COMPARATIVE STUDY OF PYROLYSIS AND THERMAL DISSOLUTION OF ESTONIAN AND MONGOLIAN KHOOT OIL SHALES

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Abstract. Two oil shale (OS) samples with different organic matter (OM) content from the Khoot deposit, Mongolia were characterized, their pyrolysis and thermal dissolution experiments were carried out and the results compared with those obtained for the Estonian oil shale sample in the same experimental conditions. The thermal decomposition of the organic matter of oil shale samples starts in the temperature range of 200–300 °C, while the highest yield of liquid products (tar and pyrolysis water) and the lowest yield of solid residue are obtained at 500–600 °C, which can be considered an optimal temperature range for the pyrolysis of OS samples. In this temperature region, 23% of tar is obtained from the Estonian oil shale sample, which is more than the yield from Mongolian Khoot oil shale samples. The higher tar yield from the Estonian oil shale sample is due to its lower ash and higher organic content compared to Mongolian Khoot oil shale samples.

The results of the thermal dissolution experiments for the three OS samples show that the yield of liquid product (tar) is the lowest at 350 °C, the highest at 400 °C and lower again at 450 °C. So, 400 °C can be considered an optimal temperature for the thermal dissolution of all the samples in tetralin as a hydrogen-donor solvent. The optimal temperature of thermal dissolution decreased almost 200 °C compared to that of pyrolysis due to the use of an autoclave, which is more suitable for carrying out the thermal decomposition of oil shale organic matter than the retort. Also, the yield of tar upon thermal dissolution is higher than that in pyrolysis, because the hydrogen in tetralin molecules favours its formation.

Keywords: thermal dissolution, pyrolysis, Estonian oil shale, Mongolian Khoot oil shale, hydrogen-donor solvent.

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1. Introduction

Oil shale (OS), which is distributed in many places worldwide, is a sedimentary rock containing organic matter (OM) called kerogen and belongs to the group of sapropel solid fuels [1, 2].

Usually oil shale is utilized for the thermal decomposition (pyrolysis) of its OM [1]. Therefore it is very important to determine OS thermal characteristics [3].

The methods mostly used for determining OS thermal characteristics include techniques such as differential scanning calorimetry (DSC), pressurized differential scanning calorimetry (P-DSC), thermogravimetry (TG), etc. [4, 5].

The geological surveys of coal and oil shale in Mongolia started in 1940. It has been found that significant oil shale resources lie in the central, eastern and southern parts of Mongolia and there are 13 oil shale-bearing basins and more than 40 oil shale deposits. 20% of these oil shale areas comprise an estimated resource of 788 billion tons [6].

In 1980, the first program for studying oil shale in Mongolia began, and during this period a number of oil shale deposits, including Khoot, Eedemt, Ovdogkhooloin gashuun, Bayanerkhet, Chagzaliin khudag, Nariin gol, Ulaan tolgoi, Zuun shavartiin ovoo, Beliin jas, Togrog, Bayanjargalan and Sumiin nuur, have been studied more intensively, and some of the selected oil shale samples were sent to Estonia and Japan for more detailed chemical investigations [6].

Located near the Bayanjargalan village of Dundgobi province in the central economic region of Mongolia where there are large reserves of brown coal and oil shale, the oil shale deposit found at Khoot is distinguished from the other abovementioned ones by that it also comprises brown coal. In this deposit, brown coal underlies oil shale. To enable brown coal to be extracted through open cast mining, oil shale is removed and treated as spoil [7].

More detailed investigations of oil shales from the above deposits and their pyrolysis experiments have been carried out in the Laboratory of Coal Chemistry and Technology, Mongolian Academy of Sciences within the framework of the aforesaid program for oil shale research. During the studies within the program the characteristics of oil shale samples from eight deposits and the yields of their pyrolysis products were determined for the first time [7].

The mechanism of thermal destruction of oil shale from the Khoot deposit was studied by thermogravimetric analysis (TGA) and its thermal stability indices were determined [8, 9]. Also, the petrographic and mineral composition of Khoot oil shale [10] and the chemical composition of its organic matter [11], as well as pyrolysis tar [12] were determined.
At present, the Khoot deposit belongs to the MAK Company, Mongolia and they are carrying out a feasibility study for utilization of brown coal and oil shale of the deposit.

We received two oil shale samples (Khoot-1 and Khoot-2) with different OM content from the MAK Company, and a sample of Estonian oil shale from Estonia during our visit to the country. It seemed interesting to us to make use of this possibility and we decided to carry out a comparative investigation of the characteristics and liquefaction of these oil shale samples by using pyrolysis and thermal dissolution methods [13].

