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PYROLYSIS AND THERMOGRAVIMETRIC INVESTIGATION OF THE MONGOLIAN KHOOT OIL SHALE

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Oil shales from eight deposits in the central economic region of Mongolia were characterized and their pyrolysis experiments and thermogravimetric study were carried out. The Khoot deposit oil shale was chosen as the best-quality one with maximum shale oil yield. The optimum conditions (heating temperature 550 °C, heating rate 92 °C/min) were determined. Shale oil fractions with different boiling temperature intervals and hard residue were obtained by using ordinary distillation. These products can be used as gasoline, diesel, oil materials and binding materials (bitumen-like hard residue) after isolation of organic bases, acids and phenolic compounds. The Khoot deposit oil shale was investigated by thermogravimetric analysis enabling to explain the mechanism of oil shale thermal destruction process in detail. Thermal decomposition had the characteristics of a first-order reaction with activation energy 22.98 kcal/mol (96.28 kJ/mol) calculated from the oil shale thermogram.

Introduction

The importance of oil as a source of energy and as a chemical feedstock is well known. The lack of appreciable oil reserves obliges some countries to develop alternative energy sources, e.g. synthetic oil from coal and other fossil fuels. Oil shales represent an enormous energy potential being an extractable hydrocarbon reserve of approximately 2.72×10^{14} t of oil [1]. For the potential to be maximized, the process of oil shale conversion to oil should be undertaken under optimal conditions but also with consideration of economic and environmental factors. In recent years, many studies on oil shales have

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been conducted in countries with abundant resources, e.g. USA, Estonia, China, Australia, Turkey, Israel and Morocco [2–8].

Mongolia, with estimated reserves of 7×10^{11} t, is increasingly interested in oil shales as an alternative energy source [9]. However, until now there have been no suggestions or projects for any kind of utilization of these great resources and pyrolysis of Mongolian oil shale has not been intensively studied previously.

Thermogravimetric analysis (TGA) has been extensively used as a means to determine the characteristics of devolatilisation and also kinetic parameters [10–15]. Most previous works have examined the thermal degradation of oil shales only in inert atmospheres or in oxygen.

This work was aimed at studying the Mongolian oil shales including their pyrolysis process. Thermal degradation mechanism of the Khoot oil shale was investigated using a variety of methods including DTA, TG in both inert and air atmospheres.

Experimental

The samples for investigation were taken from the following Mongolian deposits: Ovdog Khooloin Gashuun (OKG), Bayanerkhet (BE), Chagtsaliin Khudag (CK), Nariin Gol (NG), Ulaantolgoi (UT), Zuun Shavartiin Ovoo (ZSO) and Beliin Jas (BJ), and particularly from the Khoot (Kh) deposit – from the 46th ditch and Eedemt.

The Khoot deposit of the Choir-Nyalga Basin is the largest and most investigated one. Its oil shale belongs to the Jurassic period of the Mesozoic era. Its estimated resources reach 612 million t, which is equivalent to 42 million t of shale oil. On the present level of the liquid fuel consumption (about 0.4 million t/year) it will be enough to meet the country's requirements for 105 years [16].

The main technical specifications (content of moisture W^a , ash A^d , volatile matter V^a , organic matter, $(CO_2)^d_M$ and sulfur, and calorific value Q) of oil shale samples from the above-mentioned deposits were determined by the standard methods described in [17].

Pyrolysis of oil shale samples was carried out in a small laboratory retort (height 50 mm, diameter 15 mm) at different temperatures (from 300 to 650 °C) and heating rates from 7 to 254 °C/min. Before retorting the initial sample was ground into 3–5 mm particles and dried at 105 °C for 2 h.

Shale oil was obtained at a large-scale retort designed in our laboratory – a vertical cylindrical stainless steel apparatus (height 250 mm, diameter 100 mm), which could hold about 1.0 kg of oil shale sample. The $CaCl_2$ -dried shale oil was distilled via ordinary distillation in a laboratory flask into three

fractions: light (20–180 °C), middle (180–280 °C) and heavy (280–320 °C). Hard residue (over 320 °C) was also collected.

Thermal analyses were carried out on a *Thermoplus* Model TG 8120 thermal analyzer (*Rigaku*, Japan) at the following conditions: temperature interval 20–1200 °C, heating rate 10 °C/min, air atmosphere; and MOM derivatography system (Hungary) at the following conditions: temperature interval 20–900 °C, heating rate 10 °C/min, nitrogen atmosphere.

