

Sweeping Gases Influence on Liquid Product and Sulfur of Oil Shale

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ABSTRACT

Oil Shale samples from Ellajun Area were pyrolysed in different pyrolysing environments. Nitrogen, steam, mixture of steam and nitrogen, and mixture of hydrogen and steam used as sweeping mediums. The experimental conditions were, 500 gram of sample weight, one atmospheric operating pressure, and 410 to 550°C temperature range. Total weight loss of samples recorded as function of temperature. Condensed liquid products distilled in a simple distillation. Un-condensable gases vented without analysis.

The total weight loss of sample increased with increasing retorting temperature, and the oil yield passed through a maximum value with total weight loss and increasing temperature. The distillation results showed a clear impact of the reaction environment on the percent volume distilled and the sulfur content of the liquid fraction.

Key Words: Sweep gas, Pyrolysis, Distillation, Sulfur, Oil Shale.

INTRODUCTION

Several researchers have studied the effect of sweep gas earlier. Ekinici et al. (1995) investigated the influences of steam and nitrogen sweep gases in a fixed bed reactor on the oil yield and product distribution. They reported an increase in oil yield and higher concentration of n-alkane and increase in aromatic character of the non-paraffinic product materials. Hershkowitz et al. (1983) have reported 20% increase in kerogen conversion when hydrogen is used as pyrolysis atmosphere in their study of Colorado oil shale; in addition, they reported 90% organic carbon conversion in 823-873K temperature range. Eastman and Schlinger, Texaco researchers, (1964) obtained 126% (vol. %) oil yield of Fischer assay when they used high hydrogen pressure during pyrolysis. El-hafi et al. (1999) reported a 33% increase in oil yield when oil shale was pyrolysed in steam environment compared to nitrogenous atmosphere. The decomposition reactions, which occur during pyrolysis of oil shale are breaking of the least stable bonds within structure such as methylene, oxygen and sulfur-bridges between the aromatic building blocks. Free radical formation due to decomposition reactions insight secondary reactions in presence of hydrogen or steam results in different produce component structure. El harfi et al. (2000) have studied the effect of steam on product distribution of oil shale pyrolysis. They found that oil yield increases with

addition of steam to nitrogen sweeping gas. Similar findings were reported by Carter and Taulbee (1985). Earlier works of Al-Ayed (2006) showed a profound effect of sweeping gases on the total weight loss; oil yield, product composition and liquid oil sulfur content.

EXPERIMENTAL

Oil shale samples from Ellajjun area southern region of Jordan were studied and investigated in this work. The original oil shale specimens, were ground in a ball mill, and sieved to the particle size 0.5 - 2.1 mm. The size selection based on diffusional influences and mass transfer studies.

All experiments were conducted in a stainless steel fixed bed retort. Five hundred gram 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. The type K thermocouple inserted from the top side of the retort to the middle point of the oil shale sample for monitoring purposing, 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 introduced at the top of the retort for preheating while passing downward to the bottom of the retort, and then allowed to disperse to sweep the generated products toward the retort topside outlet. Oven temperature was controlled and monitored by thermocouples as indicated in figure 1. The pyrolysis runs were conducted in 410 to 550°C temperature range.

The generated hydrocarbon driven by the virtue of the sweep gas to pass through glass condenser. The circulating coolant is maintained at 2 °C ± 2 to condense the liquid hydrocarbons that are condensable while the light organic and non-organic gases were vented to atmosphere. At the end of each run, the retort emptied and the spent shale weighed for total weight loss oil and oil yield measurements.

