

Effect of Oil Shale Particle Size on Oil Yield, Sulfur and Distillation Fractions

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Abstract

The effect of particle size on sample total weight loss, gas loss, and oil yield of oil shale has been investigated at a constant heating rate of 1 – 2 °Cmin⁻¹. Particles sizes of 37.5, 31.5, 25.0, 19.0, 9.5 mm were used during the pyrolysis of Ellajjun oil shale specimens. The total weight loss at 550°C final pyrolysis temperature decreased from 28% to 21% as particle diameter increased from 9.5 mm to 37.5 mm. Gas loss percent also decreased from 9% to 6% in the investigated range. Oil yield measured by Fischer Assay decreased from 90% to 67% with increased particle size.

Atmospheric distillation of the produced shale oil shows a decrease in the naphtha and gasoline fraction by 4% by volume, whereas the percentage of diesel fraction decreased from 50% to 42% as particle diameter increased. On the other hand, the percent kerosene increased from 22% to 34%, as particle size increased. Sulfur content and density decreased with increasing particle diameter. The sulfur in liquid hydrocarbon decreased from 10.9% wt. in liquid hydrocarbons to 9.9% wt. as particle size increased.

1. Introduction

Oil shale, a fine-grained sedimentary rock with organic matter termed kerogen is found worldwide (Dyini, 2003). Oil shale has been an interest of many investigators in recent times due to the increase in crude oil prices (Li and Yue, 2003; Al-Ayed, 2005; Johannes, et al., 2006; Johannes, et al., 2007; Kok and Iscan, 2007). Studies of oil shale have dealt with the various influencing factors and operating conditions. Reaction temperature, heating rate, mineral composition, hydrocarbon content and kerogen content and grain size are among the most important variables that have a direct impact on the amount of extractable shale oil.

Particle size is one of the most important variables affecting the pyrolysis of oil shale. Several investigators studied the effect of particle size on the oil yield and weight loss. The size of the oil shale particles has a direct impact on the nature of the reactions of kerogen decomposition. The cracking reactions due to

the thermal inertia and the secondary reactions catalyzed by the mineral matter of the shale are affected by the size of the oil shale particle undergoing pyrolysis. Due to the complexity and compositional heterogeneity of oil shale, it is difficult to isolate and investigate the effect of each individual factor away from the minor influences of other factors. This nature of oil shale has contributed to the disagreement of several researchers' results and conclusions. The most studied factors in general are the effect of temperature, heating rate and particle size on the total weight loss and oil yield during pyrolysis reaction.

Most research conducted on oil shale deals with weight loss, oil yield, sulfur production, and heating rates. Bhargava et al. (2005) recently have reported total weight loss of oil shale as function of temperature and attributed the lost to losses of moisture, interlayer water from clay minerals, decomposition of certain minerals, and decomposition of kerogen

into pyrolytic bitumen, which further decomposes into gas and liquid products. These losses do not include carbonate decomposition as oil shale pyrolysis is accomplished below 550°C. On the other hand, (Allred, 1966) has reported that the process of oil evolution during oil shale pyrolysis is a sum of two separate steps. The first involves degradation and the second is the evaporation of the products. Braun and Rothman (1975) reported 487°C reaction temperatures for decomposition of bitumen, which involves breaking of relatively weak chemical bonds, whereas higher temperature reactions involve breaking of much stronger chemical bonds in kerogen.

Physical changes, such as softening and molecular rearrangement that are associated with the release of gases and structural water also have been reported (Jaber et al., 1999) at temperatures lower than 500°C. The peak of loss occurring early in the vapor is attributed to the rapid evaporation of the organic material not chemically bonded to the kerogen network.

Some investigators (Russell, 1990) have found shale oil yield increased as particle size was increased whereas other researchers (Wallman, 1981; Guffey, 1984; Rubel and Davis, 1985; Campbell, et al., 1978) reported a decrease in oil yield with an increase in particle size. On the other hand, Dogan and Uysel (1996) and Drescher et al. (1983) reported independence of oil yield from the particle size.

2. Experimental Setup

Oil shale samples investigated in this work were obtained from the Ellajjun area in the southern part of Jordan. The original oil shale samples were ground in a ball mill, and sieved to selected particles sizes ranging from 9.5 mm to 37.5 mm.