2. Experimental

The analytical samples of Estonian and Mongolian Khoot oil shales were prepared according to Mongolian National Standards (MNS 2719:2001) and their main characteristics, including the contents of moisture (MNS 656-79), ash (MNS 652-79), volatile matter (MNS 654-79) and sulphur (MNS 895-79), as well as calorific value (MNS 669-87), were determined.

The pyrolysis experiments with oil shale samples were performed in a laboratory small-scale quartz retort (tube), which contained 1 g of air-dried oil shale sample powdered to a particle size < 0.2 mm. The retort was placed in a horizontal electric tube furnace with a maximum heating temperature of 950 °C. A chrome-alumel thermocouple was immersed in the tube furnace to measure the actual heating temperature. The pyrolysis experiments were carried out at different heating temperatures ranging from 200 to 700 °C and at a heating rate of 20 °C/min. First, the quartz retort containing the oil shale sample was heated to 600 °C at a heating rate of 20 °C/min and kept at this temperature for 80 min. The retort was connected to a thermostable glass tube which was also heated in the electric tube furnace at 80 °C in order to collect tar, and was also connected to an air-cooled glass vessel for collecting pyrolysis water. The latter vessel was connected to a thin glass tube for catching non-condensable gases.

The yields of pyrolysis products, including solid residue (char), tar (condensed liquid product) and pyrolysis water, were determined by weighing. The yield of gases was found by the differences.

Larger-scale pyrolysis experiments of oil shale samples were performed in a laboratory vertical cylindrical retort made of stainless steel, which could contain 1000 g of sample material. The retort was placed in an SNOL electric furnace (Lithuania) with a maximum operating temperature of 950 °C. A chrome-alumel thermocouple was immersed in the oil shale bed to measure the actual heating temperature, and the temperature was controlled by a potentiometer. The retort was connected to an air-cooled iron tube, a water-cooled laboratory glass condenser and a vessel for collecting the condensate of tar (pitch) and pyrolysis water. The non-condensable gases after a water-cooled condenser left the system through a thin glass tube. The
experiments were carried out at 520 °C, the heating rate was 20 °C min⁻¹. The yields of pyrolysis products, including solid residue (char), tar and pyrolysis water, were determined by weighing. The yield of gases was found by the differences.

The mineral content of oil shale samples was determined by burning the samples slowly and continuously in the furnace at 200–850 °C. The content of mineral oxides in the ash of oil shale samples was found by X-ray fluorescence (XRF) spectrometry.

The thermal dissolution of oil shale samples was carried out in a laboratory standard stainless steel autoclave, using tetralin as a hydrogen-donor solvent. Air dried for 24 h and powdered to a particle size < 0.2 mm, 1 g of an oil shale sample was mixed with 2.8 g of tetralin (mass ratio 1:2.8) in the autoclave and heated in a laboratory furnace at temperatures of 350, 400 and 450 °C for 2 h. After completion of the experiment the autoclave with the sample was cooled to room temperature and weighed. After weighing the gases, which remained uncondensed during the thermal dissolution, were removed by opening the valve of the autoclave and the autoclave was weighed again to calculate the gas yields. The resulting liquid products and solid residue were completely removed from the autoclave by washing with chloroform and filtered, and the solid residue on the filter was subjected to sequential extraction with chloroform in a Soxhlet apparatus. The dried solid residue after extraction was weighed to calculate the yield of solid residue. An extract of liquid products from the thermal dissolution of oil shale in tetralin was distilled using a laboratory rotary evaporator for the complete removal of chloroform. The degree of oil shale conversion was determined by the loss of oil shale OM after extraction. Also, the change in the ash content of the OS samples as well as in the insoluble residue content was found. The tar from OS thermal dissolution contained unreacted tetralin and transformed naphthalene because there was no separation of these substances from each other. Therefore in material balance calculations, the weight of the oil shale sample included also that of tetralin.

3. Results and discussion

The results of ultimate and proximate analyses of Estonian and Mongolian Khoot oil shale samples are presented in Tables 1 and 2.