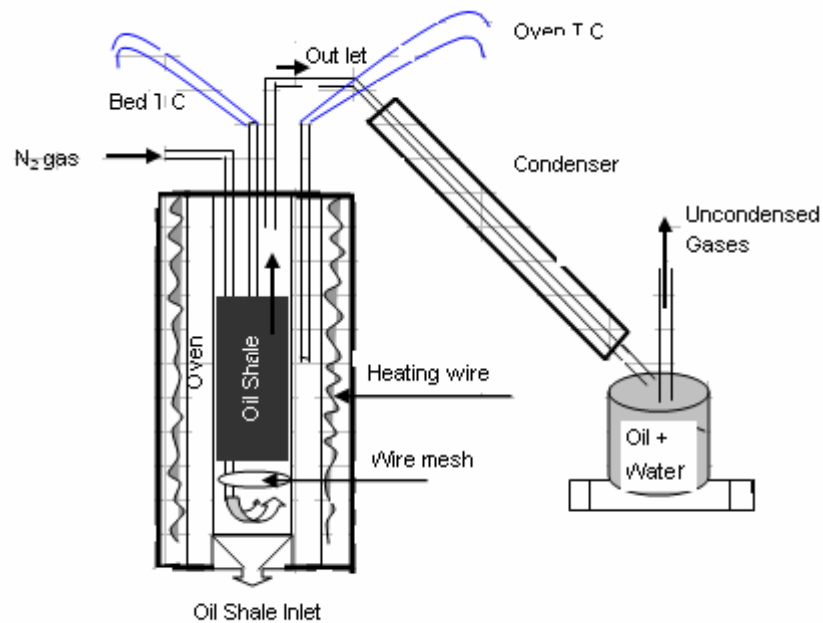


Figure (1) Experimental Setup

In order to fractionate shale oil in a simple atmospheric distillation apparatus, a 500 cm³ were needed for each retorting temperature. The required quantities of oil for distillation were collected at selected temperatures. In nitrogen-steam runs, the nitrogen gas was bubbled

in distilled water for saturation and allowed into the reaction zone after preheating while hydrogen runs were allowed without bubbling in water. Steam runs, were conducted by allowing vaporized pure water into the bottom of the reactor. The volume of the condensed hydrocarbon and water were measured, separated and shale oil sent to simple atmospheric distillation .

RESULTS AND DISCUSSION

In this research work, the influence of several parameters such as temperature, reaction environment on total weight loss, oil yield, and fractions distilled and sulfur content of the produced oil shale have been investigated.

Weight Loss Measurement

The total weight loss of oil shale specimens was measured as function of pyrolysis temperature. The experimental conditions selected were normal atmospheric pressure and 410 - 550°C temperature range. All experimental runs were conducted in presence of different pyrolysing environments. Each run was conducted for several hours where the final reaction temperature is maintained at the desired level for at least 2 hours. Several runs were conducted at each temperature to achieve reproducibility of data for weight loss measurement and to collect the required amount of shale oil volume required for simple atmospheric distillation.

Typical results of weight loss versus kerogen reaction temperature are shown in figure 2. As it can be seen from the figure, that, the total sample weight loss increases as the pyrolysis temperature is increased in the specified temperature range. It is quite clear that the total weight loss of oil shale increases with increasing temperature. This total weight loss encompasses losses of intermolecular water, vaporization of volatile matter and hydrocarbon evolution. The decomposition of both calcium and magnesium carbonates do not contribute to the total weight loss below 550°C. The total weight loss curve shown in figure depicts the impact of different sweeping gases on the total weight percentage loss of oil shale sample. In addition, it can be observed, that the increase in weight loss percentage is higher for sweeping mixtures rather than a single component at the same reaction temperature; this might be ascribed to the secondary reactions due to free radical formation.

The impact of secondary reactions is reflected on the liquid product. Furthermore, upon distillation, the Initial Boiling Point (IBP) of the liquid shale oil produced is lower in case of mixtures sweeping gas than that of single component sweeping medium. This is an indication of lighter hydrocarbon production due to the secondary reactions that are augmented in presence of water vapor. Reaction of water with carbon element or the carbon that deposited from cracking reactions, the catalyzing effect of the several mineral components of the oil shale; these factors collectively resulted in an increase in the total weight loss and production of lighter hydrocarbons.

