

## THERMAL BEHAVIOR OF KHOOT OIL SHALE IN DIFFERENT CONDITIONS

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*The Khoot oil shale has been non-isothermally pyrolyzed in a thermogravimetric analyzer to determine the influence of temperature, heating rate and purge gas (N<sub>2</sub> or CO<sub>2</sub>) employed on thermal degradation of the sample. The heating rates investigated were 10–50 K min<sup>-1</sup> to final temperature of 950 °C. The oil shale was also pyrolyzed in a wire-mesh reactor to determine the yield of volatile compounds. The oil shale and shale oil were characterized by size-exclusion chromatography.*

### Introduction

Because of petroleum crises in last twenty years and predicted exhaustion of the world's plentiful resources of petroleum, new attention is being focused on coal, asphaltite and oil shales as potential future supplies of energy and chemical raw materials. Investigations to develop technologies and modernize existing ones have been renewed.

Oil shale deposits occur widely throughout the world, the most extensive ones being in Colorado in the USA and at Sao Paulo in Brazil [1]. In Mongolia, the current total estimated resource is 700 billion tonnes of oil shale reserves in central and eastern areas [2].

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For the energy potential of any oil shale to be maximized, the conversion process of oil shale to oil should be undertaken under optimal process conditions. A range of pyrolysis process conditions has been investigated to ensure the maximum and efficient extraction of oil. These parameters include pyrolysis temperature, heating rate, pyrolysis atmosphere, particle grain size, type of reactor, etc. [3]. Heating rate and pyrolysis temperature were shown to have the most influence on the yield and composition of oil in oil shale pyrolysis studies [1, 3–8].

The oil shale pyrolysis is a complicated process because the shale is a complex mixture. Oil shales are composed of organic matter distributed in an inorganic matrix. The majority of the organic matter in oil shale is in the form of kerogen. Kerogen is a high-molecular-weight heteropolymer, which is insoluble in common organic solvents. Kerogen contains different maceral groups that behave differently in pyrolysis reactions [3]. The heterogeneity of kerogens and their insolubility in usual organic solvents render the determination of the structure of this sedimentary organic matter very difficult.

There are a number of techniques for determining molecular masses (MM), although when applied to such complex mixtures as fossil fuels, most are only capable of giving an average value. However, two techniques, size-exclusion chromatography (SEC) and mass spectrometry, reveal the molecular distribution of such mixtures which can be far more informative. SEC has been used in coal research as the data about the molecular mass, or molecular size of the species present in coal and its derivatives is important in the design of processes for coal conversion, particularly at selection and preparation of porous catalysts, and in assessing the effectiveness of such conversions [9].

The present investigation is an experimental study using a TGA (thermogravimetric analysis) apparatus (under non-isothermal conditions) to determine the influence of temperature, heating rate and purge gas employed on the thermal degradation of the sample. The purpose of this work was also to determine the behavior of oil shale in wire-mesh reactor (WMR). The oil shale and shale oil were characterized by SEC.

## Experimental

The Khoot oil shale deposit has been surveyed and analyzed comprehensively for exploitation purposes. The oil shale samples have been examined in a preliminary pyrolysis study using fixed-bed retort [2]. The laboratory standard Khoot oil shale sample (Table 1) has been used in the experiments described below. In addition, the main characteristics of the treated (oxidized) oil shale are given.

A WMR and a TGA were used for the majority of the experimental work of this study. Conditions used in the reactors during the present set of experiments are summarized in Table 2.

**Table 1. Main Characteristics of the Samples, wt.%**

Characteristics	Oil shale	Oxidized oil shale
Moisture	5.2	–
Ash	59.8	45.8
Volatile matter	31.8	–
DAF volatile matter	90.9	–
Sulphur	0.32	0.68
Chlorine	0.02	–
Phosphorus	0.05	–
Carbon	21.1	20.85
Hydrogen	2.66	3.52
Nitrogen	0.6	0.36
Oxygen (by difference)	10.25	–
H/C	1.51	–

**Table 2. Reactor Operating Conditions**

Parameter	Wire-mesh reactor	TG analyzer
Gaseous environment	He or CO <sub>2</sub>	N <sub>2</sub> or CO <sub>2</sub>
Heating rate, K s <sup>-1</sup>	1000	10–50
Temperature, °C	1000	950
Hold-up time, s	10	3600
Sample size, µm	106–152	< 100
Sample weight, mg	6	500–600

### Thermogravimetric Analysis

Thermogravimetric analysis of the oil shale sample was investigated using a *DMT Hochdruck Thermowaage TG* analyzer. In this work, a ~0.5-g sample was heated to 1000 °C at heating rate 10, 20, 30, 40 and 50 K min<sup>-1</sup> using nitrogen and carbon dioxide as the purge gas.