Results and Discussion

Chemical analysis (Table 1) showed that oil shales studied differ in the organic matter content being an important specification. Oil shales of the Kh, OKG and NG deposits contain higher amounts of organic matter than the others tested, and these shales are comparable as for the content of organic matter with oil shales exploited in other countries [18]. Comparing to high-sulfur oil shales containing over 2.5 % sulfur [19], sulfur content in all samples analyzed was low, which is desirable from the environmental standpoint.

Table 1. Main Characteristics of Oil Shales

Deposit	W^a , %	A^d , %	V^a , %	Organic matter, %	$(CO_2)^d_M$, %	S, %	Q , kcal/kg
Mongolian:							
OKG	3.97	71.0	22.23	28.6	1.64	0.44	1808.7
BJ	3.72	84.5	10.90	15.03	2.76	0.22	1176.6
ZSO	2.22	88.88	7.20	10.87	1.80	0.19	849.5
CK	3.58	83.27	14.39	16.10	0.84	0.45	1262.2
Khoot:							
46th ditch	5.88	61.12	33.18	28.82	10.06	0.19	2120.0
Eedemt	5.52	62.46	28.67	26.27	11.27	0.45	2010.0
NG	5.45	75.75	12.70	22.80	4.03	1.56	1792.1
UT	3.96	84.00	5.94	15.35	1.35	0.08	1186.2
BE	2.81	87.44	10.98	13.50	1.29	0.31	1444.5
Estonian (Estonia)	10.00	47.00	–	35.5	18.00	1.5	3150.0
Green River (USA)	0.20	59.80	–	13.8	4.90	0.8	1220.0
Fushun (China)	5.0	78.5	–	18.6	3.8	0.5	1390

Pyrolysis experiments were carried out with a number of geological samples from each deposit. Table 2 presents their averaged values, as well as those for the above-mentioned oil shales from other countries for comparison.

Oil shales from the Kh and OKG deposits produce more shale oil than those of other Mongolian, and Green River (USA) and Fushun (China) deposits, but not as much as Estonian shale. All deposits differ in resources

and properties. For instance, BE and ZSO have rich resources, but their shale oil yield of is relatively low. On the contrary, the NG and OKG deposits have less resources with higher content of organic matter than those of BE and ZSO.

Table 2. Yields of Oil Shale Pyrolysis Products

Samples	Oil shale pyrolysis products, %			
	Shale oil	Pyrolysis water	Hard residue	Gas and loss
OKG	9.63	5.01	78.80	6.30
BJ	2.50	0.78	95.26	2.66
ZSO	0.89	1.57	94.63	2.90
CK	2.49	4.02	90.81	2.68
Kh-46th ditch	15.62	3.93	73.45	6.99
Kh-Eedemt	13.28	3.82	75.72	7.17
NG	4.49	2.89	84.26	8.34
UT	1.28	0.78	95.26	2.66
BE	2.50	3.21	90.44	3.81
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Estonian	25.5	2.90	63.80	7.80
Green River	10.3	1.40	85.80	2.50
Fushun	6.6	3.40	86.70	3.30

The results presented in Tables 1 and 2 attest that oil shale from the Khoot deposit can be processed technologically, from the OKG deposit – energy-technologically, and oil shales from other deposits – for producing power. The Khoot deposit oil shale contains the biggest amount of organic matter and its resources are richer than in all other investigated deposits. For this reason it was chosen as a best-quality oil shale and objected to detailed investigations.

A specific feature of the Khoot deposit is the occurrence of large resources of good-quality brown coal underlying oil shale. That is why a thorough investigation of its oil shale is important from both theoretical and practical points of view.

Detailed pyrolysis experiments with the Khoot 46th ditch oil shale were carried out at different temperatures and heating rates (Figs 1 and 2).

Pyrolysis at different temperatures and constant heating rate (18 °C/min) (Fig. 1) have shown that with the temperature rise the shale oil yield increases and reaches its maximum at 550 °C. In other words, thermal decomposition of oil shale was completed at 550 °C, and this temperature was chosen as the optimum one for pyrolysis. Certainly, the shale oil yield was less at lower temperatures, because thermal decomposition was not sufficient, and also over 550 °C, because at higher temperatures the volatile products underwent second-stage pyrolysis [20].

