Oil Shale, 2013, Vol. 30, No. 2, pp. 136–146
doi: 10.3176/oil.2013.2.04
ISSN 0208-189X

OIL SHALE PYROLYSIS AND EFFECT OF PARTICLE SIZE ON THE COMPOSITION OF SHALE OIL

ADNAN M. KHALIL*

Al-Balqa Applied University
Faculty of Engineering Technology
Department of Chemical Engineering
4146 Amman 11953 Jordan

Abstract. *Samples of Ellajjun oil shale were pyrolysed under nitrogen environment to the final pyrolysis temperature of 550 °C. The particle size of the samples under study was varied from 10 to 40 mm. The effect of particle size on weight loss and oil yield was investigated at a constant heating rate of 2–3 °C/min. Increasing particle size from 10 to 40 mm decreased the total sample weight loss from 27 to 21% at the same final pyrolysis temperature. At the same time, gas weight loss decreased from 10 to 6%. Oil yield was found to decrease with increasing particle size in the studied range from 92 to 70%.*

The shale oil produced was distilled in a simple atmospheric distillation unit to give naphtha, gasoline, diesel and residue. The naphtha fraction was found to decrease with increasing particle size. The diesel fraction decreased by 8%, i.e. from 50 to 42%, when particle size was increased from 10 to 40 mm. The kerosine percentage decreased from 35 to 22% with increasing particle size.

Keywords: *oil shale, pyrolysis, particle size, retorting, shale oil.*

1. Introduction

Oil shale is a fine-grained sedimentary rock which contains an organic matter called kerogen and from which shale oil, a mixture of hydrocarbons, can be obtained upon heating. Oil shale is found worldwide [1]. In recent times, oil shale has been the focus of many investigators due to the increase of crude oil prices [2–6]. Studies of oil shale have been dealing with various factors that influence its pyrolysis. Some researchers [7, 9] used HPTG, TG/DG and DSC to study the pyrolysis kinetics of crude oil and oil shale under different conditions. Other investigators [10, 11] determined the kinetic parameters and studied the reaction mechanism in different condi-

* Corresponding author: e-mail *dr_adnan_khalil@hotmail.com*

tions. Reaction temperature, heating rate, mineral composition, hydrocarbon content and grain size are among the most important parameters 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 oil yield and weight loss. The size of oil shale particles has a direct impact on the nature of the decomposition reactions of kerogen. The cracking reactions due to thermal inertia and secondary type reactions, or reactions that are catalyzed by the mineral matter of the shale are affected by the particle size of the oil shale sample undergoing pyrolysis. Due to the complexity and compositional heterogeneity of oil shale resources, it is difficult to isolate and investigate the effect of each individual factor away from minor interferences of other factors. This nature of oil shale has contributed to the disagreement between the results obtained and conclusions made by several researchers. The effect of such factors as pyrolysis temperature, heating rate and particle size on total weight loss and oil yield has been addressed most thoroughly in oil shale pyrolysis kinetics studies.

Researches conducted on oil shale dealt with determining sample weight loss, oil yield, sulfur content and effect of heating rates. Recently, Bhargava et al. [12] reported the total weight loss of oil shale to be a function of temperature and it is attributed to the 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 since oil shale pyrolysis is accomplished below 550 °C. On the other hand, Allred [13] has reported that the process of oil evolution during oil shale pyrolysis is a sum of two separate steps. The first step involves degradation and the second is the evaporation of products. Braun and Rothman [14] reported the reaction temperature of 487 °C for decomposition of bitumen, which involves the breaking of relatively weak chemical bonds of kerogen, while higher temperature reactions involve the breaking of much stronger chemical bonds.

Physical changes such as softening and molecular rearrangement that are associated with the release of gases and structural water have also been reported [15] 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 [16] have found shale oil yield to increase with increasing particle size, while other researchers [17–20] reported a decrease in oil yield with increasing particle size. On the other hand, Dogan [21] and Drescher et al. [22] have reported independence of oil yield from particle size change.

In this research work, the effect of increasing particle size on weight loss, oil yield and product distribution will be investigated for Jordanian oil shale samples taken from Ellajjun area.

