation in different conducted runs varied between 13.0 to 14.6 with an average value of 13.8%. Slight differences were observed for different heating rates for the same range, i.e. higher heating rate within a small range resulted in a higher liquid total weight loss percentage at the end of a run. The total weight loss was calculated as the difference between input weight and spent shale weight at the end of the run. Similar behavior was observed for other heating rate values. When the heating rate was increased to 1.8–2.8 °C min⁻¹, the rate of liquids' accumulation increased while its maximum shifted close to 700 K. The maximum value of liquids' accumulation rate 0.65 g min⁻¹ was measured at the highest heating rate in the low heating rate range. The initial rise in the rate of weight loss to a maximum value followed by a decrease is ascribed to the kinetics-controlled reaction zone at low pyrolysis temperature, whereas the decrease is related to the depletion of hydrocarbons from kerogen due to reaction progress and complexity of the entangled hydrocarbons in the kerogen matrix. Undoubtedly lower heating rate run requires more time to approach higher reaction temperature, so the decrease in the rate of liquids' accumulation when reaction temperature increases will not affect the final quantity of the liquid produced but definitely alters the product distribution. The calculated total weight loss for low heating rate runs were found to vary between 13% to 15%, which is acceptable. The estimated average total weight loss is 14.0% for low heating rate experimental runs.

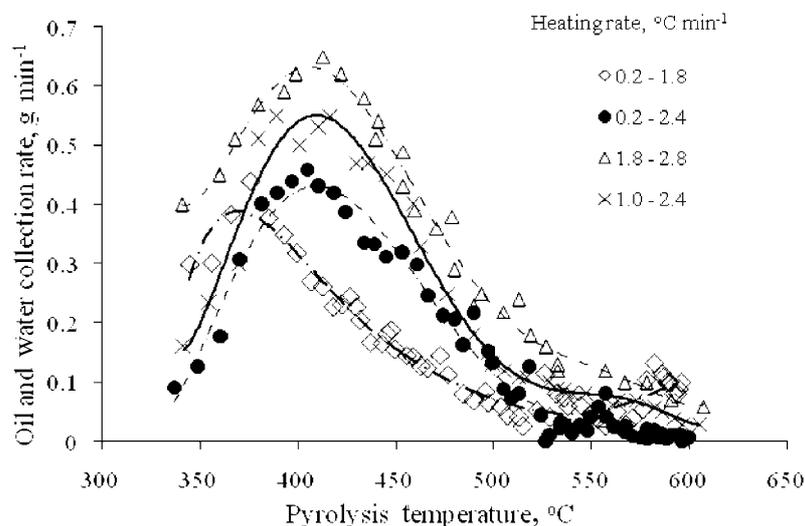


Fig. 2. Effect of low heating rates on the rate of weight loss as function of pyrolysis temperature.

Figure 3 is depicting similar behavior for the intermediate heating rate, e.g. 2.2-5.0. It is quite clear from the figure that the magnitude of the rate of liquid accumulation increased. It is clear from Figures 2 and 3 that the increment in the rate is more than two folds in magnitude in the range 2.2–5.0 °C min⁻¹ in the entire experimental temperature range. It is evident that the highest rate of weight loss increased in the magnitude with a slight shift in location of the pyrolysis temperature. Similar results are reported [14] for hydrocarbon release shift with increasing heating rate.

The maximum magnitude of the rate of weight loss observed is 1.55 g min⁻¹ for 3–5 °C min⁻¹ as it can be inferred from Fig. 3. On the other hand, the total weight losses for the 2.5–4 and 3–5 °C min⁻¹ were calculated to be 15.6% and 16.6% respectively, while the total weight loss for 2–2.2 °C min⁻¹ heating rate was found to be 15%. The estimated average total weight loss for the intermediate heating rate would be 15.7%.

Higher heating rates resulted in the highest magnitude of the rate of weight loss during this investigation (Fig. 4). It can be observed that due to experimental procedure and high rate of liquids' accumulation, the produced data suffer from scattering and spread. Comparing scattering on the three above-mentioned graphs, it can be seen that the higher the heating rate, the more scattered the data are. As it is clear from the graph, the magnitude of the weight loss rate, 2.5 g min⁻¹, was observed with the 11–13 °C min⁻¹ heating rate. The higher the heating rate, the higher the magnitude of the rate of oil shale mass loss. The rate of liquids' accumulation increased from 0.65 g min⁻¹ in the low heating rate range to higher than 2.2 g min⁻¹ in the high heating rate range in the present study. Kök [11] has reported similar