### Table 1. Proximate analysis of oil shale samples

<table>
<thead>
<tr>
<th>Oil shale sample</th>
<th>Moisture, %</th>
<th>Ash, %</th>
<th>Volatile matter, %</th>
<th>Calorific value, kcal/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Aₐ</td>
<td>Aₜ</td>
<td></td>
</tr>
<tr>
<td>Estonian</td>
<td>0.43</td>
<td>41.96</td>
<td>42.14</td>
<td>56.49</td>
</tr>
<tr>
<td>Mongolian Khoot-1</td>
<td>2.09</td>
<td>76.82</td>
<td>78.45</td>
<td>21.04</td>
</tr>
<tr>
<td>Mongolian Khoot-2</td>
<td>2.15</td>
<td>81.37</td>
<td>83.15</td>
<td>16.66</td>
</tr>
</tbody>
</table>

Note: a – air-dried, d – dry, daf – dry ash free basis.
Table 2. Ultimate analysis of oil shale samples, %

<table>
<thead>
<tr>
<th>Oil shale sample</th>
<th>Carbon</th>
<th>Hydrogen</th>
<th>Nitrogen</th>
<th>Sulphur</th>
<th>Oxygen (by difference)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Estonian [1]</td>
<td>77.3</td>
<td>9.8</td>
<td>0.4</td>
<td>1.7</td>
<td>10.8</td>
</tr>
<tr>
<td>Mongolian Khoot-1</td>
<td>70.4</td>
<td>9.1</td>
<td>1.7</td>
<td>0.7</td>
<td>18.1</td>
</tr>
<tr>
<td>Mongolian Khoot-2</td>
<td>58.2</td>
<td>6.6</td>
<td>1.6</td>
<td>1.7</td>
<td>31.9</td>
</tr>
</tbody>
</table>

From Table 1 it can be seen that the moisture content of all samples is low. The ash content of Mongolian Khoot-1 and Khoot-2 OS samples is twice higher than that in the Estonian oil shale sample. It is for this reason that the content of V_d of Mongolian oil shale samples is also 2–3 times lower than that of the Estonian oil shale sample. Furthermore, the calorific value of the former is 4.3–7.5 times lower than that of the Estonian oil shale sample. These results show the Mongolian Khoot oil shale to be of lower quality than the Estonian oil shale.

The photographic images of Estonian and Mongolian Khoot oil shale samples are shown in the Figure.

It is clear from Table 1 and the Figure that Estonian and Mongolian oil shales differ in characteristics as well as appearance (photographic image). The Estonian oil shale is a “rock-like” sediment of yellow-brown color and the Mongolian Khoot oil shale is a black-green “paper-like” fossil.

The calculated dry ash-free values of the volatile matter of both oil shales (V_daf ≈ 94–97%) are indicative of the low thermal stability of their organic matter.

The results of organic elemental analysis in Table 2 show that the content of C and H of Mongolian Khoot-1 and Khoot-2 samples is lower and that of N and O higher than the respective figures in the Estonian oil shale sample. This organic elemental composition of Mongolian Khoot oil shale is similar to that of oil shale from the Kashpir deposit in Russia [1]. The S content of

![Photographic images](image-url)
all the OS samples under study is similarly low, which is favourable from an environmental point of view. After completely burning the oil shale samples, the mineral elements content of the produced ash was determined. The contents of mineral oxides of ash as established by XRF analysis are presented in Table 3.

The data in Table 3 demonstrate that the ash of Estonian oil shale has the highest content of CaO, while SiO₂ is abundant in the ash of Mongolian Khoot oil shale. At the same time, SiO₂ and Al₂O₃ are present in the ash of Estonian oil shale in moderate quantities, as is the case with Fe₂O₃, CaO and also Al₂O₃ in the ash of Mongolian Khoot oil shale. The content of all the other oxides is similarly low in the ash of both oil shales. The ratio of \((\text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O})/(\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2)\) was found to be more than 1 (2.26) for the Estonian oil shale ash, and less than 1 for the ash of Khoot-1 (0.34) and Khoot-2 (0.35). These results indicate that the ash of Estonian oil shale is alkaline and the Khoot oil shale ash is acidic in nature.

The above results are indicative of that Estonian and Mongolian oil shales greatly differ in physical properties, appearance, as well as organic and inorganic composition.

It is known that oil shale is a suitable raw material for liquefaction of various substances. The pyrolysis and thermal dissolution (hydrogen-donor solvent refining) are two different processes of liquefaction for production of petroleum-like liquid product (as the main product) from solid fossil fuels, including oil shale. For this reason the Estonian and Mongolian oil shale samples were tested in pyrolysis experiments in a small-scale quartz retort to determine the optimal heating temperature for oil shale in the absence of oxygen. The yield of tar (liquid condensed petroleum-like product) as the most important pyrolysis product was determined. The yields of pyrolysis products of oil shale samples (hard residue, tar, pyrolysis water, gas) obtained in pyrolysis experiments at different temperatures and a constant heating rate (20 °C/min.) are given in Table 4.