### The Wire-Mesh Reactor

The WMR (Fig. 1) has been described elsewhere [10–13]; brief descriptions are given below. The oil shale sample is placed as a mono-layer on the folded mesh, which is a heated resistance between water-cooled electrodes. Gas is introduced through the bottom and directed through a flow smoothing section into the mesh. Two thermocouples are attached to the mesh for lateral temperature measurements and temperature control. During pyrolysis (in helium) and CO<sub>2</sub> gasification, the gas stream flowed through the mesh at a velocity of 0.1 m s<sup>-1</sup>. A stainless steel (AISI 304) mesh was used for the pyrolysis and gasification experiments.

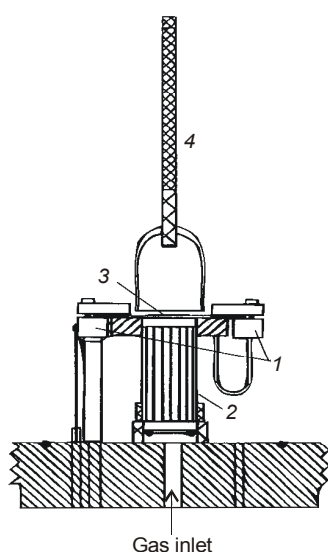


Fig. 1. Schematic diagram of the wire-mesh pyrolysis reactor:

- 1 – electrodes clamping the mesh,
- 2 – gas flow distributor (ensures even distribution and suppresses turbulence in the dense gas supplied to the mesh),
- 3 – sample holder,
- 4 – liquid-nitrogen-cooled tar trap

### Treatment of Oil Shale

The Khoot oil shale sample was treated with  $\text{KMnO}_4$  in water for 8 h. Thereafter aqueous phase (water-soluble oil shale) was separated from solution and dried. *n*-Methyl-2-pyrrolidinone (NMP) was added to the water-soluble part and the solution analyzed by SEC.

### Size-Exclusion Chromatography

SEC using NMP as solvent was carried out using a 5- $\mu\text{m}$  particle-size polystyrene/polydivinylbenzene column (“Mixed-D”; *Polymer Laboratories Ltd.*, Shropshire, UK) [14, 15] with the flow rate of  $0.5 \text{ mL min}^{-1}$  at a column temperature of  $80 \text{ }^\circ\text{C}$ . Two different detectors in series: a variable wavelength *Perkin-Elmer LC 290 UV* at 450 nm and an *Applied Biosystems 1000S* diode array detector set at 280, 300, 350 and 370 nm were used.

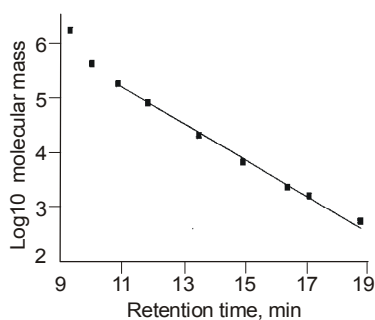


Fig. 2. Polystyrene calibration line in “Mixed-D” column with NMP as eluent

The same sample injection was used to record all the profiles in order to compare the spectra at different wavelengths. Data were collected simultaneously from both detectors into a computer. The calibration curve is shown in Fig. 2. The polystyrene MM-standards from 100 up to 300,000  $\mu$  are retained by the column and eluted with a linear relation between  $\log_{10}$  MM and elution time. Larger MM polystyrene standards up to 2,000,000  $\mu$  elute at shorter times with a different relation between MM and time and they are classed as not depending on column porosity.

## Results and Discussion

### Non-Isothermal Thermogravimetry of the Mongolian Khoot Oil Shale under Different Processing Conditions

Khoot oil shale sample has been non-isothermally pyrolyzed using a TG analyzer. A typical variation of the conversion percentage and differential weight loss (i.e. the TG and DTG curves) in nitrogen with temperature is shown in Fig. 3a, while Fig. 3b shows the curves in carbon dioxide for the Khoot oil shale.

The weight losses during pyrolysis and gasification of oil shale sample with regard to heating rate and the temperature at which the maximum rate of decomposition occurred, are presented in Table 3.