All experiments were conducted in a stainless steel fixed bed retort. Four hundred grams of oil shale sample was electrically heated in 800 cm³ volume cylindrical retort. Reactor and furnace temperatures were controlled to obtain

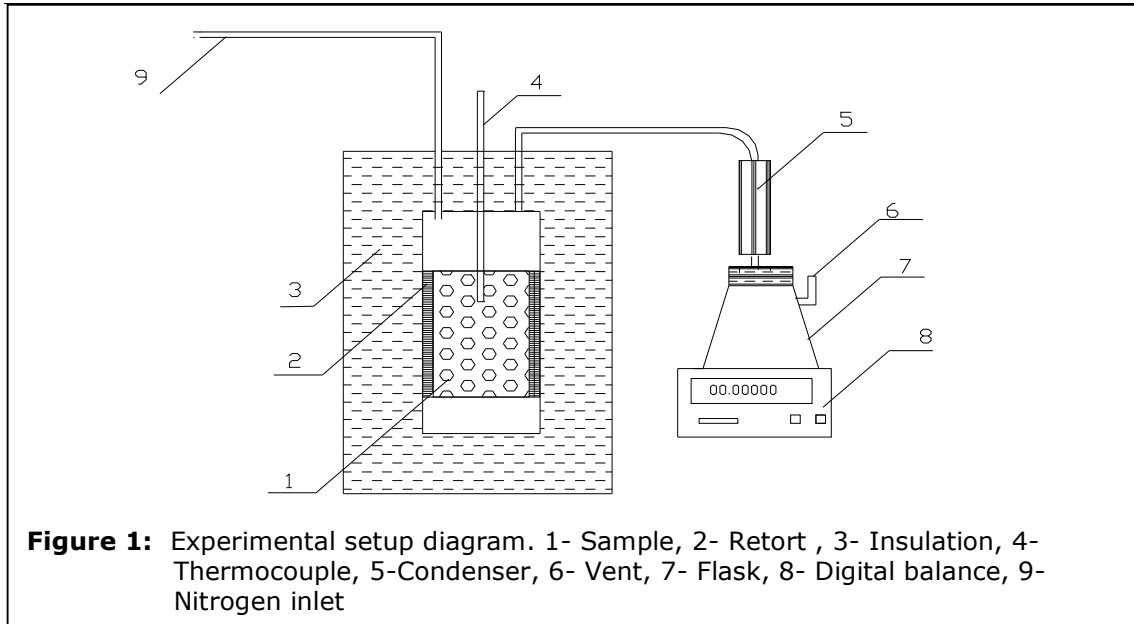
the desired retorting temperature. A Type K thermocouple was inserted from the top side of the retort to the midpoint of the oil shale sample for monitoring purposes, whereas another thermocouple was situated between the external body of the retort and the inner side of the ceramic cylinder for controlling the retort temperature. The retort was heated at 1-2 °Cmin⁻¹ rate in all runs. Sweep gas was introduced from the top of the retort at 50 cm³ min⁻¹ through an 8 mm pipe for preheating while passing downward to the bottom of the retort, and then allowed to sweep the generated products toward the retort topside outlet. Oven temperature was controlled and monitored by a digital temperature controller indicated as oven T°C in Figure 1.

The circulating coolant was maintained at 2 ± 2 °C to condense the liquid hydrocarbons and water transported from the reaction zone by nitrogen gas. Condensable hydrocarbons and water are collected while the uncondensable light organic compounds and other non-condensable gases were vented to the atmosphere. The weight of the condensed liquid shale oil and water were recorded continuously as a function of time and retort temperature as the digital balance indicated 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 total weight loss measurement.