2. Experimental

The oil shale samples investigated in this work were obtained from Ellajjun area, which is located in the southern region of Jordan [24]. The original oil shale samples were ground in a ball mill and sieved to the selected particle size of 10 to 40 mm. The characteristics of the studied samples are presented in Table 1.

Table 1. Characteristics of Ellajjun oil shale samples

Characteristic	
Moisture content, wt%	1.21
Total water, wt%	2.5
Total oil, wt%	16.0
Gas loss, wt%	3.4
Spent shale, wt%	81.3
Calorific value, kJ/kg	5487

All experiments were conducted in a stainless steel fixed bed retort. A 400 g sample of oil shale was electrically heated in a 800 cm^3 cylindrical retort. The reactor and furnace temperatures were controlled to obtain the desired retorting temperature. A type K thermocouple was inserted from the top of the retort to the middle point of the oil shale sample for monitoring purposes, while 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 a 2–3 °C min^{-1} rate in all runs. Sweep gas at a rate of 50 cm^3 min^{-1} was introduced from the top of the retort in a 8 mm pipe for preheating while passing downward to the bottom of the retort, and was then allowed to sweep the generated products toward the retort topside outlet. The 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 0 ± 2 °C to condense the liquid hydrocarbons and water transported from the reaction zone by nitrogen gas. The condensable hydrocarbons and water were collected while noncondensable light organics and other noncondensable gases were vented to the atmosphere. The weights 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 was weighed for total weight loss measurement.

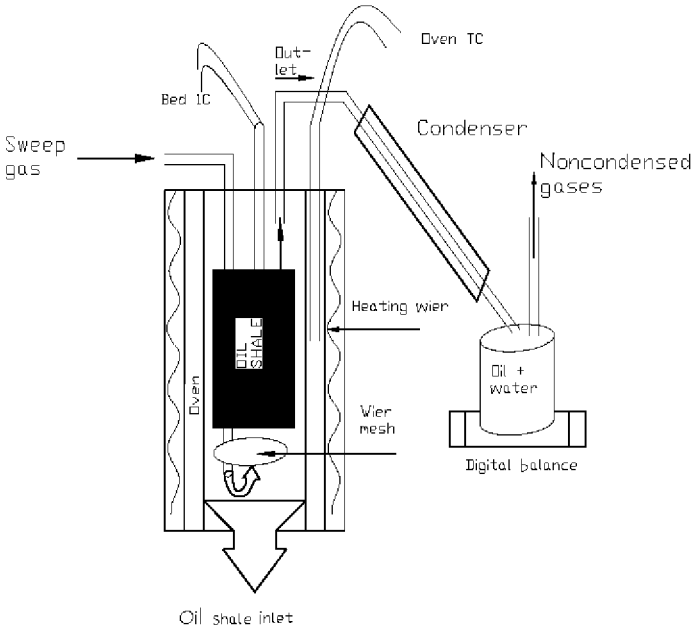

Fig. 1. Experimental setup diagram.

3. Results and discussion

3. 1. Total weight loss percent

Several investigators [5, 23] have studied the effect of particle size on total weight loss for different oil shale origins, including Ellajjun oil shale. The total weight loss of sample is normally measured as the weight difference between the fresh sample and sample after pyrolysis with respect to its original weight. In the present work, the final pyrolysis reaction temperature was kept at 550 °C in all runs. The oil shale weight loss of the sample encompasses the loss of moisture, volatiles, structural water in all its forms, and hydrocarbons evolution during the reaction under the selected experimental conditions. The effect of particle size on the total weight loss that includes the weight loss of water and liquid hydrocarbons (shale oil) during the run is depicted in Figure 2. The gas weight loss is calculated as the weight difference between total loss and that of the liquid collected and measured at the end of each run.