Table 3 shows the data of weight loss in the low-, medium- and high-temperature regions of the pyrolysis and gasification of oil shale in TG. Thermal decomposition of oil shale below 200 °C produced weight loss attributed to the loss of moisture and of interlayer water from clay minerals. Some authors have assigned low-temperature weight loss to physical changes in the kerogen occurring prior to its decomposition to pyrolytic bitumen, these changes being expressed as softening of the kerogen, molecular rearrangement accompanied by the release of gas [3]. The main weight loss in the region from about 200 to 550 °C occurs due to the loss of hydrocarbon

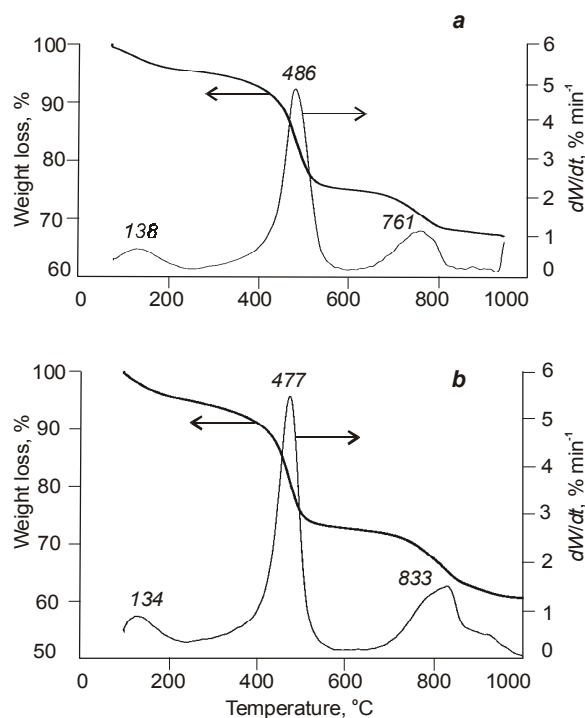


Fig. 3. TG profiles of the Khoot oil shale with respect to pyrolysis temperature, heating rate 20 K min<sup>-1</sup>: a – in N<sub>2</sub>; b – in CO<sub>2</sub>

material and evolution of gases and oil vapor. In addition, the great weight loss due to carbonate decomposition takes place between 550–950 °C.

Table 3. TGA of Khoot Oil Shale

Heating rate, K min <sup>-1</sup>	Weight loss, %				Temperature of maximum rate of decomposition, °C
	at pyrolysis temperature range, °C			Total	
	30–200	200–550	550–950		
Purge gas N <sub>2</sub>					
10	6.152	21.925	7.917	35.994	463
20	4.117	20.460	8.681	33.258	486
30	3.489	22.049	11.956	37.494	505
40	2.386	20.095	13.392	35.873	516
50	3.013	19.269	15.342	37.624	521
Purge gas CO <sub>2</sub>					
10	4.752	22.055	13.042	39.849	455
20	4.342	22.510	12.589	39.441	477
30	3.643	22.892	13.314	39.849	498
40	3.784	22.941	13.092	39.817	513
50	1.795	21.338	15.608	39.741	533

The maximum rate of decomposition shifts to higher temperature at increasing heating rate. Table 3 shows slightly greater weight losses occurring as a result of using CO<sub>2</sub> instead of N<sub>2</sub> to purge the TGA system, as CO<sub>2</sub> is more reactive than N<sub>2</sub> [4].

### Tests on Wire-Mesh Reactor

During Khoot oil shale pyrolysis in helium in WMR (two replications), the following yields were obtained, wt.%: total volatile yields 36.9 and 37.7, and shale oil yields 15.5 and 18.3, respectively. During Khoot oil shale CO<sub>2</sub> gasification in WMR (also two replications), the total volatile yields were 47.9 and 45.3 wt.%, respectively, oil shale yields were not measured.

The yields of volatiles were substantially higher in the WMR compared to TGA and laboratory glass retort (fixed-bed reactor) experiments [2]. Particularly the WMR yield of shale oil exceeds that of fixed-bed reactor due to, primarily, lower heating rates, a less close gas-solid contact and the effect of secondary reactions leading to repolymerization and charring of shale oil in the fixed-bed reactor. The behavior of oil shale in WMR was determined for the first time. However, a more detailed investigation on WMR in relation to pressure and effect of sweep gas has to be carried out.

### SEC Analysis

The heterogeneity of kerogens and their insolubility in the usual organic solvents make the determination of the structure of this sedimentary organic matter very difficult. This insoluble fraction is the basic material of oil shales and cannot be extracted by ordinary solvents simply, but after treatment is suitable for use as feedstock. So, Khoot oil shale was treated with  $\text{KMnO}_4$  and thereafter tested by SEC. The pyrolysis oil was also characterized by SEC (Fig. 4).