3. Results and Discussion

3.1 Total Weight Lost Percent

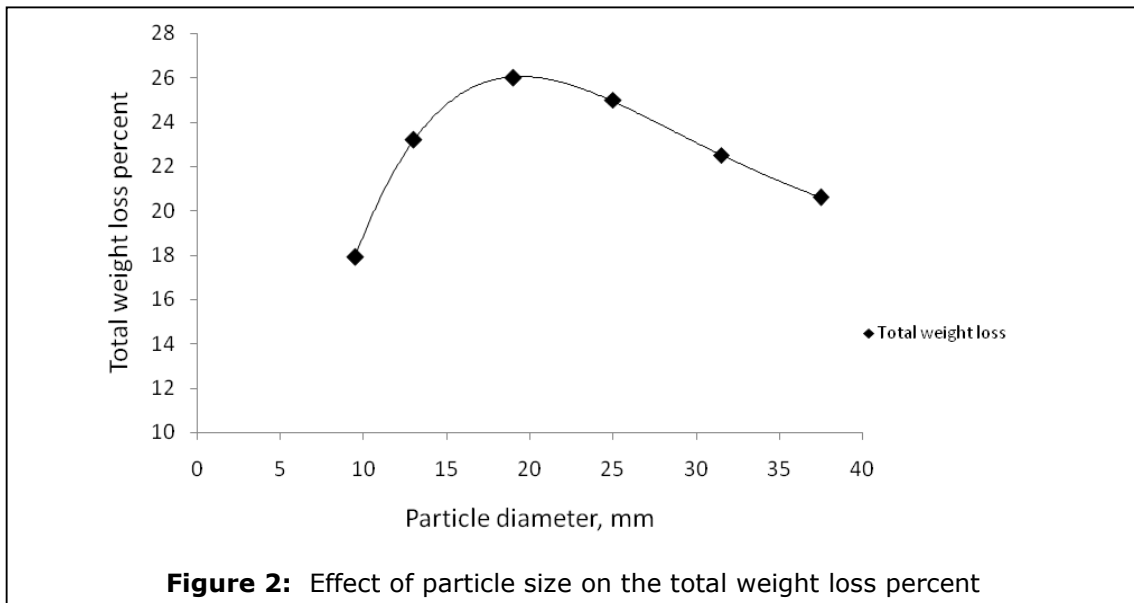
Several workers (Jaber, et al. 1999; Al-Ayed, 2005) have studied the effect of particle size on total weight loss in general and samples from Ellajjun oil shale in particular. The total weight loss of the sample is normally measured as the weight difference between the fresh sample and the sample after pyrolysis divided by the original weight of the sample. In the present work, the reaction temperature was kept in all runs as high as 550°C with constant heating rate.



The weight loss of the sample encompasses the losses of moisture, volatiles, structural water in all its forms, and hydrocarbon evolution during reaction. At the selected experimental temperatures it is important here to rule out the possibility of carbonate (dolomite and calcite) decomposition, as these reactions initiate at temperatures higher than 650°C and terminate at 810°C. The experiments determined the effect of particle size on the total weight loss, the weight of water and liquid accumulated during the run and the gaseous weight loss, which is calculated by weight difference.

As depicted in Figure 2, the total weight loss of the samples show a maximum value with increasing particle size. It can be seen from figure 2; that increasing the particle diameter from 9.5mm to 19mm increases the total weight loss of sample from 18% to about 26%. This increase is attributed to the secondary reaction rates increasing with increasing particle size, which produces more char and gaseous hydrocarbons due to cracking reactions that are taking place in the pores of the oil shale.

It is possible that at this value of diameter, the time required for the bulk of



molecules to travel from the reaction sites to the external surface area of the particle is optimized within the domain of the reaction time in the retort.

A further increase of particle size from 19mm to 38mm affects both primary and secondary reactions; the result appears to be a decrease in the product diffusion from the inner parts of the oil shale particles to the external surface. The process of products travelling to the external surface of the reacting particles is tortuous and time consuming and hence leads to a decrease in the total weight loss as products are apparently trapped in the particle. This observed decrease in weight loss from 26% to about 21% as the particle size increased from 19mm to 38mm is also accompanied by a decrease in the gaseous weight loss as indicated in Figure 3.

