

Investigation of the Properties of Products of Estonian Oil Shale Decomposition through the Bitumen Stage

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Abstract

Aspects of applying bituminization in the temperature range 370–410 °C to Estonian oil shale as the preliminary stage to hydrogenation process are described. The obtained products of the bitumen stage are compared with products produced by present technologies of oil shale thermal treatment. The bitumen stage of Estonian oil shale as a step toward possible combined use of oil shale for energy and chemical products as Best Available Techniques (BAT) are provided in a schematic diagram. The obtained products are compared at different conditions of the bituminization process in the laboratory retort.

Technology

In Estonia, retorting or semicoking of oil shale is the main process of thermal treatment to produce shale oil. The retorting is accomplished in two different forms, either processing lump oil shale with a gaseous heat carrier, or processing small particle size shale oil with a solid heat carrier. The principal differences between the processes include the method of oil shale drying, the use of different heat carriers, and different handling of retorting residue (combustion and partly gasifying). Updated technology combines the two developed technologies for retorting both big and small particle size oil shale. This technology would achieve the best solution with practically clean solid waste and no gaseous CO₂ emission. Heat carrier flow would be combined in an efficient way, as well as joint gasification and condensation, and oil, gas and water processing units. Gas will be converted to synthesis gas and then to liquids using the Fisher-Tropsch process.

In addition to the above-mentioned retorting technology, developments are provided with influence on the solid fuel high temperature (~800 °C) heat carrier, during which a considerable part of the oil shale

organic matter cracks to gas and carbon, as well as a low yield of liquid products.

In the oil shale industry the retorting temperature is 500-550 °C. The yield of oil is about 60% of organic matter (OM), which could be increased by decreasing the process temperature to minimize secondary processes during oil formation. However, at the same time the content of organic compounds in the retorting residue increases. TOC content in semicoke is up to 14%. Spent shale contains harmful constituents: cancerogenic polyaromatics (2.6-9.8 mg/kg), and water soluble sulfides (0.3-1.1 g/kg). Additional CO₂ emissions are formed by burning retorting residue. An added perspective for direct liquefaction of the organic matter could be the hydrogenation process, developed in coal processing technology.

Coal hydrogenation technology consists of these main stages:

- Drying of solid fuel
- Two stage hydrogenation of the paste of solid fuel with oil fraction, using iron-based catalyst
- Liquid product extraction
- Hydrogenation of the liquid product to obtain the necessary quality end products (*e.g.*, engine fuels)