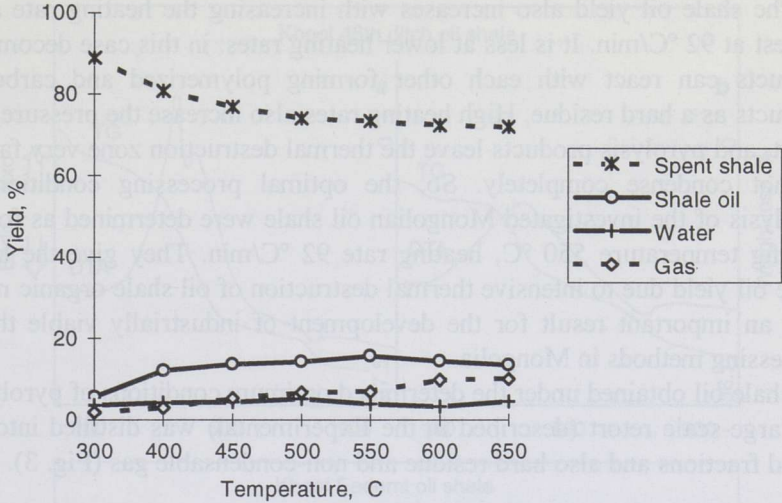


Fig. 1. Yields of the pyrolysis products of the Khoot 46th ditch oil shale at different temperatures

The shale oil yield depends also on the heating rate, mechanism of thermal decomposition, polymerization and carbonization reactions in the retort, and the exit conditions of pyrolysis products.

Next series of experiments was carried out at the constant temperature (550 °C) and different heating rates (Fig. 2).

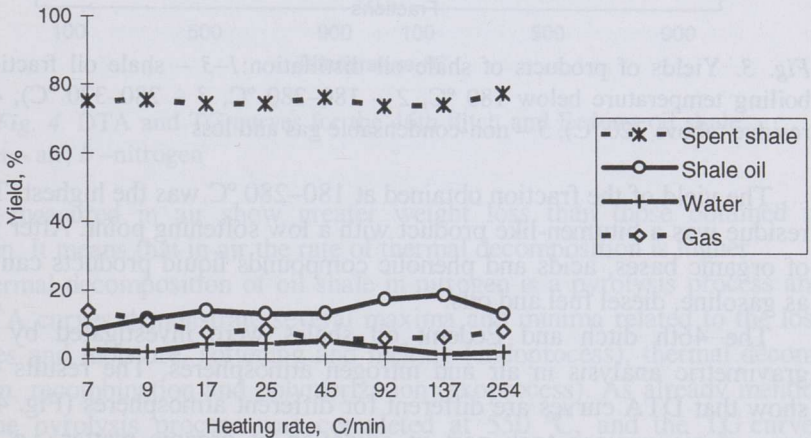


Fig. 2. Yields of the pyrolysis products of the Khoot 46th ditch oil shale at different heating rates

The shale oil yield also increases with increasing the heating rate and is highest at 92 °C/min. It is less at lower heating rates: in this case decomposed products can react with each other forming polymerized and carbonized products as a hard residue. High heating rates also increase the pressure in the retort, and pyrolysis products leave the thermal destruction zone very fast and do not condense completely. So, the optimal processing conditions for pyrolysis of the investigated Mongolian oil shale were determined as follows: heating temperature 550 °C, heating rate 92 °C/min. They give the highest shale oil yield due to intensive thermal destruction of oil shale organic matter. It is an important result for the development of industrially viable thermal processing methods in Mongolia.

Shale oil obtained under the determined optimum conditions of pyrolysis in the large-scale retort (described in the Experimental) was distilled into three liquid fractions and also hard residue and non-condensable gas (Fig. 3).

