

## LOW-TEMPERATURE SUPERCRITICAL CONVERSION OF KUKERSITE OIL SHALE

MIHHAIL FOMITŠOV\*

Oil Shale Competence Center, Virumaa College, Tallinn University of Technology, Estonia

**Abstract.** *The thermal decomposition of Estonian Kukersite oil shale under supercritical conditions was carried out using a continuous flow tubular reactor. The effects of the retorting times of 0, 30, 60 and 120 minutes on the yield of thermobitumen (TB), solid residue, oil, gas, coke and undecomposed kerogen at temperatures of 390 °C and 420 °C were investigated. The maximum yield of organics was 93.8% by using the benzene solvent at 420 °C. The influence of physicochemical factors on the efficiency of liquefaction under supercritical conditions was studied. The reaction conditions and solvent for maximum extraction were established.*

**Keywords:** *oil shale conversion, thermobitumen, supercritical, solvents, liquefaction.*

### 1. Introduction

Currently, crude oil reserves are depleting, and oil products continue to become more expensive. The use of unconventional fuels, such as oil shale, is considered not only as a source of alternative energy for electricity generation but also as a promising source for producing synthetic liquid fuel and valuable chemical products.

Oil shale is an organic-rich sedimentary rock containing kerogen, a solid mixture of organic chemical compounds, most of which are of high molecular weight (more than 1000 g/mol), some can be extracted easily, and others are probably present in small quantities. Oil shale can be found around the world, including major deposits in the United States, China, Russia, Brazil, Morocco, Jordan, Australia and Estonia [1, 2]. There are approximately 2.8–3.3 trillion recoverable barrels of oil in oil shale deposits across the world. These contain at least three times more oil than conventional crude oil reserves, which are estimated to be approximately 1.2 trillion barrels [1, 3].

---

\* Corresponding author: e-mail [mihhail.fomitsov@taltech.ee](mailto:mihhail.fomitsov@taltech.ee)

Oil shale is a dense-layered rock of sedimentary origin, having an ash content of at least 33 wt% of organic matter (OM) and volatiles. Heating oil shale causes thermal decomposition of organic matter to produce tar that is not collected in appreciable amounts during extraction [4]. The main indicators of quality and technological properties that determine the practical significance of oil shale are related to the content of organic matter. Oil shales of different deposits differ significantly in many aspects such as appearance, composition and properties. [1] The specific feature of combustible shale is the interbedding of organic-rich and -poor layers.

Normally, in oil shale deposits, the mineral part significantly predominates over the organic matter portion [5–7]. The main groups of minerals are carbonates (mainly calcite and dolomite), silicates and aluminosilicates (primarily hydromica, mica, feldspars, montmorillonite and kaolinite), quartz and sulfides (mostly pyrite) [3]. There are also various sulfates, phosphates, sometimes halides, amorphous silica and other minerals present in oil shale.

## 2. Thermal decomposition

The thermal decomposition process of kerogen macromolecules resembles that of polymers, with fundamentally similar structural features [3, 8, 9]. When oil shale is heated, a certain part of organic matter transforms into a fusible and soluble state, the so-called thermobitumen (TB) and other products [9] as indicated in Table 1. The release of volatiles and other products due to kerogen thermal decomposition at different temperatures during oil shale heating is also given in Table 1.

Thermobitumen is formed in a wide range of temperatures, 300–450 °C [10–12]. The output and composition continuously change since the decomposition reactions of thermobitumen proceed in parallel with its formation step. The final products of semicoking are formed both directly from kerogen and during transformation of thermobitumen. Oil shales of different deposits are characterized by varying degree of bituminization.

**Table 1. Stages of thermal decomposition of kerogen**

Temperature range, °C	Process
100 to 105	Evaporation of moisture (drying step)
170 to 180	Release of absorbed gases
270 to 290	Release of pyrogenetic water, CO <sub>2</sub> and SO <sub>2</sub>
325 to 350	Extraction of tar and hydrocarbon gases
325 to 390	Main stage of thermobitumen formation
420 to 450	Active point of thermal decomposition
450 to 500	Semicoking ends
> 500	Secondary pyrolysis processes of semicoking products

The most important factors affecting the yield and properties of shale distillation products are temperature, rate of heating, conditions of evacuation of the steam-gas mixture, reaction gaseous environment and system pressure [4, 13, 14].

The gaseous environment has a great influence on the degree of semicoking of solid fuels and this is especially sharply manifested under high pressures. Thus, the use of elevated pressure is an effective means of influencing the process and associated chemical reactions. These factors can be used in organizing the directional semicoking of solid fuels.

### 2.1. Oil shale characteristics

The results of Fischer Assay, elemental and associated analysis of raw oil shale are presented in Table 2.