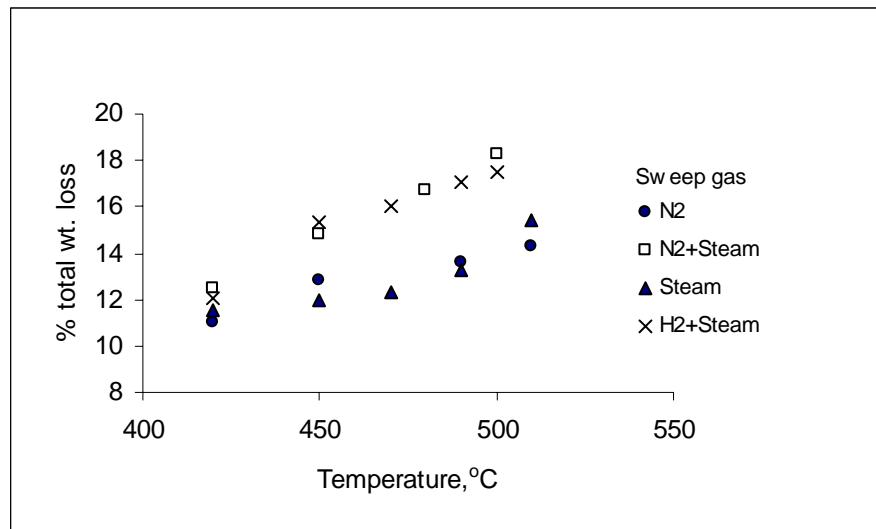


Figure (2) Temperature effect on weight percentage loss for different sweeping mediums

Oil Yield Measurement

Oil yield calculations are based on Fischer Assay measurement. According to tests performed in the Laboratories of Natural Resources Authority, Jordan, the oil content of the studied samples was measured to be 14%. Figure 3 shows the oil yield as function of retorting temperature for different sweeping gases.

It can be seen from the figure that oil yield increases initially with increasing pyrolysis temperature, passes through a maximum and then decreased. These findings are in agreement with the results of El-hafie et.al (2000). The maximum oil yield is not associated with a single retorting temperature but vary slightly with sweeping gas and temperature. Furthermore, the single component sweeping gases gave higher oil yield compared to mixture sweeping gases for same reaction temperature. It is worth noting here, that mixture-sweeping gases resulted in higher percentage total weight loss and lower oil yield compared with single component sweeping gas. This behavior is attributed to the presence of water or hydrogen and its direct effect on the reacting components or its role in gasification and secondary reactions that are taking place during pyrolysis. Dung et. al (1986) and Dung (1990) had reported independent oil yield of temperature for both steam and nitrogen.

On the other hand, the relationship between the total weight percentage loss and the oil yield is interesting. The weight loss percentage effect on the oil yield is shown in the figure 4. In general, It is quite clear, that higher the total weight loss percent, lower is the oil yield. A single component sweeping gas gave higher oil yield than multi-component system. From the figure, it can be seen that, nitrogen-sweeping gas resulted in low total weight loss percent but highest oil yield although, steam suppressed kerogen decomposition to produces liquid oil and resulted in the lowest weight loss percent.

Steam as pure component and its probable activity at such low reaction temperature favoring gasification resulted in lower oil yield compared with nitrogen single component sweep gas.

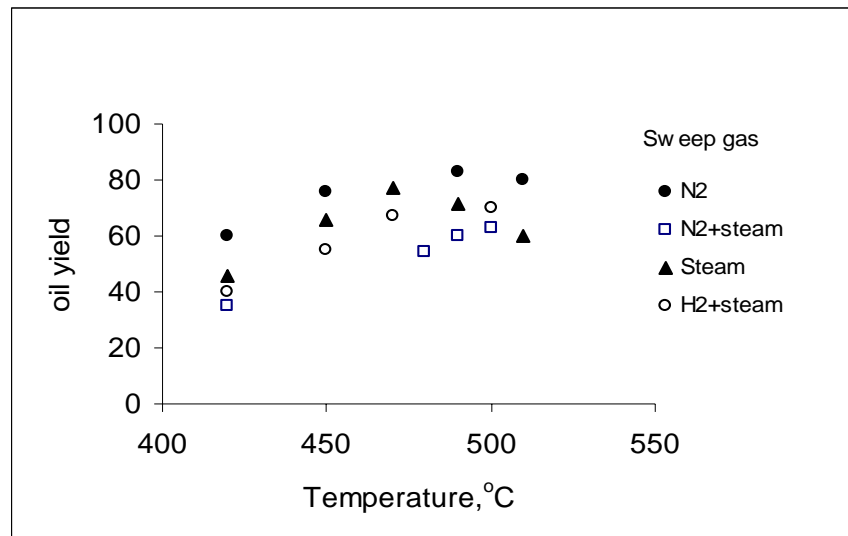
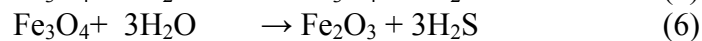
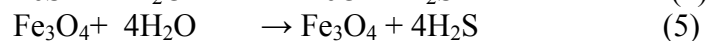
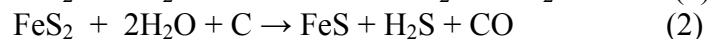