Co-retorting of lump oil shale and oil shale fines

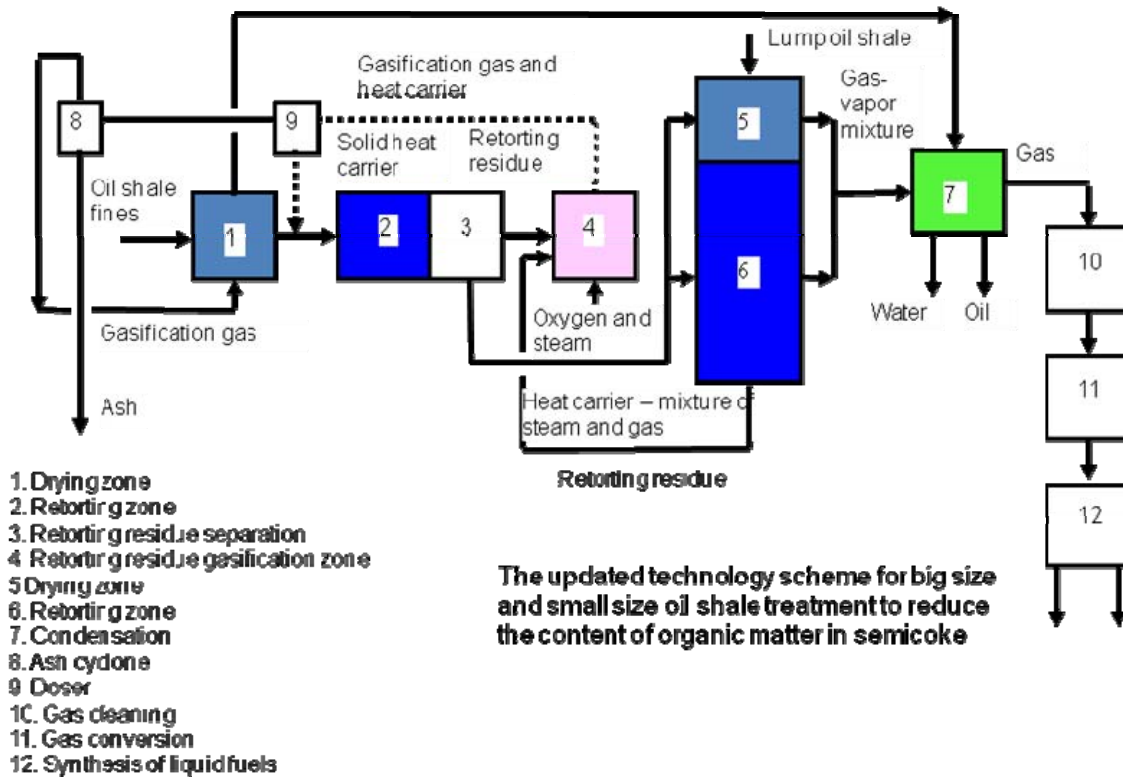


Figure 1: Co-retorting of lump oil shale and oil shale fines

In practice there are strict requirements for feed of hydrogenation processes: water content: 1.0-1.5%; mineral (ash) content: 10-12%; oxygen content: 12-13%.

Preparation of solid fuel with high ash and oxygen content (characteristic of oil shale before the hydrogenation process) under thermal solution could be performed under pressure and temperature $t=380-450\text{ }^{\circ}\text{C}$, with H_2 or an H_2 -donor (for example tetralin) added, which could be the preliminary stage of the hydrogenation process. The yield of liquid products could be 60-90 % of solid fuel. The basis of our investigation is the property of oil shale to form a bitumen stage. Many kinds of solid fuels go through the bitumen stage under thermal treatment. The formation of a soluble state of Estonian oil shale in organic solvents occurs in the temperature range $350-420\text{ }^{\circ}\text{C}$ and the separation of organic matter from the mineral part could

take place. To begin to investigate this possibility, experiments to prepare oil shale for hydrogenation through the bitumen stage were done in a laboratory.

Laboratory Experiments and Results

The general scheme of the laboratory experiments is shown in Figure 2. An analytical sample of oil shale (50 g) was charged into the Fischer's retort and heated to $370-410\text{ }^{\circ}\text{C}$. Isothermal retention intervals were 20, 30 and 60 minutes. During the experiment the following products were formed: oil, thermobitumen, solid residue, gas, and pyrogenetic water. Thermobitumen was extracted from the solid residue by ethanol-benzene mixture and after solvent regeneration thermobitumen was subjected to thermal decomposition experiments. Analytical instrumental methods were used to analyze the obtained products. Initial oil shale contained 32% OM. Solvent was evaporated on a

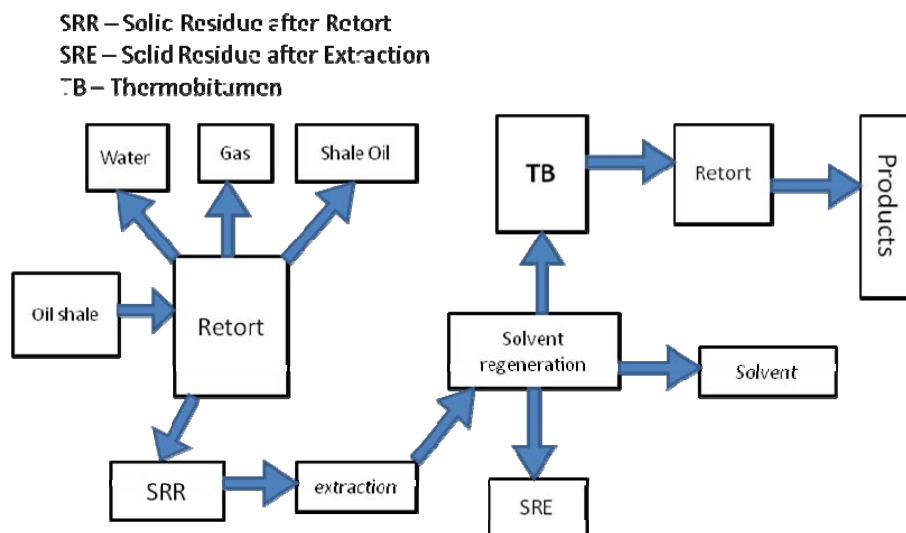


Figure 2: Principal scheme of laboratory experiments

glycerol bath and dried to constant weight in a vacuum drying box. Thermobitumen used in thermal decomposition tests was obtained under conditions of its maximum yield from oil shale.