3.2 Water and Oil Weight Loss Percent

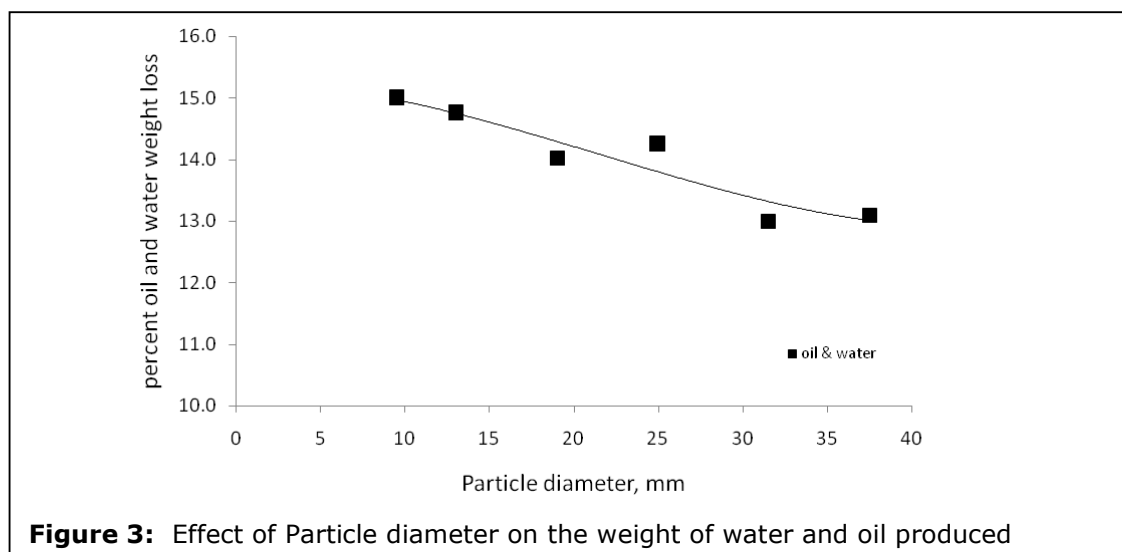
As indicated in figure 3, the combined weight loss of water and liquid oil decreases from 15% to almost 14% for particles size increase from 9.5mm to 19mm. This decrease is not appreciable as it lies within the experimental error. In other words, the decrease in the amount of oil and water does not give a clear indication of a decreasing trend. Here, it can be surmised that the

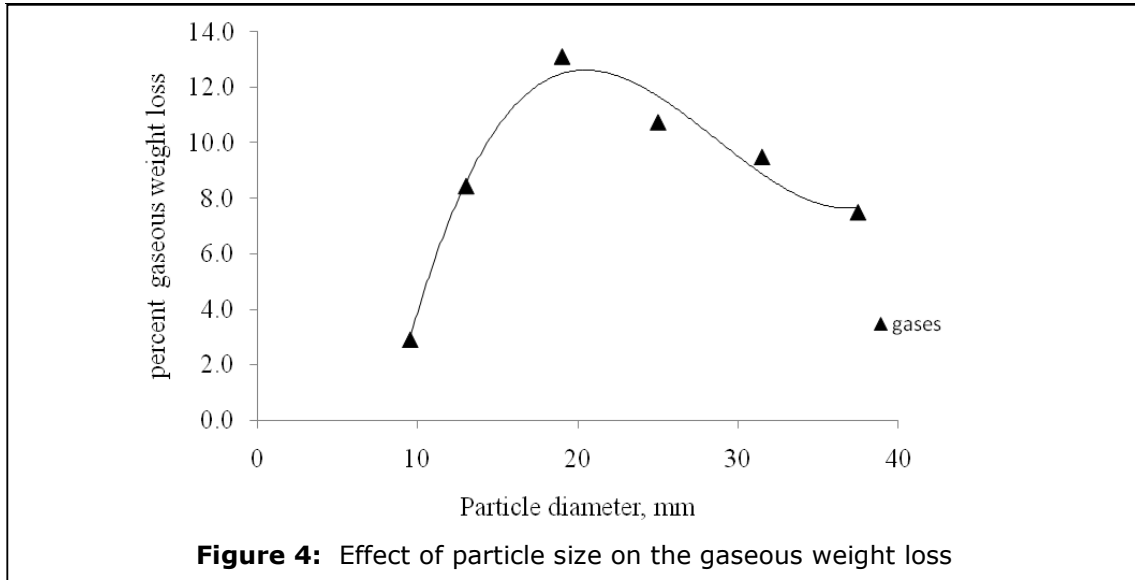
increase in total weight loss for the same range of particle size as shown in figure 2 is due to the increase in gaseous production although the total weight loss percent is increased.