As shown in Figure 2, the total weight loss percent shows a maximum value with increasing particle size. The total weight loss of samples is calculated as indicated earlier and it accounts for the losses of moisture, volatiles, water associated clay, structural water and, finally, the hydrocarbons evolution. It can be seen from Figure 2 that increasing the particle size from 10 to 20 mm increases the total weight loss of sample from 18 to about 26%. This increase is attributed to the increase of the rate of secondary

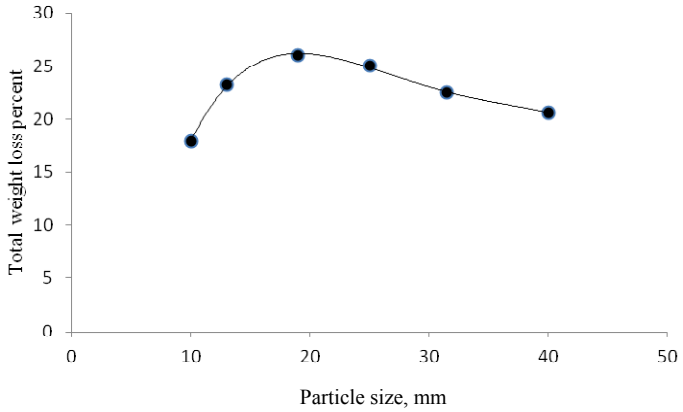

Fig. 2. Effect of particle size on total weight loss percent.

reactions with increasing particle size, which produces more char and gaseous hydrocarbons due to cracking reactions that are taking place in the pores of oil shale. It is possible that at this value of particle size, the time required for bulk of molecules to travel from the reaction sites to the external surface area of the particle is acceptable within the domain of the reaction time in the retort. A further increase of particle size from 20 to 40 mm affects both primary and secondary reaction types. This influences the product diffusion from the inner parts of oil shale particles to the external surface. The process of products travel to the external surface of the reacting particles is tortuous and time-consuming and hence leads to a further decrease in the total weight loss. This decrease in weight loss from 26 to about 21% as the particle size increased from 20 to 40 mm is also accompanied by a decrease in the gas weight loss as indicated in Figure 4.

3. 2. Water and shale oil weight loss percent

As indicated in Figure 3, the combined weight loss of water and liquid oil has decreased from 15 to almost 14% with particle size increasing from 10 to 20 mm. This decrease is not appreciable since it lies within the experimental error. In other words, the decrease in the amount of oil and water is not supportive to give a clear indication of the decreasing trend. Here, it can be surmised that the increase in total weight loss for the same range of particle sizes as shown in Figure 2 is due to the increase in gases production although the total weight loss percent is increased. For this particle size range, i.e. 10 to 20 mm, the increase in total weight loss is due to an increase in cracking reactions and it could be due to the 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 leads to the observed increase in the weight loss of gases. On the other hand, the decrease in the combined weight loss of both liquids for particle sizes of 20 to 40 mm is 13%. Overall, it can be said that the amount of water and liquid

hydrocarbons collected during runs is almost constant since the decrease is within 2%.

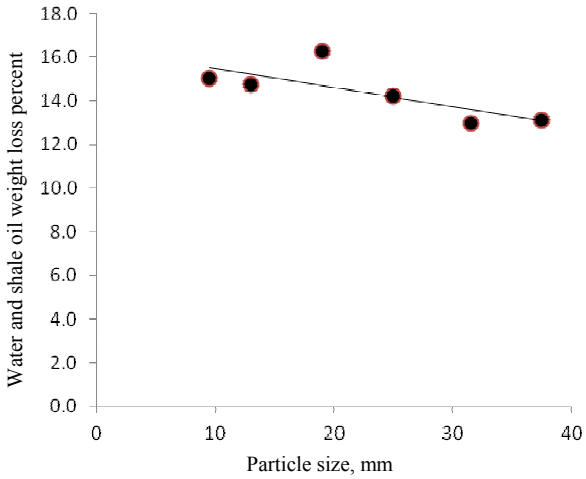

Fig. 3. Effect of particle size on the weight of shale oil and water produced.