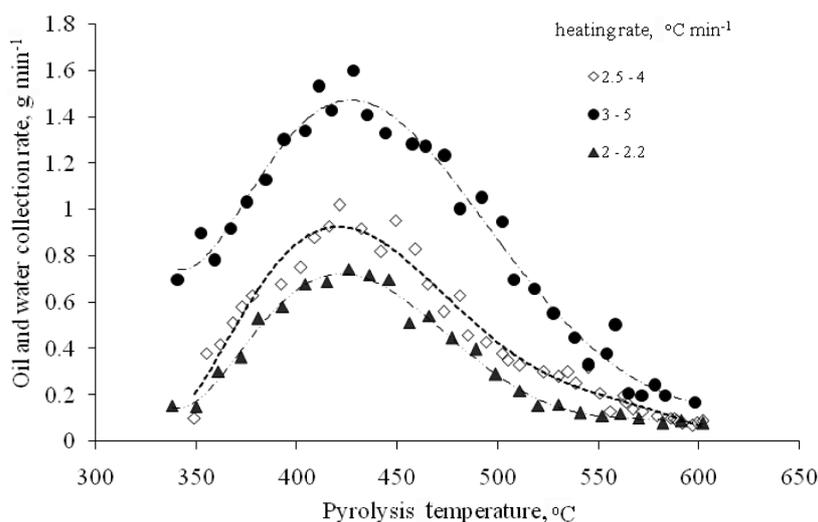


Fig. 3. Effect of intermediate heating rates on the rate of weight loss as function of pyrolysis temperature.

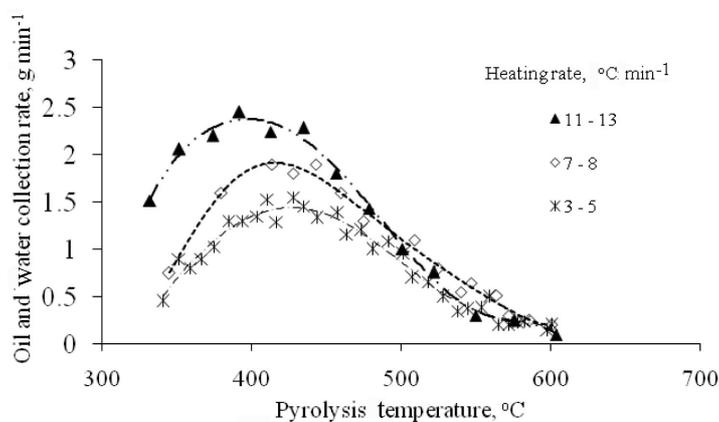


Fig. 4. Effect of high heating rates on the rate of weight loss as function of pyrolysis temperature.

results: higher heating rates resulted in higher reaction temperatures and higher heat of reactions. Maximum weight loss peaks shifted to higher temperatures with increasing heating rate.

Heating rate affected both conversion and oil yield. The influence of heating rate on total conversion of oil shale that included liberation of intermolecular water and kerogen decomposition is shown in Fig. 5. As it can be seen from the figure, at low heating rates, i.e. less than $4\text{ }^{\circ}\text{C min}^{-1}$, conversion of oil shale was remarkably less. On the other hand, conversion percentage was not affected by heating rates higher than $4\text{ }^{\circ}\text{C min}^{-1}$. Higher than $13\text{ }^{\circ}\text{C min}^{-1}$ heating rates were not examined since control over reaction temperature was difficult.

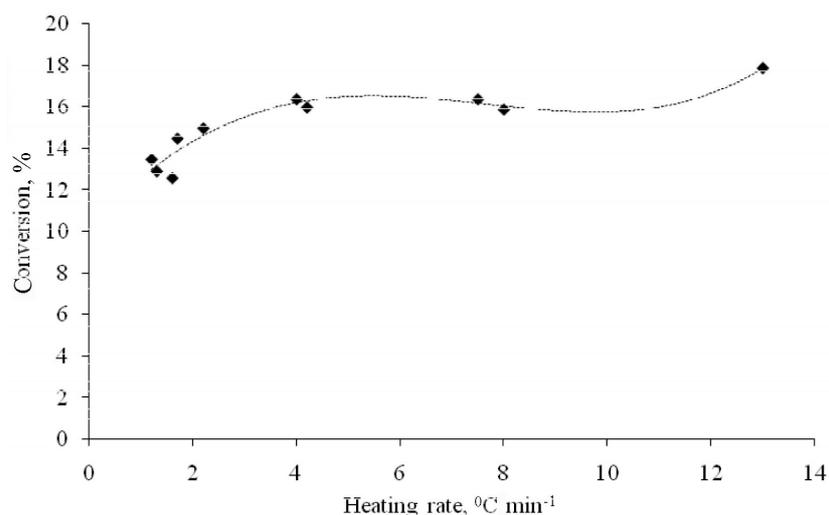


Fig. 5. Effect of heating rate on conversion percentage.

On the contrary, oil yield calculation based on the quantity of oil generated in Fisher Assay test [15] was affected negatively by the heating rate. As indicated in Fig. 6, the oil yield calculated based on Fischer Assay for Ellajun samples decreased with increasing heating rates in the studied range. The highest oil yield measured in this work was 90% corresponding to the lowest heating rate in this work. The decrease in the oil yield is accompanied by variation in composition and physical properties of the produced oil. Conversion percentage increased with increasing heating rate while oil yield decreased. This behavior is ascribed to the increase in secondary cracking reaction such as dehydrogenation of components of heavy fraction of the produced oil and subsequent coke deposition, the dealkylation, reforming reactions are also possible candidates.