**Table 2. Fisher Assay, elemental and associated analysis of raw oil shale**

Parameters (on dry basis)	Wt%
Fischer Assay	
Oil content	17.6
Semicoke	76.0
Pyrogenetic water	1.1
Gas + losses	5.3
Heat of combustion, MJ/kg	10.192
Ash, at 815 °C	51.7
Volatiles	47.8
Organic matter, OM = 100 – (CO <sub>2</sub> + ash)	27.6
OM residue after pyrolysis in Fischer retort at 520 °C	4.7
Carbon dioxide, (mineral)	20.7
Elemental analysis (C, H, N)	
C	28.0
H	2.8
N	0.075
Organic carbon	22.3
Inorganic carbon	5.7
Total sulfur	1.66
Organic sulfur	0.48
Sulfur in pyrite	1.14
Sulfur in sulfates	0.04

### 3. Experimental

The main objective of the experimental work is to explore the possibility of maximizing the extraction of organic matter from oil shale through continuous distillation of shale by action of solvents in inert nitrogen gas stream environment at the stage of thermobitumen formation [9]. The critical parameters of solvents employed are as follows: benzene 562 K (289 °C) and

4.89 MPa, methanol 513 K (240 °C) and 7.85 MPa, and water 647 K (374 °C) and 21.78 MPa.

A Parr Instruments installation as depicted in Figure 1 was used to investigate oil shale thermal decomposition in supercritical conditions. The installation consists of a high-pressure vertical tubular reactor, 400-ml volume (1) with external heating, a water cooler (2) and a 2-litre vessel for collecting products (3) where the gas-liquid mixture is separated. During the process, it is possible to feed any solvent/liquid by using a high-pressure pump to remove products from the reaction zone.

The liquid product is collected, excessive pressure and generated gases are discharged through a valve (7). The adjustable process parameters are temperature, heating rate (PID controller), pressure (gauge and back pressure regulator), gas consumption rate (needle valve and flow meter) and solvent consumption rate (liquid high-pressure piston pump).

Oil shale particle size fraction of 2–4 mm was placed in the reactor, and then heated to the desired set temperature (390 or 420 °C). The solvent pumping flow rate of 3 ml/min was achieved as soon as the predetermined temperature was attained. The oil shale sample was kept in the solvent vapor under supercritical conditions for various times (60 and 120 minutes). In one set of experiments, the solvent was injected in the reactor immediately, i.e. starting at room temperature until reaching the specified temperature followed by rapid heating (indicated by zero time). After the reactor was cooled, the reaction products (solid residue and oil) were collected and analysed.

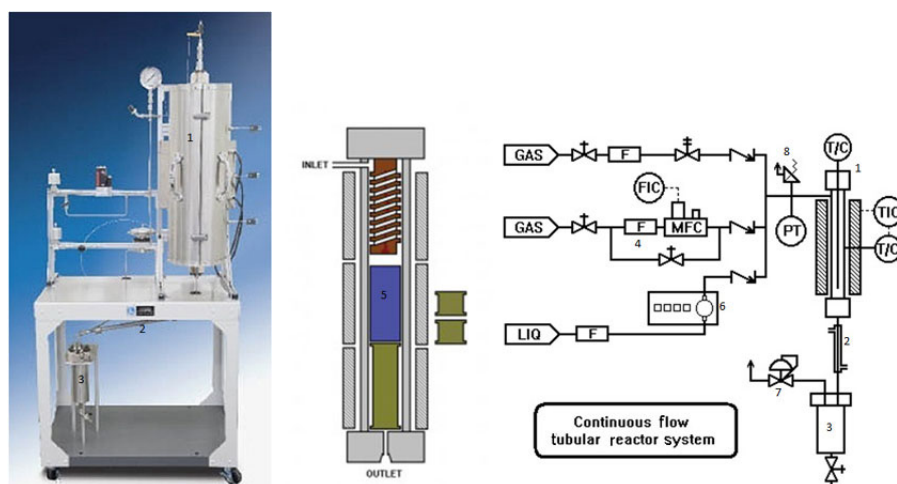


Fig. 1. Parr Instruments installation: 1 – tubular reactor; 2 – condenser; 3 – gas-liquid mixture separator; 4 – gas compressor; 5 – raw material collector; 6 – high-pressure piston liquid pump; 7 – back-pressure regulator; 8 – safety valve.

The tubular-reactor experiments measured the thermobitumen extracted from the reacted mass by solvent immediately after its stage of formation [6, 9, 15].