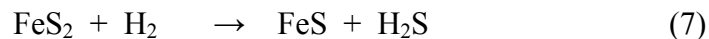
Figure (3) Temperature effect on oil yield for different sweeping gases

It is interesting to note that hydrogen-steam sweeping medium, gave more of total weight loss percent and higher oil yield compared with nitrogen-steam sweeping gas. The presence of both steam and hydrogen components at temperatures higher than 400 °C enhances some of possible the reactions:

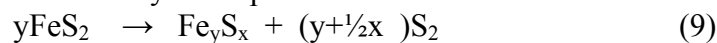
a) Steam reactions:



b) Hydrogen reactions:



c) Decomposition of Pyrite to produce elemental sulfur:



These reactions act on the sulfur of the Pyrite and Pyrrhotites of the oil shale resulting in more of sulfur leaching. The formation of hydrogen sulfide through different chemical reactions as suggested in steam reactions (1) to (6) lead to both increase in the total weight loss of sample and an increase in the sulfur content of the produced shale oil. This explanation commensurate with the experimental results indicated in figure 4. The presence of hydrogen where reactions (7) and (8) take place in addition to steam reactions enhances further the total weight loss and increase the sulfur content of shale oil and the oil yield which is quite clear in figure 4. Further more, the oil yield decreased due to formation of gaseous hydrocarbons as a result of hydrogenation reactions that might take place and the production of hydrogen sulfide, carbon dioxide and sulfur dioxide formation. The hydrogenation reactions could lead to carbon deposition due to coking reactions. These results emphasize the important role of steam during reactions. In nitrogen runs, the oil yield is highest compared with other sweep gases, while the

corresponding weight loss is more than steam only; this is ascribed to the nature of chemical reactions that are taking place. Thermal cracking reactions are dominating in nitrogen runs, while hydrogenation and steam reforming reactions are more liable to occur in presence of mixtures alleviating the impact of thermal cracking. The results shown in figure 6 support these suggestions.

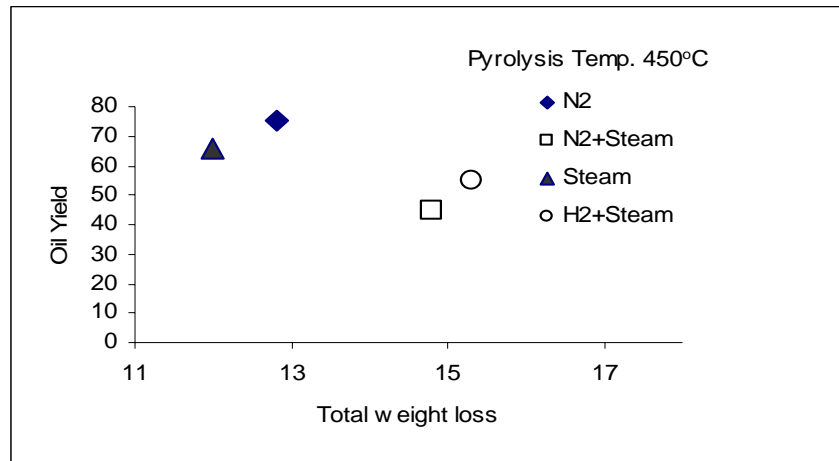


Figure (4) Relationship between the total weight loss and oil yield

SHALE OIL DISTILLATION

The produced shale oil was distilled in simple distillation computerized unit. Figure 5 depicts the fractionation of the generated shale oil samples at different sweeping gases. It should be noted here, that hydrogen-steam sweeping gas shale oil sample is not presented in the curve since no data available at 490°C. As shown in the figure, more volume percent distilled are produced for same distillation temperature in case of nitrogen sweeping gas runs compared with steam sweeping.