**Table 3. The mineral composition of ash of oil shale samples**

<table>
<thead>
<tr>
<th>Mineral oxide</th>
<th>Estonian</th>
<th>Mongolian Khoot-1</th>
<th>Mongolian Khoot-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>14.58</td>
<td>63.95</td>
<td>64.48</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.24</td>
<td>0.57</td>
<td>0.66</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>6.78</td>
<td>7.17</td>
<td>11.21</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.41</td>
<td>11.32</td>
<td>16.11</td>
</tr>
<tr>
<td>MnO</td>
<td>0.01</td>
<td>0.33</td>
<td>0.47</td>
</tr>
<tr>
<td>MgO</td>
<td>1.81</td>
<td>2.57</td>
<td>2.07</td>
</tr>
<tr>
<td>CaO</td>
<td>38.78</td>
<td>6.9</td>
<td>4.97</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.12</td>
<td>0.79</td>
<td>0.82</td>
</tr>
<tr>
<td>K₂O</td>
<td>5.65</td>
<td>2.94</td>
<td>3.04</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.04</td>
<td>0.18</td>
<td>0.27</td>
</tr>
</tbody>
</table>
Table 4. The yields of pyrolysis products of oil shale samples obtained in a small-scale quartz retort

<table>
<thead>
<tr>
<th>Oil shale sample</th>
<th>Heating temperature, °C</th>
<th>Heating time, min</th>
<th>Hard residue, %</th>
<th>Tar, %</th>
<th>Pyrolysis water, %</th>
<th>Gas and losses, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Estonian</td>
<td>200</td>
<td>80</td>
<td>99.48</td>
<td>–</td>
<td>0.41</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>80</td>
<td>96.50</td>
<td>0.46</td>
<td>0.95</td>
<td>2.04</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>80</td>
<td>76.90</td>
<td>10.97</td>
<td>1.80</td>
<td>10.31</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>80</td>
<td>65.49</td>
<td>18.79</td>
<td>4.00</td>
<td>11.66</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>80</td>
<td>64.23</td>
<td>23.11</td>
<td>1.68</td>
<td>10.96</td>
</tr>
<tr>
<td></td>
<td>650</td>
<td>80</td>
<td>63.15</td>
<td>17.06</td>
<td>3.44</td>
<td>16.34</td>
</tr>
<tr>
<td>Mongolian Khoot-1</td>
<td>200</td>
<td>80</td>
<td>98.69</td>
<td>–</td>
<td>0.94</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>80</td>
<td>97.25</td>
<td>0.51</td>
<td>0.62</td>
<td>1.61</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>80</td>
<td>96.17</td>
<td>0.91</td>
<td>2.11</td>
<td>0.79</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>80</td>
<td>90.57</td>
<td>2.55</td>
<td>2.50</td>
<td>1.32</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>80</td>
<td>89.99</td>
<td>3.93</td>
<td>0.72</td>
<td>5.35</td>
</tr>
<tr>
<td></td>
<td>650</td>
<td>80</td>
<td>86.85</td>
<td>4.07</td>
<td>1.62</td>
<td>7.44</td>
</tr>
<tr>
<td>Mongolian Khoot-2</td>
<td>200</td>
<td>80</td>
<td>97.59</td>
<td>–</td>
<td>1.73</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>80</td>
<td>97.15</td>
<td>–</td>
<td>2.66</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>80</td>
<td>94.92</td>
<td>0.23</td>
<td>2.34</td>
<td>2.48</td>
</tr>
<tr>
<td></td>
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<td>80</td>
<td>90.89</td>
<td>1.45</td>
<td>3.90</td>
<td>3.74</td>
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<td></td>
<td>600</td>
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<td>88.09</td>
<td>1.64</td>
<td>4.50</td>
<td>5.75</td>
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<td>650</td>
<td>80</td>
<td>86.73</td>
<td>1.44</td>
<td>3.45</td>
<td>8.36</td>
</tr>
</tbody>
</table>