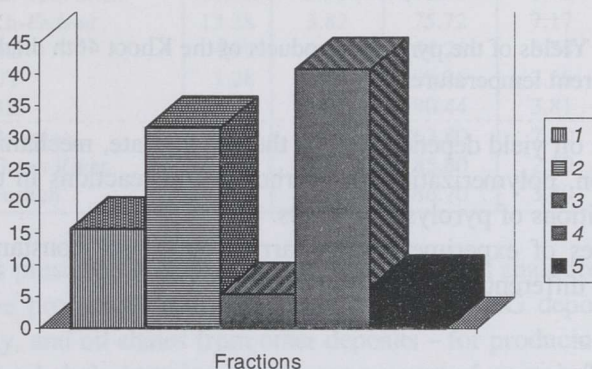


Fig. 3. Yields of products of shale oil distillation: 1–3 – shale oil fractions (1 – boiling temperature below 180 °C, 2 – 180–280 °C, 3 – 280–320 °C); 4 – hard residue (above 320 °C), 5 – non-condensable gas and loss

The yield of the fraction obtained at 180–280 °C was the highest. The hard residue was a bitumen-like product with a low softening point. After isolation of organic bases, acids and phenolic compounds liquid products can be used as gasoline, diesel fuel and oils.

The 46th ditch and Eedemt oil shales were investigated by thermogravimetric analysis in air and nitrogen atmospheres. The results obtained show that DTA curves are different for different atmospheres (Fig. 4): in the case of air, oxygen took part in oxidation of organic matter, i.e. thermo-oxidative destruction took place.

DTA curves have 2–3 maxima. The first one can be related to the oxidation process at a comparatively low temperature and in such conditions a decrease in hydrogen content takes place, which has some influence on decreasing the shale oil yield. The second and third maxima are related to the combustion of organic matter with decreased hydrogen content. The TG

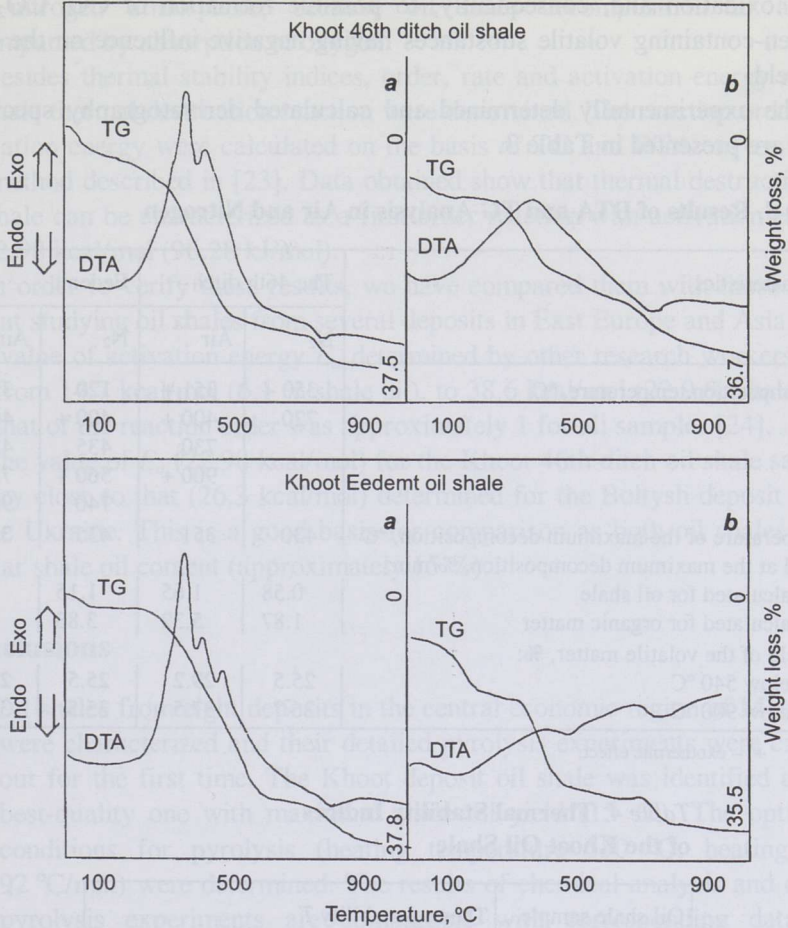


Fig. 4. DTA and TG curves for the 46th ditch and Eedemt oil shale: a – air; b –nitrogen

curves measured in air show greater weight loss than those obtained in nitrogen. It means that in air the rate of thermal decomposition is higher.

Thermal decomposition of oil shale in nitrogen is a pyrolysis process and the DTA curves demonstrate several maxima and minima related to the loss of gases and moisture, softening and melting (endoprocess), thermal decomposition, recombination and polymerization (exoprocess). As already mentioned, the pyrolysis process was completed at 550 °C, and the TG curves illustrate thermal decomposition of most of oil shale organic matter. The main mineral constituents of the sample are calcite, dolomite, quartz, montmorillonite and illite [21]. The small minima at 700 and 780 °C (in the DTA curve) probably belong to the decomposition of dolomite and calcite.