As indicated in figure 4, the total weight loss of sample was less for steam sweeping mixture case compared with other types of sweeping gases. On the other hand, the volume percent distilled of the shale oil produced under the influence of nitrogen-steam mixture lies in intermediate stage between the two cases of pure components. According to the results of distillation, the residue which is characterized by components that boils at higher than 370°C, varies according to the sweeping gas; for example, nitrogen and nitrogen-steam sweeping mediums gave 6% as residue, while steam produced 25 – 30 % residue. Steam-hydrogen runs also resulted in similar trend as steam sweeping gas although not depicted here in the curve since 490°C data are not available.

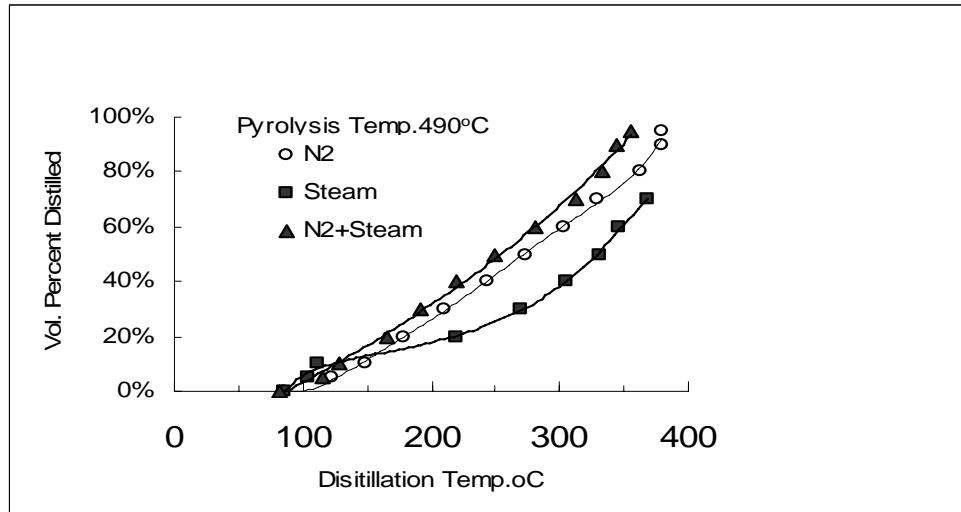


Figure (5) Simple atmospheric distillation of produced shale oils

The boiling ranges of the main fractions produced during crude oil topping process are presented in table I.

Table I: Crude oil fractions with boiling range.

Gasoline and Naphtha	0 - 140°C
Kerosene	140 - 250°C
Diesel	250 - 370°C
Residue	> 370°C

The results of simple atmospheric distillation and the impact of sweeping gas on the main fractions of the fractionation process are depicted in the column chart 5 below. It is clear from the figure that the hydrogen sweeping gas altered the volume percent distilled for kerosene, diesel and residue. Secondary reactions are main sources of changing the composition of the produced oil. As it can be seen, the main shift is the conversion of components that constituting the diesel fraction to form kerosene range components and residue. The decrease in diesel quantity is estimated to be 50% of that produced in nitrogen runs.