The data in Table 4 show that at the beginning of heating, for example at 200 °C, the yield of hard residue is 97–99% and tar yield 0.0%, which means that the thermal decomposition of organic matter of none of the oil shale samples had not started yet. The yields of pyrolysis water and gas are 0.1–0.3%, which is indicative of the evaporation of adsorbed moisture and gases from the oil shale samples. The thermal decomposition of the samples OM starts in the temperature region of 200–300 °C. The highest yield of liquid products (tar and pyrolysis water) and the lowest yield of hard residue are obtained at 500–600 °C, which can be considered an optimal temperature range for the pyrolysis of oil shale samples. Also, because of its lower ash and higher organic content, the yield of tar (23%) from Estonian oil shale in this temperature region is higher than that from Mongolian Khoot-1 (4%) and Khoot-2 (1.6%) oil shale samples. These results are in agreement with the proximate and ultimate analysis data for all oil shale samples presented in Tables 1 and 2. The lowest tar yield from Khoot-2 can be explained by its lower organic content and higher mineral content in comparison with Estonian and Khoot-1 oil shale samples.

The data in Table 4 also show that the maximum yield of tar and pyrolysis water is obtained at 500–600 °C, decreasing thereafter slightly at higher temperatures, which is indicative of completion of the thermal decomposition of OM of oil shale samples. It is interesting that at temperatures up to 650 °C the yield of gas still increases, which, in our opinion,
is because some gases, for example CO$_2$, may be formed from the CaCO$_3$ and MgCO$_3$ present in the OS inorganic matter.

After determining the optimal heating temperature range, 500–600 °C, 520 °C was chosen as an optimal temperature for pyrolysis of OS samples and at this temperature the next pyrolysis experiments were carried out in a larger-scale retort. The determined yields of hard, liquid and gaseous pyrolysis products of oil shale samples are given in Table 5.

From Table 5 it can be seen that the yields of tar and pyrolysis water obtained upon pyrolysis in the larger-scale retort are slightly higher than those obtained in a small-scale quartz retort (Table 4). At the same time, the yield of gas by pyrolysis in the larger-scale retort is lower than that from pyrolysis in the small-scale quartz retort. These results indicate that the thermal decomposition of oil shale was enhanced and the condensation (during cooling with water) of decomposed steam-gaseous products to liquid products (tar and pyrolysis water) was more effective in the larger-scale retort than in the small-scale quartz device.

The chemical composition of pyrolysis tar (purified from pyrolysis water) of Khoot oil shale was determined by gas chromatography-mass spectrometry (GC-MS), the results were published in our earlier work [8].

The thermal dissolution experiments with oil shale samples in tetralin as a hydrogen-donor solvent were carried out at different heating temperatures by using the method described in the chapter Experimental, the yields of the obtained hard residue, tar and gas are given in Table 6.

The results in Table 6 show that the yield of tar from all OS samples is the lowest at 350 °C, the highest at 400 °C and lower again at 450 °C. Hence, 400 °C can be considered an optimal temperature for the thermal dissolution of OS samples in tetralin. Comparison of these results with those given in Table 4 for pyrolysis demonstrates that the optimal thermal dissolution temperature decreased almost 200 °C against that of pyrolysis carried out in the autoclave, which is more suitable for the thermal decomposition of OS organic matter than the retort. Also the yield of tar from thermal dissolution is higher than that from pyrolysis, because the hydrogen in tetralin favours its formation. Due to its higher organic and lower mineral content, the yield of hard residue from the Estonian oil shale is significantly lower than that from the Mongolian Khoot oil shale.

Table 5. The yields of pyrolysis products of oil shale samples obtained in a larger-scale retort

<table>
<thead>
<tr>
<th>Oil shale sample</th>
<th>Heating temperature, °C</th>
<th>Heating time, min</th>
<th>Hard residue, %</th>
<th>Tar, %</th>
<th>Pyrolysis water, %</th>
<th>Gas, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Estonian</td>
<td>520</td>
<td>80</td>
<td>59.88</td>
<td>30.16</td>
<td>2.99</td>
<td>6.95</td>
</tr>
<tr>
<td>Mongolian Khoot-1</td>
<td>520</td>
<td>80</td>
<td>87.41</td>
<td>5.55</td>
<td>4.79</td>
<td>2.23</td>
</tr>
<tr>
<td>Mongolian Khoot-2</td>
<td>520</td>
<td>80</td>
<td>90.04</td>
<td>3.16</td>
<td>4.39</td>
<td>2.35</td>
</tr>
</tbody>
</table>
Table 6. The yields of hard residue, tar and gas obtained upon the thermal dissolution of oil shale samples in tetralin