For this particle size range, i.e. 9.5mm to 19 mm, the increase in total weight loss is due to an increase in cracking reactions and it could be due to exothermic heat of reaction for certain reactions inside the particle. The increase in the reaction temperature inside the particle due to the exothermic heat of reactions lead to the observed increase in weight loss of gases. On the other hand, the decrease in combined weight loss of both liquids for particle size 19mm to 38mm is 13%. Overall, it can be said that the amount of water and liquid hydrocarbon collected during runs is almost constant since the decrease is within 2%.

3.3 Gaseous Weight Loss

The weight loss of gases has been calculated by difference. It can be seen from figure 4 that the weight loss of gases increased from 3% to 13% as the particle diameter increased from 9.5mm to 19mm. This increasing trend can be attributed to the secondary reactions of further cracking of kerogen hydrocarbon that evolved due to the thermal effects.





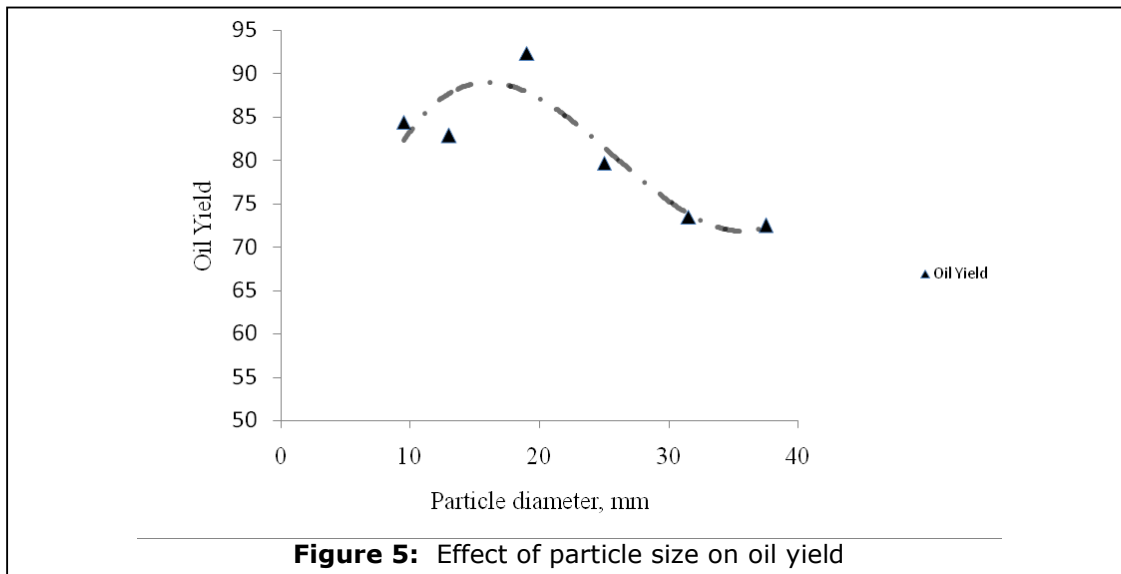
This explanation is supported by the trends of the earlier figures of total weight loss and oil & water losses in which total weight loss increased whereas liquid losses decreased slightly. It can be inferred from the curves of figures 2 and 3 that the increase in gaseous weight loss is a result of cracking reactions due to the diffusional resistance to the produced liquid hydrocarbons. On the other hand, increasing the particle size from 19mm to 38mm decreased the weight loss of gases from 13% to 8%. This decrease is a result of increasing the diffusional resistance to the formed products which require more time to diffuse to the external surface of the oil shale

particle.

3.4 Oil Yield

Oil yield is measured with respect to the amount of oil that can be destructively distilled by Fischer Assay. Standard Fischer Assay indicated that 16% of the sample is oil. As a result of that, the oil yield is calculated relative to the 16% oil content.