A rotary evaporator was used to remove solvents from the product mixture which was composed mainly of thermobitumen and solvent. Since TB is a chemically active intermediate product, reduced pressure (25 mbar) was used to lower the evaporation temperature and shorten the reaction time. The quantity of extracted organics was calculated by the difference between total organic matter in raw material and solid residue organic content.

#### 4. Results and discussion

The results obtained under various pyrolysis conditions, such as time duration, solvent type and reaction temperatures, are presented in Table 3. Operation conditions play a decisive role in shaping the properties of the final products of shale and largely determine their yield. The components of the primary gas-vapor mixture are thermolabile and prone to further thermal transformations, mainly in the direction of compaction or polymerization of liquid products.

It can be seen from Table 3 that the maximum yield of organics from Kukersite oil shale was obtained using benzene solvent as shown in Figure 2 at a temperature of 420 °C. The figure reveals that at the reaction temperature of 420 °C, increasing time onstream increases the weight percent of solid residue for benzene and methanol solvent, whereas for water, the weight percent of total organic carbon (TOC) residue decreases when the reaction time is increased. It is apparent that increasing reaction time for super extraction allows the extracted thermobitumen to transform to other more unextractable stable products. For the water extraction process, increasing time onstream increases the extracted amount.

**Table 3. Experimental conditions and data**

Component	Temperature, °C	Isothermal reaction time, min	Solid residue, % mass	Ash of solid residue, % mass	TOC of solid residue, % mass
Benzene	420	0	74.25	77.18	2.9
Water	420	0	77.39	74.16	4.9
Methanol	420	0	74.70	76.90	3.3
Benzene	420	60	76.46	75.19	4.3
Water	420	60	76.45	75.15	4.4
Methanol	420	60	77.07	74.53	4.5
Benzene	420	120	76.18	75.36	4.5
Water	420	120	75.96	75.65	4.1
Methanol	420	120	76.57	75.05	4.2
Benzene	390	30	77.04	74.55	4.7
Water	390	30	79.39	72.15	5.9
Methanol	390	30	78.17	73.42	4.2

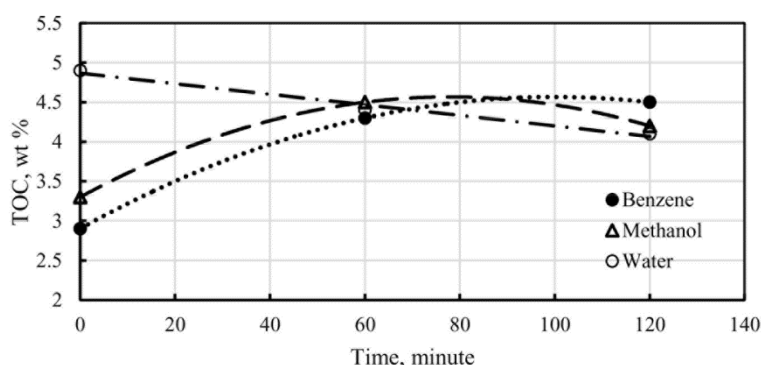


Fig. 2. Effect of the reaction time on solid residue extraction at the constant reaction temperature of 420 °C.

Also, it is clear from Figure 2 that the amount extracted is almost constant at 60 minutes of time onstream irrespective of the solvent used, being between 4.3 and 4.5 wt%. A similar trend is also observed at 120 minutes with slightly greater differences between the extracted amounts. These observations are clear for benzene and methanol solvents whereas the water solvent showed a linear decrease with time onstream at the constant reaction temperature of 420 °C.

The rate of the gas-vapor mixture removal from the reaction zone of high temperatures increases the yield of the resin and reduces its degree of compaction, as confirmed by the results of this work. A shorter time at a higher temperature affords a higher yield of the desired product.

The maximum yield of organics was found to be 93.8% (based on total organic matter) in the tubular flow reactor using benzene as a solvent during liquefaction at 420 °C.

During benzene flow through the tubular reactor, the physical interactions and chemical reactions start before reaching maximum temperature, which prevent an additional decomposition of oil shale and thermobitumen to gaseous products, oil and coke. This resulted in 15% higher yield than the yield obtained in the same conditions by using Fischer retort and subsequent TB extraction with a suitable solvent [16].

In this work, the basis for a new supercritical extraction technology is described where TB is extracted with organic solvents and/or water in the thermobituminization stage. It has been found that more than 85% of organic matter can be liquefied, and the demand for oil shale and the amount of hazardous semicoke wastes per unit oil shale can be both substantially decreased. Thermobitumen is a chemically active intermediate product, and its yield exceeds maximum under conditions of optimum temperature and time duration. The composition of TB depends on the pyrolysis conditions and changes during storage.