The processes or mechanisms of thermo-oxidative decomposition (in air) and pyrolysis (in nitrogen) are different. The presence of oxygen leads to oil

shale oxidation and, consequently, to possible formation of CO, CO₂ and oxygen-containing volatile substances having negative influence on the shale oil yield.

The experimentally determined and calculated derivatography specifications are presented in Table 3.

Table 3. Results of DTA and TG Analysis in Air and Nitrogen

Characteristics	The 46th ditch		Eedemt	
	N ₂	Air	N ₂	Air
Decomposition temperature, °C	350 + 720	351 + 400 + 730 900 +	120 400 + 435 560 + 740	350 + 405 + 480 + 750 900 +
Temperature of the maximum decomposition, °C	430	351	435	350
Yield at the maximum decomposition, %/min:				
Calculated for oil shale	0.58	1.65	1.15	1.37
Calculated for organic matter	1.87	5.32	3.83	4.56
Yield of the volatile matter, %:				
Below 540 °C	25.5	29.2	25.5	28.6
Below 900 °C	36.7	37.5	35.5	37.8

Note: '+' – exothermic effect.

Table 4. Thermal Stability Indices of the Khoot Oil Shale

Oil shale sample	Thermal stability <i>T</i>			
	In air		In nitrogen	
	<i>T</i> _{5%}	<i>T</i> _{30%}	<i>T</i> _{5%}	<i>T</i> _{30%}
The 46th ditch	280 °C	560 °C	150 °C	620 °C
Eedemt	300 °C	600 °C	145 °C	690 °C

Thermal destruction is most intensive at about 350 °C that agrees with the data for Urtbulak oil shale (Uzbekistan) and a number of other oil shales except Estonian kukersite (460 °C). The comparatively easy oxidation is connected with the kerogen structure. Kerogen of the Khoot oil shale contains more aliphatic hydrocarbons than aromatic ones and is therefore easy to oxidize. The higher content of aliphatic carbon in kerogen was confirmed by IR, NMR and GC-MS investigations [22].

Thermal stability characteristics of the Khoot oil shale (Table 4) were determined from the thermogram. The 5-% weight losses are different for air

and nitrogen atmosphere, because oil shale decomposition in air is accompanied by absorption of oxygen.

Besides thermal stability indices, order, rate and activation energy of the oil shale thermal destruction reaction were determined. The reaction order and activation energy were calculated on the basis of TG and DTA curves using the method described in [23]. Data obtained show that thermal destruction of oil shale can be characterized as a first-order reaction with activation energy E_a 22.98 kcal/mol (96.28 kJ/mol).

In order to verify these results, we have compared them with those obtained at studying oil shales from several deposits in East Europe and Asia [23]. The value of activation energy E_a determined by other research workers ranged from 14.7 kcal/mol (6.1 % shale oil), to 38.6 kcal/mol (22.9 % shale oil), and that of the reaction order was approximately 1 for all samples [24].

The value of E_a (22.98 kcal/mol) for the Khoot 46th ditch oil shale sample is very close to that (26.3 kcal/mol) determined for the Boltsh deposit shale in the Ukraine. This is a good basis for comparison as both oil shales have similar shale oil content (approximately 15 %).

Conclusions

1. Oil shales from eight deposits in the central economic region of Mongolia were characterized and their detailed pyrolysis experiments were carried out for the first time. The Khoot deposit oil shale was identified as the best-quality one with maximum shale oil yield (15 %). The optimum conditions for pyrolysis (heating temperature 550 °C, heating rate 92 °C/min) were determined. The results of chemical analysis and of the pyrolysis experiments are comparable with corresponding data for industrially exploited oil shales from other countries.
2. The Khoot deposit oil shale was studied by thermogravimetric analysis. Its thermal destruction can be characterized as a first-order reaction with activation energy E_a 22.98 kcal/mol (96.28 kJ/mol). Thermal stability indices of oil shale were determined as well.
3. Shale oil fractions of different boiling temperature intervals and hard residue were obtained by using ordinary distillation. These products can be used as a gasoline, diesel, oil materials and binding materials (bitumen-like hard residue), after isolation of organic bases, acids and phenolic compounds.

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