The effect of increasing particle size on oil yield is shown in figure 5. It is quite clear that there was an initial increase in the oil yield from 82% at particle size 9.5mm to a maximum value of 88% at particle size of 19mm, whereas a further increase in the particle size resulted in a



drop in oil yield. As particle size increased from 19mm to 37.5mm, the amount of oil released decreased. Increasing the particle size leads to increasing diffusional resistance and hence reduction in percent of kerogen decomposition. The decrease in oil yield was approximately 15% as the particle diameter was increased from 19mm to 37.5mm.

3.5 Distillation of Shale Oil

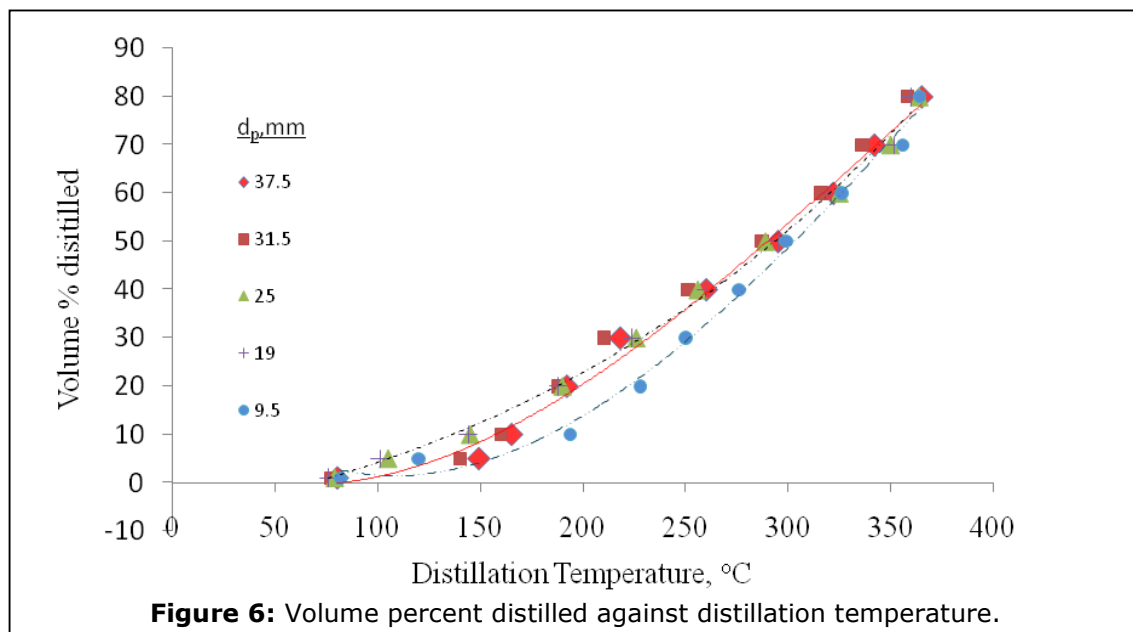
The generated liquids of water and hydrocarbons during pyrolysis were separated into water and liquid shale oil. Sufficient amount of the petroleum liquid was sent for simple atmospheric distillation in the laboratories of Jordan Petroleum Refinery. The data obtained from the distillation are plotted on different graphs. The distillation data has been depicted as curves of volume percent distilled versus distillation temperature. These curves give information about the boiling range of the oil fraction, which will be compared with cuts of crude oil distillation.