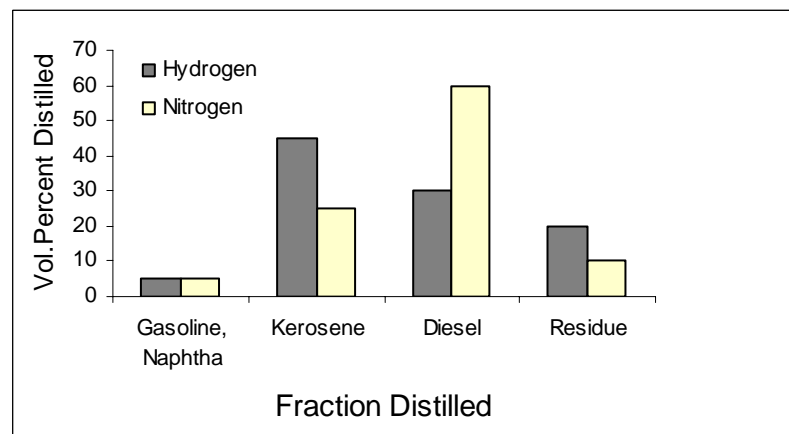


Figure (6) Effect of sweeping medium on shale oil fractions

SULFUR CONTENT

X-ray Fluorescence used to estimate the sulfur content of the produced shale oil. The sulfur analysis carried out on the liquid fraction of the produced oil shale. The impact of sweeping gas on the sulfur content of produced oil is shown in figure 7 below. As it can be seen that the weight percent of sulfur in the liquid shale oil is higher with relatively active components of the sweep gas such as water vapor and hydrogen gas. The highest percent sulfur, which is close to 9%, was associated with steam and hydrogen mixture sweeping medium.

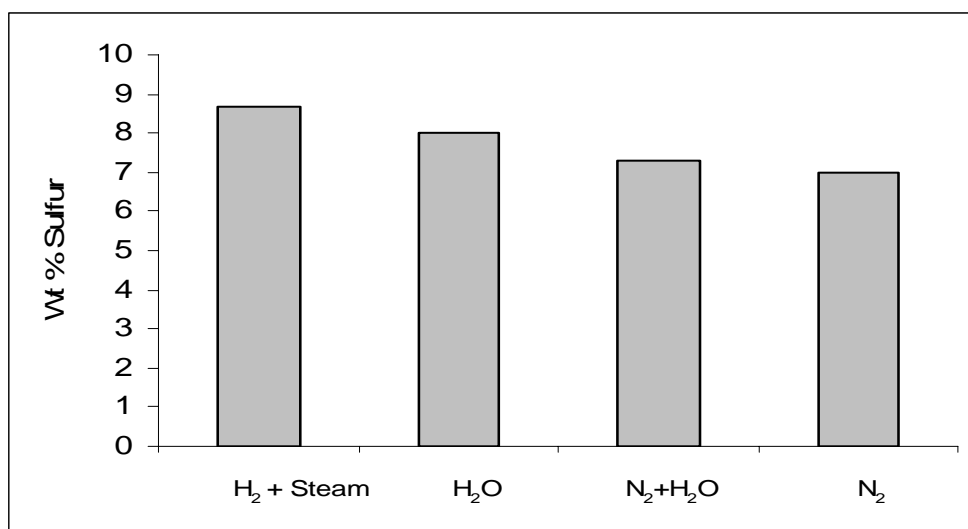


Figure7 Effect of sweeping gas on the sulfur content of shale oil.

As it can be seen from the figure, that the sweeping medium has a profound effect on the percent sulfur found in the produced shale oil. It can be surmised here, that the reactive medium such as hydrogen and/or steam plays a significant role during pyrolysis. This role, through oil shale chemical reactions with the sweeping medium and the catalyzing effect of the mineral matter, results in leaching more of sulfur content of the oil shale with the shale oil. In order to obtain more concrete analysis on sulfur, spent shale and gaseous analysis must be performed to obtain an over whole picture of sulfur scenario.

CONCLUSIONS

The reaction environment during pyrolysis of oil shale has a significant effect on the liquid product distribution and its sulfur content. The total sample weight loss and the oil yield are affected by the sweeping medium. The type of sweep gas or sweeping mixture employed during pyrolysis influenced the percentages of fractions and the sulfur content. Hydrogen-steam mixture showed highest leaching ability for sulfur from kerogen, whereas pure nitrogen medium gave highest oil yield and lowest weight loss.

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