3.3. Gas weight loss percent

The weight loss of gases is calculated as the difference between total weight loss and that of accumulated shale oil and water at the end of each run. It can be seen from Figure 4 that the weight loss of gases increased from 3 to 13% with increasing particle size from 10 to 20 mm. This increasing trend can be attributed to the secondary reactions of the further cracking of kerogen hydrocarbons that evolved due to the thermal effects. This explanation is supported by the trends illustrated in the above figures of total weight loss,

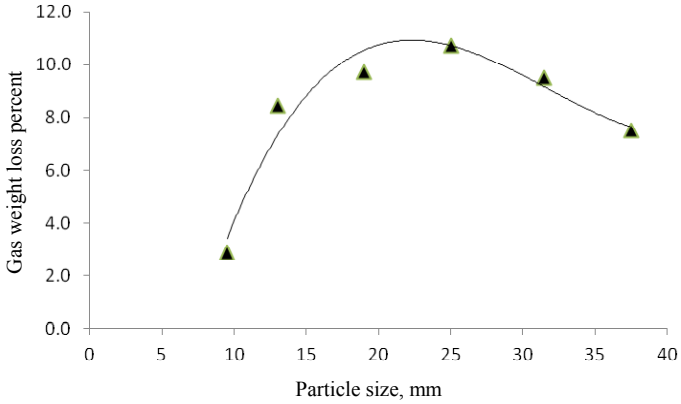

Fig. 4. Effect of particle size on gas weight loss.

and water and shale oil weight losses. From these figures it can be seen that total weight loss increased while that of liquids decreased slightly. It can be inferred from the curves in Figures 2 and 3 that the increase in gas weight loss is the result of cracking reactions due to the diffusional resistance to the liquid hydrocarbons produced. On the other hand, increasing the particle size from 20 to 40 mm decreased the weight loss of gases from 13 to 8%. This decrease is the 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 amount of oil that can be destructively distilled in Fischer Assay. A standard Fischer test indicated that 16% of the sample was shale oil. As a result, the oil yield in this work was calculated on the basis of the 16% sample oil content.

The effect of increasing particle size on oil yield is shown in Figure 5. It is quite clear that there is an initial increase in oil yield to a maximum value and a further increase in particle size results in a drop in oil yield. The oil yield increased from 82% at a particle size of 10 mm to 88% as maximum at a particle size of 20 mm. When the particle size is increased from 20 to 40 mm, the amount of oil released is decreased and this is reflected on the oil yield. Some investigators [5] studied the effect of Ellajjun oil shale particle size on oil yield and reported no change in oil yield and weight loss when particle size was increased up to 12 mm. At the same time, other researchers [23] reported an increase in oil yield with increasing particle size. Increasing the particle size leads to increasing diffusional resistance and hence reduction in the percentage of kerogen decomposition. The decrease in oil yield is proximate to 15% when the particle size is increased from 20 to 40 mm.

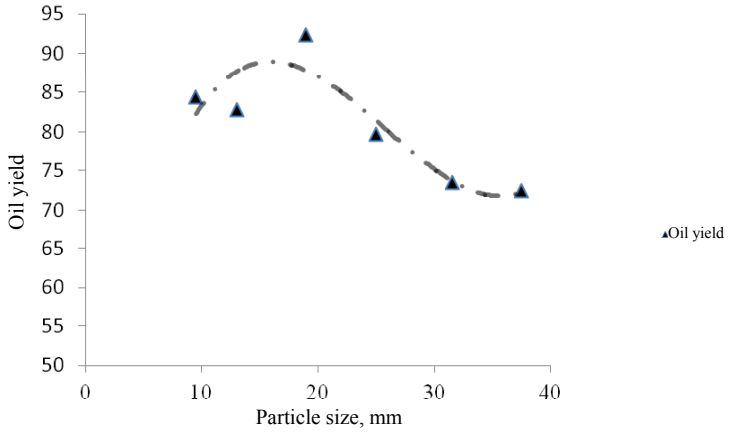

Fig. 5. Effect of particle size on oil yield.

3.5. Distillation of shale oil

The mixtures of water and liquid hydrocarbons generated during pyrolysis were separated into water and liquid shale oil. A sufficient amount of a petroleum-like liquid was sent for simple atmospheric distillation in Jordan Petroleum Refinery laboratories. The obtained data from the distillation has been plotted on different graphs. The distillation data has been depicted as curves of distilled volume percent 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.

According to the crude oil fractionation, the different cuts obtained are characterized in Table 2.

Table 2. Crude oil fractionation

Fraction	Temperature range, °C
Naphtha and gasoline	0–140
Kerosene	140–250
Diesel	250–370
Residual	> 370

The distilled volume percent versus distillation temperature curve assists in determining the corresponding fractional percent of each cut.