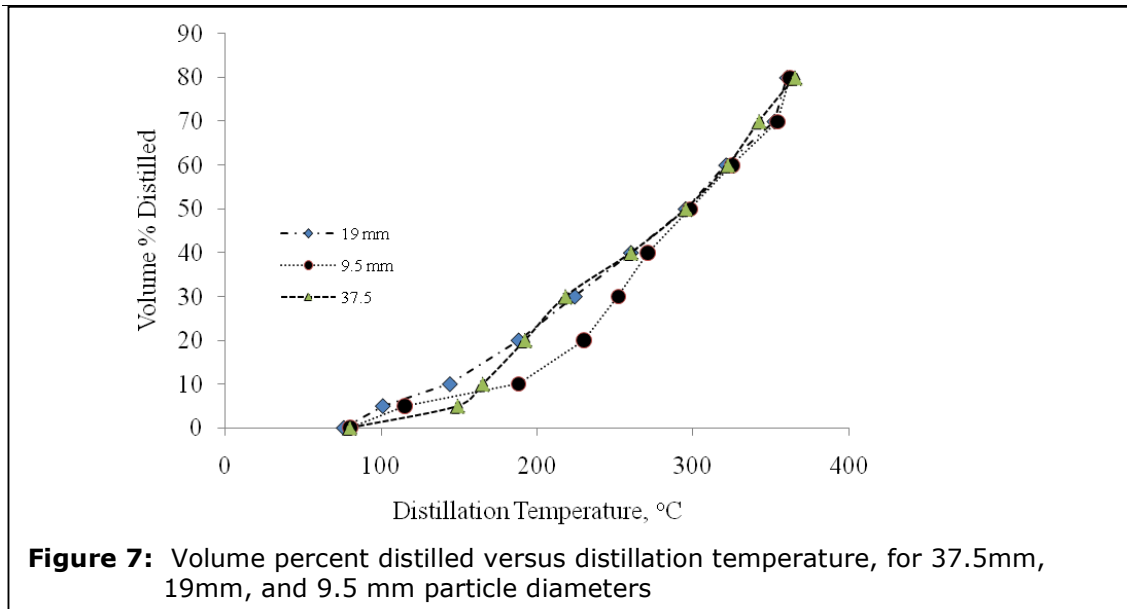
Figure 6 presents the volume percent distilled against distillation temperature for different particle sizes used in this research work. The percent recovery of all runs has been estimated through the distillation data and found to be 87% or slightly less. The residual fraction of the distillation process which boils at

temperature higher than 370 degree centigrade was found to be 13%.

It is clear from Figure 6 that small particle sizes such as 9.5mm have resulted in lower volume percent up to 70% volume distilled compared with larger particle sizes such as 31.5mm and 37.5mm for the same distillation temperature. This difference is attributed to the absence of diffusional influences in small size particles whereas strong diffusion resistance is present in particle sizes larger than 31.5mm. An intermediate behavior for 25 mm particle size further supports the suggested explanation.

In order to demonstrate the effect of diffusion in enhancing the opportunity for occurrence of secondary reactions, Figure 7 has been plotted for largest and smallest particle sizes used in this work. As an example to further show the effect of diffusion on the lighter hydrocarbon formation, we consider 190°C distillation temperature. As it can be seen in Figure 7 below, the larger size produced 20% volume of liquid hydrocarbons which boils below 190°C whereas pyrolysis of small oil shale particles resulted in 10% volume for same distillation temperature. This increase in volume percent distilled is likely a result of diffusional influences on products delaying exit to the external surface of the particle and the subse-





quent induced secondary cracking reactions.

The different cuts obtained during crude oil fractionation are shown in Table 1. The volume percent distilled versus distillation temperature curve assists in determining the corresponding fractional percent of each cut.

Simple calculations show that 37.5 mm particle size has resulted in 4% volume distilled as naphtha and gasoline fraction, whereas the smallest particle size (9.5mm) produced 8% volume distilled naphtha and gasoline fraction. The amount of kerosene produced during pyrolysis of large particle size was found to be 34% volume distilled whereas 22% volume distilled was reported for smallest size used. Diesel fraction has been found to constitute 42% volume distilled for largest particle size employed in this work whereas 50% volume distilled was reported for smallest particle size. These

results are summarized in Table 1. It is evident that the product from the larger particles reflects the additional reaction of the heavier hydrocarbons, producing a lighter oil.