Material balance for each experiment was compiled on the basis of three parallel experiments conducted at specified temperature and isothermal retention times. Table 1 shows extracted thermobitumen yield as percent of oil shale organic matter.

Table 1: Material balance of thermobitumen and oil on OM

T °C	Time	TB on OM	Oil on OM	TB+Oil on OM
370	20	25.90	8.65	34.55
380	20	55.29	19.27	74.56
390	20	61.61	23.10	84.71
400	20	60.40	28.15	88.55
410	20	58.90	30.12	89.02
370	60	55.11	23.07	78.18
390	60	57.00	32.51	89.51
410	60	47.80	36.66	84.46
380	30	58.00	22.38	80.38
390	30	62.10	27.86	89.96
400	30	56.90	30.39	87.29
410	30	54.90	31.73	86.63

The data in Table 1 show that the maximum amount of conversion products (oil+TB) is formed at 390 °C and isothermal retention time of 30 minutes. For maximum product yield at lower temperatures, the retention time should be increased and vice versa. Table 2 presents the material balance of tests in the retort, which distinctly show the rise in oil and gas yields with increased temperature.

Figure 3 represents the potential liquid product yield formed via thermobitumeni-

Table 2: Material balance of retort

T °C	Time	Oil	Solid Residue after Retort	Water	Gas+ Losses
370	20	1.4	96.6	0.6	1.4
380	20	2.6	94.4	0.8	2.2
390	20	4.6	92.5	1.0	1.9
400	20	7.8	88.2	1.2	2.8
410	20	11.1	85.2	1.4	2.4
380	30	3.6	93.8	0.7	1.9
390	30	4.4	92.8	0.5	2.2
400	30	10.3	86.3	1.0	2.4
410	30	14.2	81.4	1.2	3.2
370	60	7.2	88.9	0.9	3.0
390	60	10.5	85.3	1.0	3.2
410	60	16.5	79.0	1.6	2.9

zation extraction stage. The blue curve (circles) shows product yield at temperatures 380-410 °C and retention time 20 min, the red curve (squares) at 30 min and the green curve (triangles) at 60 min.

Elemental composition of thermobitumen obtained under different temperatures and different isothermal times is presented in Table 3. Carbon content in thermobitumen is in the range of 76-82% and hydrogen content 9-10%. These values depend on

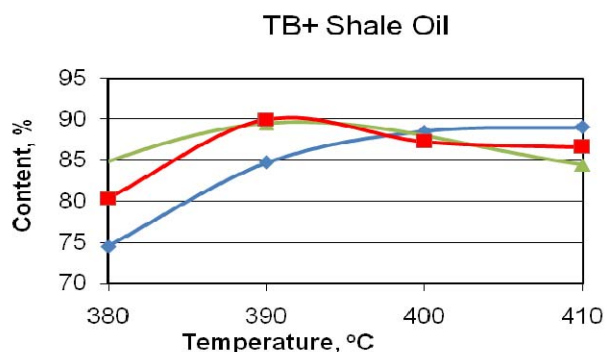


Figure 3: Potential liquid product yield. Blue line – 20 min, red – 30 min, green – 60 min.

Table 3. Elemental composition of thermobitumen

T (°C)	Isothermal time, min	Element					rate C/H
		C	H	N	S	O	
370	20	76.4	9.7	0.26	0.9	12.74	7.87
380	20	79.5	9.9	0.30	0.8	9.50	8.03
390	20	80.3	9.5	0.27	0.8	9.13	8.45
400	20	81.1	8.9	0.25	0.6	9.15	9.11
410	20	81.2	8.8	0.26	0.7	11.00	9.22
370	60	80.8	9.2	0.27	0.6	9.16	8.78
390	60	82.5	8.8	0.26	0.7	7.74	9.38
410	60	83.2	8.9	0.28	0.6	7.02	9.35
380	30	79.7	9.6	0.30	0.7	9.70	8.30
390	30	81.3	9.1	0.27	0.8	8.53	8.93
400	30	81.6	9.3	0.23	0.5	8.37	8.77
410	30	82.1	8.9	0.24	0.6	8.16	9.22

experimental conditions.