Figure 7 shows the variation of shale oil density with heating rate. As it can be seen from the figure, the contribution of the heavy component increased with increasing heating rate. Oil density increased from 0.947 g cm^{-3} at low heating rate to 0.982 g cm^{-3} at high heating rate. This change is ascribed to the change in composition of the produced hydrocarbons and the formation of heavier components.

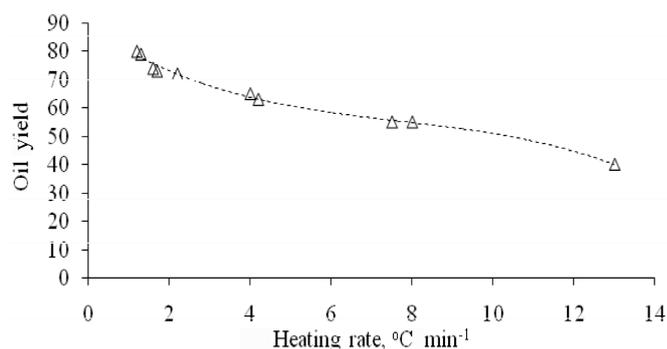


Fig. 6. Influence of heating rate on oil yield.

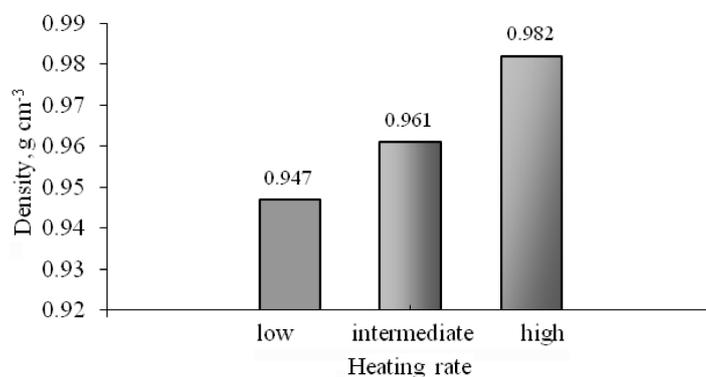


Fig. 7. Influence of heating rate on density of shale oil.

Sulfur content of the produced liquid shale oil was measured and results are depicted in Fig. 8. It is quite clear from the figure that sulfur content of the produced hydrocarbons decreased from 7.4 wt.% to 6.5 wt.% when both heating rate and pyrolysis temperature were increased in the studied range.

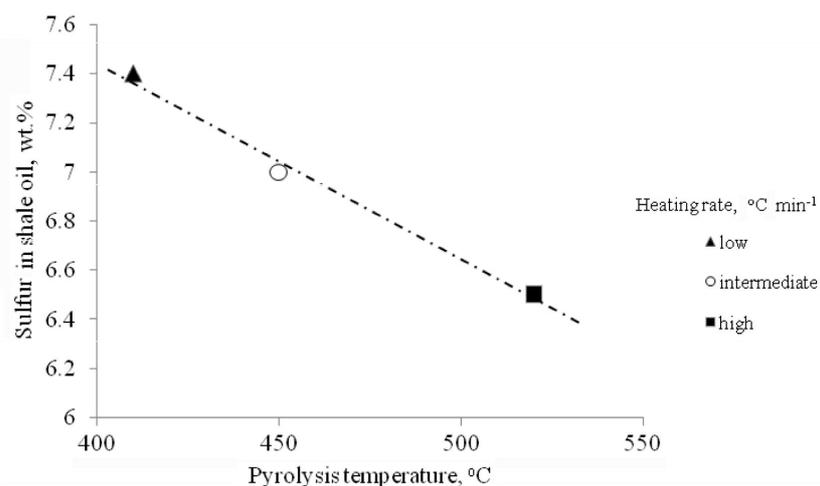


Fig. 8. Effect of pyrolysis temperature on sulfur content of shale oil.

Conclusions

Heating rates have a direct impact on the rate of oil formation and water loss from oil shale (see Table). The results have demonstrated that increasing heating rate increases conversion slightly. A maximum magnitude of the oil and water loss rate was observed for all heating rates although the corresponding pyrolysis temperature where the maximum occurs is different. A steady decrease was observed for oil yield with increasing the heating rate in the studied range. The density of the produced liquid hydrocarbons increased with increasing the heating rate. Pyrolysis temperature decreased sulfur content when the temperature increased.

Table. Experimental data, heating rate versus total weight loss and collected oil & water

Heating rate range, C min ⁻¹	Total weight loss, % (Conversion)	Oil & water, wt.%
0.2–1.8	13.5	7.3
0.2–2.4	12.93	7.7
1.0–2.4	14.5	7.8
2.0–2.2	12.6	8.5
1.8–2.8	15	11.1
3.0–5.0	16	9.4
7.0–8.0	16.4	10.7
11.0–13.0	17.9	7.8

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