3.6 Density Measurement

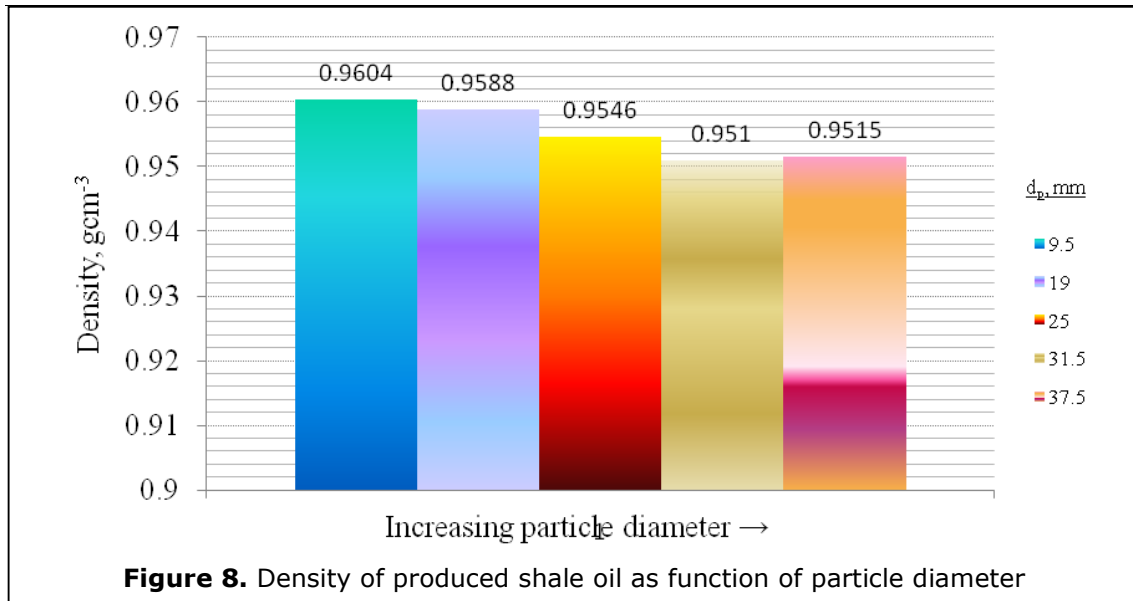
Density of liquid hydrocarbon is indicative of lightness and heaviness of its hydrocarbon content. As can be seen from figure 8 below, the increasing particle size results in decreasing oil density. Here, it can be said that this decrease in density augments the earlier suggested explanation of diffusional influences on the nature and type of hydrocarbon that has been generated or reformed.

3.7 Sulfur Results

The sulfur content of the samples has been determined in Jordan Petroleum Refinery laboratories using x-ray fluorescence. Sulfur content of the generated

Table 1: Crude oil fractionation

| Fraction | Temperature Range, °C | 9.5 mm fraction | 37.5 mm fraction |
|----------------------|-----------------------|-----------------|------------------|
| Naphtha and Gasoline | 0 – 140 | 8% | 4% |
| Kerosene | 140 – 250 | 22% | 34% |
| Diesel | 250 – 370 | 50% | 42% |
| Residual | >370 | 20% | 20% |



shale oil is determined and the results are depicted in Figure 9. It is quite clear from the figure that increasing the particle size up to 19 mm increases the sulfur content of the oil. This increase is associated with the nature of hydrocarbon generated. In this range of particle size, where the diffusional resistance is not predominant, the hydrocarbon compounds bearing sulfur are released from kerogen without further cracking. This could explain the increase in the weight percent of sulfur in the liquid shale oil as has been found in earlier studies (Dogan and Uysel, 1996). The decrease in sulfur content at larger particle sizes might reflect selective retention of the sulfur compounds in the particles due to diffusional resistance.

4. Conclusion

The results of this study indicate that changes in particle size do not necessarily result in a unidirectional change in the mass losses and oil properties of oil shale. The combined liquid loss (oil + water) decreases monotonically as particle size increases, and the product density appears to do the same (although the data show a slight increase in density at the largest particle size). However, the gas loss first increases then decreases with increasing particle size. The oil yield and sulfur content of the oil show similar patterns. The composition of the product oil changes with increasing parti-

cle size, showing decreases in the light naphtha/gasoline and heavier diesel fractions and an increase in the mid-range kerosene fraction.

These results are interpreted as due to the effects of increasing time for diffusion of products out of the particle. Increasing from small- to medium-sized particles increases the reaction time for reaction products, making more gas oil, and less total liquid product, but also releasing more sulfur into the product. Further increase in grain size appears to result in trapping of the gaseous products in the particle, reducing the gas and oil and further reducing total liquid yields, but reducing the sulfur content as well.

The liquid fractions show the effects of both the diffusion-increased reaction time and the diffusion resistance trapping of products across the range of particle sizes. Lower naphtha/gasoline fraction may be due to reaction to non-condensable gases, whereas the lower diesel fraction may be due to the heavier compounds being trapped in the larger particles.

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