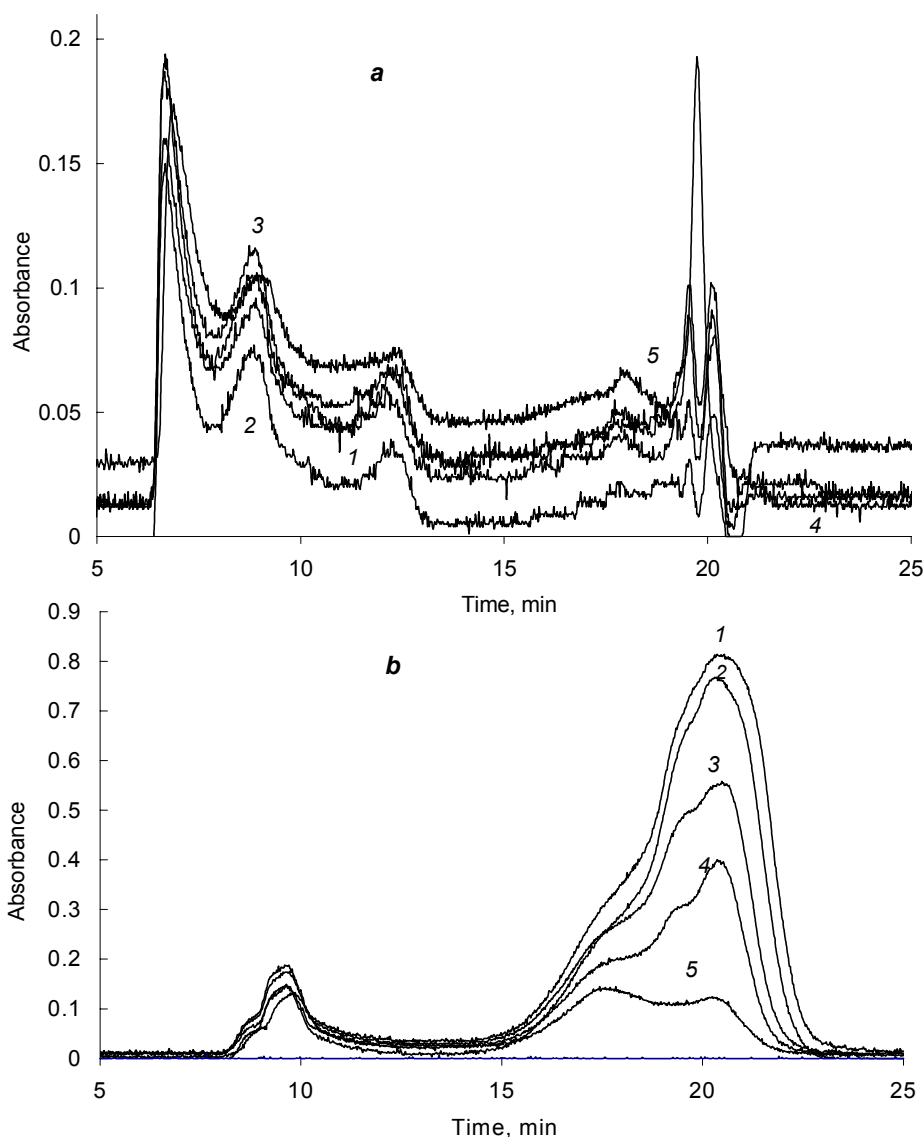


Fig. 4. SEC of the Khoot oil shale (a) and shale oil (b) at different wavelengths: 280 (1), 300 (2), 370 (3), 350 (4), and 400 (5) nm

Figure 4 shows the size-exclusion profiles of the Khoot oil shale and shale oil measured at five wavelengths in NMP, and also shows the differences between molecular masses of oil shale and shale oil, i.e. how the molecular mass is changing during the pyrolysis. The polystyrene calibration suggests the first peak to correspond to large molecular species which are being excluded from the packing material pores. In the oil shale SEC, the peak between 19 and 21 min corresponds to small molecules. Their molecular mass is between 100–300  $\mu$ . The peak of major intensity corresponds to large (over 30,000  $\mu$ ) molecular species. The shale oil SEC has a major peak between 15 and 23 min and the molecular mass below 1000  $\mu$ . The SEC has a little peak at 10 min, which corresponds to large molecules. The chromatograms in Fig. 5 show that oil shale has a large molecular mass.

## Conclusions

The Khoot oil shale from Mongolia was processed in the WMR and TG analyzer. The WMR oil yield exceeds that obtained using TGA and fixed-bed reactor. A slightly greater weight loss occurred as a result of using CO<sub>2</sub> instead of N<sub>2</sub> to purge the TGA system.

The results show that SEC may be used for the oil shale analysis and that the molecular mass is changing during pyrolysis, i.e. the molecule of oil shale is decomposing to small molecules.

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