The distillation data has been plotted in different figures. Figure 6 presents the distilled volume percent against distillation temperature for different particle sizes.

In this research work, the effect of particle size and subsequent diffusional inflences on the nature of the produced organic compounds were investigated using a wide range of particle sizes, viz. 40, 31.5, 25.0, 20.0, 10.0 mm.

The percent recovery of all runs has been estimated through the distillation data and found to be 87% or slightly lower. The residual fraction

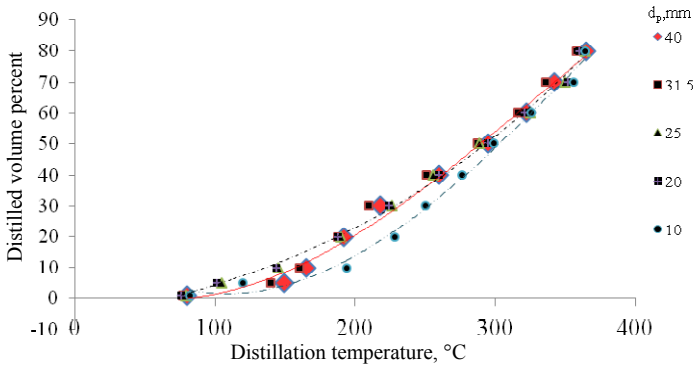

Fig. 6. Distilled volume percent against distillation temperature.

of the distillation process, which boils at a temperature higher than 370 °C, was found to be 13%.

It is clear from Figure 6 that at the same distillation temperature, small-sized particles, such as 10 mm, afforded lower distilled volume percent, up to 70%, compared with large-sized particles, such as 31.5 and 40 mm. This difference is attributed to the absence of diffusional influences in small-sized particles whereas a strong diffusion resistance is present in particles larger than 31.5 mm in size. An intermediate behavior was observed in case of 25 mm particles, which further supports the truthfulness of the suggested explanation. At the same distillation temperature, oil shale of larger particle size produced 20% liquid hydrocarbons which boil below 190 °C, whereas pyrolysis of oil shale of small particle size yielded 10%. This increase in distilled volume percent is with no doubt the result of diffusional influences on product exit to the external surface of the particle and subsequent induced secondary cracking reactions.

Simple calculations show that 9.5 mm particles afforded 8% distilled volume whereas larger, 37.5 mm particles produced 4% distilled volume of naphtha and gasoline fractions. During pyrolysis of oil shale of larger particle size, the distilled volume of the produced kerosene was 34%, while 22% was distilled during pyrolysis of oil shale of the smallest particle size. Upon pyrolysis of oil shale of the largest particle size, 42% of the produced diesel fraction was distilled, whereas 50% was distilled during pyrolysis of oil shale of the smallest particle size.

Conclusion

It is quite clear from this study that increasing the particle size does not have a clear increasing effect on total weight loss, as well as on that of oil, water, and gas in the oil shale samples investigated. The increase in particle size resulted in a decrease in the percentage of naphtha and gasoline products. Kerosene production was increased with increasing particle size and this is the result of diffusional influences on the products generated due to the pyrolysis process whereas the diesel fraction decreased with increasing particle size. The impact of diffusional influences during pyrolysis is reflected on the percentage change of different fractions during distillation.

REFERENCES

1. Dyni, J. R. Geology and resources of some world oil shale deposits. *Oil Shale*, 2003, **20**(3), 193–252.
2. Johannes, I., Kruusement, K., Veski, R. Evaluation of oil potential and pyrolysis kinetics of renewable fuel and shale samples by Rock-Eval Analyzer. *J. Anal. Appl. Pyrol*., 2007, **79**(1–2), 183–190.