A method has been developed for the liquefaction of organic matter of oil shale, including low-calorific value, at low temperatures in an environment of low-boiling temperature solvents (benzene, water, alcohol).

Unlike liquefaction in the liquid phase (for example, tetralin), the resulting product is released from the system in the gas/vapor phase and, therefore, separation of oil from the solid residue does not pose any difficulties.

Recovery of OM in oil shale is important economically and ecologically. The dependence of TB on oil yield, bituminization temperature and residence time demonstrates that higher temperatures make TB and oil more easily extractable from the solid residue, with a higher loss of OM to solid coke. On the other hand, it is clear that more oil is extracted with shorter reaction times at higher temperatures.

Under certain conditions of solvent extraction, organic compounds (thermobitumen) more easily dissolve in the pores and reduce the strength of donor-acceptor interactions between individual fragments of the organic polymer matrix, which contributes to milder thermal decomposition conditions.

## 5. Conclusions

Treating oil shale under supercritical vapour steam allows for more rapid removal of products from the reaction zone, avoiding their further decomposition to gaseous products and coke. Additionally, solvent vapours reduce the temperature gradient between the outer surface and the inner part of the particle, eliminating diffusional influences and enhancing heat transfer, which eventually results in a dynamic extraction process. Fast pyrolysis and withdrawal of solvent vapours from the thermal processing zone enhance organic matter extraction.

## REFERENCES

1. *Oil Shale. Spheres of Use of Combustible Shales. Characteristics and Indicators of the Quality of Oil Shale.* <https://knowledge.allbest.ru/physics/c-2c0a65635b3ac68b4d43b89521316c36.html>, accessed on 24.10.2017 (in Russian).
2. *Enefit. What is Oil Shale?* 2014. <https://enefitutah.com/project/what-is-oil-shale/>, accessed on 01.10.2018.
3. SA Innove. *Chemical Technology: A Training Manual for Chemical-Technological Specialities of Professional Centers*, 2012 (in Russian).
4. Muratov, V. N. *Geology of Caustobioliths*. Moscow, 1970 (in Russian).
5. *Handbook of Oil Shale.* (Rudin, M. G., Serebryannikov, N. D., eds.). Khimiya, Leningrad, 1988 (in Russian).
6. Strizakova, J. A. *Development and Improvement of the Processing of Oil Shales to Produce Valuable Chemical Products and Components of Motor Fuels.* PhD Thesis, Ufa, 2011. <http://www.dislib.ru/himiya/18301-1-razvitie->

- sovershenstvovanie-pererabotki-goryuchih-slancev-s-polucheniem-himicheskikh-produktov-komponentov-motornih-topliv.php ,accessed on 17.03.2018 (in Russian).
7. Knowlton, F. H. *The Laramie Flora of the Denver Basin*. United States Geological Survey, Professional Paper 130, Government Printing Office, 1922, 121–122.
  8. Johannes, I., Tiikma, L., Zaidentsal, A. Comparison of the thermobituminization kinetics of Baltic oil shale in open retorts and closed autoclaves. *Oil Shale*, 2010, **27**(1), 17–25.
  9. Pavlusha, E. S. *Thermal Dissolution of Oil Shales in the Supercritical Fluids*. PhD Thesis, Kemerovo, 2012 (in Russian).
  10. *Composition and Properties of Oil Shales*. <http://www.studsell.com/view/34107/>, accessed on 28.08.2018 (in Russian).
  11. Dyni, J. R. *Geology and Resources of Some World Oil-Shale Deposits*. Reprint of USGS Scientific Investigations Report 2005-5294. <https://geology.com/usgs/oil-shale/>, accessed on 03.03.2018.
  12. Tiikma, L., Sokolova, Yu., Vink, N. The effect of organic matter on the output of thermobitumen from the Baltic oil shale kukersite. *Solid Fuel Chemistry*, 2010, **2**, 25–30 (in Russian).
  13. Chistyakov, A. N. *Chemistry and Technology of Processing of Coal Tar*. Training manual for universities. Metallurgy, Chelyabinsk, 1990 (in Russian).
  14. Zelenin, N. I., Fainberg, V. S., Chernysheva, K. B. *Chemistry and Technology of Shale Tar*. Khimiya, Leningrad, 1968 (in Russian).
  15. Efimov, V. M., Piik, E. E., Rappu, L. I. On some features of thermal processing of rich bituminous shales. In: *Chemistry and Technology of Oil Shales* (Proceedings of the Scientific Research Institute of Shales), 1973, **19**, 36 p (in Russian).
  16. Fomitšov, M. *The Possibility of Extraction of Oil Shale Organic Material During Bitumen Formation Stage*. MSc Thesis, Tallinn University of Technology, 2014.

Received January 13, 2019