<table>
<thead>
<tr>
<th>Oil shale sample</th>
<th>Mass ratio of oil shale:tetralin</th>
<th>Heating temperature, °C</th>
<th>Heating time, min</th>
<th>Yield of hard residue, %</th>
<th>Yield of tar, %</th>
<th>Yield of gas, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Estonian</td>
<td>1:2.8</td>
<td>350</td>
<td>2</td>
<td>85.0</td>
<td>15.0</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>1:2.8</td>
<td>400</td>
<td>2</td>
<td>68.0</td>
<td>32.0</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>1:2.8</td>
<td>450</td>
<td>2</td>
<td>65.0</td>
<td>28.0</td>
<td>7.0</td>
</tr>
<tr>
<td>Mongolian Khoot-1</td>
<td>1:2.8</td>
<td>350</td>
<td>2</td>
<td>95.0</td>
<td>5.0</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>1:2.8</td>
<td>400</td>
<td>2</td>
<td>90.0</td>
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<td>90.0</td>
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<tr>
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4. Conclusions

Based on the study of Estonian and Mongolian oil shale samples, the following conclusions can be drawn:

1. The ash content of Mongolian Khoot-1 and Khoot-2 oil shale samples is twice higher than that in the Estonian oil shale sample. It is for this reason that the content of V$_{\text{d}}$ in Mongolian oil shale samples is also 2–3 times lower than that in the Estonian oil shale sample. Also the calorific value of the former is 4.3–7.5 times lower than that of Estonian oil shale. These results reveal the lower quality of Mongolian Khoot oil shale compared to Estonian oil shale.

2. The oil shale samples studied differ in appearance, as evidenced by photographic images. The Estonian oil shale is a “rock-like” sediment, while the Mongolian Khoot oil shale is a “paper-like” fossil.

3. The calculated dry ash-free value of the volatile matter of both oil shales ($V_{\text{daf}}^\text{d} = 94–97\%$) indicates the low thermal stability of their organic matter.

4. The results of organic elemental analysis demonstrate that in Mongolian Khoot-1 and Khoot-2 oil shale samples the content of C and H is lower and that of N and O higher than the respective figures in the Estonian oil shale sample. The S content of both oil shales is similarly low, which is favorable for the environment.

5. The ash of Estonian oil shale has the highest content of CaO, while SiO$_2$ is the most abundant mineral compound in the ash of Mongolian Khoot oil shale. Moreover, the contents of SiO$_2$ and Al$_2$O$_3$ in the ash of Estonian oil shale and those of Fe$_2$O$_3$, CaO and also Al$_2$O$_3$ in the ash of Mongolian Khoot oil shale are similarly moderate. All the other oxides are present in the ash of both oil shales in similarly low concentrations. The ratio of \((\text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O})/(\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2)\) was calculated to be more than 1 (2.26) for the Estonian oil shale ash and less than 1 for the ash of Khoot-1 (0.34) and Khoot-2 (0.35). This gives
evidence of the alkaline nature of the ash of Estonian oil shale and of the acidic nature of Mongolian Khoot oil shale ash.

6. The thermal decomposition of the organic matter of oil shale samples starts in the temperature region of 200–300 °C. The highest yield of liquid products (tar and pyrolysis water) and the lowest yield of hard residue are obtained in the temperature range of 500–600 °C, which is chosen as an optimal temperature interval for the pyrolysis of oil shale samples. In this temperature region, 23% of tar is obtained from the Estonian oil shale, which is higher than that from both Khoot-1 (4%) and Khoot-2 (1.6%) oil shale. The higher tar yield from the Estonian oil shale sample is due to its lower ash and higher organic content compared to both Mongolian oil shale samples.

7. The yields of tar and pyrolysis water obtained upon pyrolysis in the larger-scale retort are almost the same or slightly increased than those obtained in the small-scale quartz retort. The slightly increased liquid products yields and the decreased gas yield obtained in the larger-scale retort compared to those obtained in the small-scale quartz retort show that the thermal decomposition of oil shale, as well as the condensation of decomposed steam-gaseous products to liquid products are more efficient in the former.

8. The results of thermal dissolution experiments for the three oil shale samples under study show that the yield of tar is the lowest at 350 °C, the highest at 400 °C and lower again at 450 °C. So, 400 °C can be considered an optimal temperature for the thermal dissolution of oil shale samples in tetralin as a hydrogen-donor solvent. This is almost 200 °C lower than the optimal temperature of pyrolysis due to using an autoclave, which is more suitable for the thermal decomposition of oil shale organic matter than the retort. Also the yield of tar from thermal dissolution is higher than that from pyrolysis because the hydrogen from tetralin contributes to its formation.

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