3. Johannes, I., Kruusement, K., Veski, R., Bojesen-Koefoed, J. A. Characterisation of pyrolysis kinetics by Rock-Eval basic data. *Oil Shale*, 2006, **23**(3), 249–257.
4. Kök, M. V., Iscan, A. G. Oil shale kinetics by differential methods. *J. Therm. Anal. Cal.*, 2007, **88**(3), 657–661.
5. Al-Ayed, O. S. Distillation curves under the influence of temperature and particle size of Ellajjun oil shale. *Proc. International Green Energy Conference* 12–16 June 2005, Waterloo, Ontario, Canada.
6. Al-Ayed, O. S, Matouq, M., Anbar, Z., Khaleel, A. M., Abu-Nameh, E. Oil shale pyrolysis kinetics and variable activation energy principle. *Appl. Energ.*, 2010, **87**(4), 1269–1272.
7. Kök, M. V., Hughes, R., Price, D. Combustion characteristics of crude oil-limestone mixtures. *J. Therm. Anal.*, 1997, **49**(2), 609–615.
8. Kök, M. V., Gundogar, A. S. Effect of different clay concentrations on crude oil combustion kinetics by thermogravimetry. *J. Therm. Anal. Calorim.*, 2010, **99**(3), 779–783.
9. Kök, M. V. Evaluation of Turkish oil shales – thermal analysis approach. *Oil Shale*, 2001, **18**(2), 131–138.
10. Kök, M. V., Pamir, R. Pyrolysis kinetics of oil shales determined by DSC and TG/DTG. *Oil Shale*, 2003, **20**(1), 57–68.
11. Kök, M. V., Guner, G., Bagci, S. Combustion kinetics of oil shales by reaction cell experiments. *Oil Shale*, 2008, **25**(1), 5–16.
12. Bhargava, S., Awaja, F., Subasinghe, N. D. Characterization of some Australian oil shale using thermal, X-ray and IR techniques. *Fuel*, 2005, **84**(6), 707–715.
13. Allred, V. D. Kinetics of oil shale pyrolysis. *Chem. Eng. Prog. S. Ser.*, 1966, **62**(8), 55–60.
14. Braun, R. L., Rothman, A. J. Oil-shale pyrolysis: Kinetics and mechanism of oil production. *Fuel*, 1975, **54**(2), 129–131.
15. Jaber J. O., Probert, S. D. Pyrolysis and gasification kinetics of Jordanian oil shales. *Appl. Energ.*, 1999, **63**(4), 269–286.
16. Russell, P. L. *Oil Shales of the World: Their Origin, Occurrence and Exploitation*. Pergamon Press, Oxford, 1990.
17. Wallman, P. H., Tamm, P. W., Spars, B. G. Oil Shale retorting kinetics. In: *Oil Shale, Tar Sand and Related Materials* (H.C. Stauffer, H. C., ed.), ACS Symposium Series 163. American Chemical Society, Washington, 1981.
18. Rubel, A. M., Davis, E. The effect of shale particle size on the products from the bench scale fixed bed pyrolysis of Kentucky Sunbury shale. In: *Proc. 1985 Eastern Oil Shale Symposium*, November 18–20, 1985. Kentucky Energy Cabinet, Lexington, Kentucky, 1985, 43–51.
19. Guffey, F. D., McLendon, T. R. Evaluation of oil yield losses during the retorting of oil shale at low void fraction: Part 1. The effects of particle size and resource grade. *Liq. Fuels Technol.*, 1984, **2**(4), 439–461.
20. Campbell, I. H., Kosinas, G. H., Coburn, T. T., Stout, N. D. Comparison of isothermal and nonisothermal pyrolysis data with various rate mechanisms: implications for kerogen structure. *In Situ*, 1978, 2, 1.
21. Doğan, O. M., Uysal, B. Z. Non-isothermal pyrolysis kinetics of three Turkish oil shales. *Fuel*, 1996, **75**(12), 1424–1428.
22. Drescher, E. A., Bassil, C. A., Rolinske, E. J. The kinetics of the thermal decomposition of Green River oil shale by thermogravimetric analysis. In:

Alternative Energy Sources V, Part D: Biomass/Hydrocarbons/Hydrogen (Veziroglu, N. T., ed.). Elsevier, Amsterdam, 1983.
23. *Oil Shale Resources Development in Jordan*. http://www.nra.gov.jo/index.php?option=com_content&task=view&id=38&Itemid=46 accessed 18/05/2012.
24. Jaber, J. O., Probert, S. D., Williams, P. T. Evaluation of oil yield from Jordanian oil shales. *Energy*, 1999, **24**(9), 761–781.

Presented by M. V. Kök
Received July 17, 2012