The IR-spectrum of thermobitumen was obtained at 390 °C and retention time 30 min. The spectrum peaks reveal the presence of aromatics, aliphatic and carbonyl compounds as well as alkanes and phenols (Figures 4, 5). Comparison between spectra of oil formed at the oil shale bitumenization stage and oil formed in the Fischer retort reveals that the phenol peak of the first is less intense than that of the second (Figure 6).

It is caused by less intense breakage of oxygen bridges during thermobitumen formation than in the course of standard oil shale retorting when the final temperature is 520 °C. Also it is noticeable that oil from the bituminization stage contains more paraffin hydrocarbons because the rate of aromatic hydrocarbon formation is not as high in this temperature range as in the Fischer retort standard test.

Elemental compositions of three oils obtained from standard oil shale retorting, from thermobitumenization, and from thermobitumen decomposition are shown

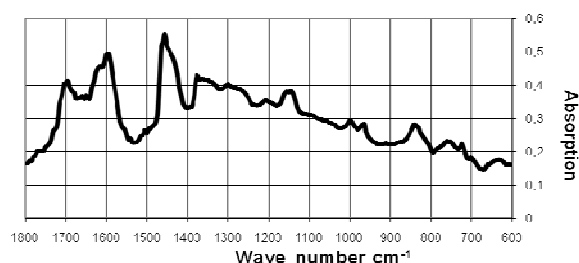


Figure 5. IR-spectra of thermobitumen from 600 to 1800 cm⁻¹.

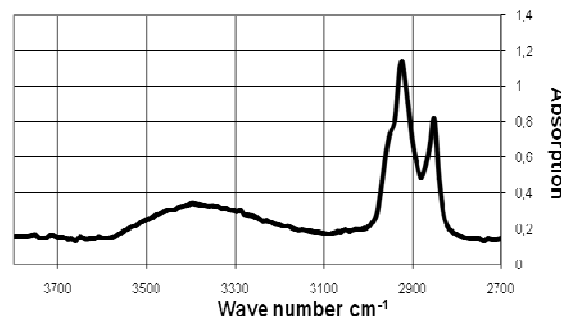


Figure 4: IR-spectra of thermobitumen from 2700 to 3700 cm⁻¹.

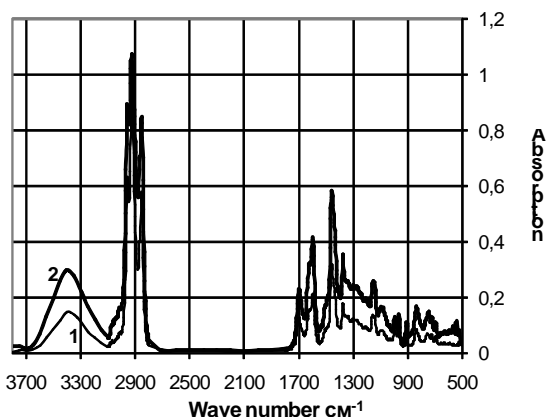


Figure 6: IR spectra comparison of shale oil of standard process (2) and shale oil obtained at bitumen process (1)

in Table 4. Table 4 data show that hydrogen content in oil from thermobitumenization is higher than in the other oils because of higher content of saturated hydrocarbons in the oil. Lower hydrogen content in the two other oils is attributed to hydrogen redistribution reactions at higher temperatures and formation of unsaturated hydrocarbons from paraffin hydrocarbons by cracking reactions.

Group compositions of oils derived from oil shale retorting in the Fischer retort and from thermobitumen decomposition are presented in Table 5.

Considerably fewer aromatic hydrocarbons

Table 4: Elemental composition of shale oils.

Product	Element				
	C	H	S	O+N	C/H
Shale oil produced in Fisher assay, %	81.20	10.1	0.6	8.0	8
Shale oil of thermobitumen decomposition, %	80.20	9.6	0.3	9.9	8.3
Shale oil of thermobitumen formation stage, %	82.52	12.04	1.31	4.13	6.9

Table 5. Shale oil group composition of standard process in Fisher assay and thermobitumen treatment.

Sample	Group content of hydrocarbons and oxygen compounds, %		
	Paraffin & olefin compounds	Aromatic hydrocarbons	Oxygen compounds
Shale Oil of std. process in Fisher assay	44	30	26
Shale Oil of thermobitumen treatment	29	38	33

are formed in the process of oil shale retorting in one stage. Comparison of the oils shows that production of liquid products by two stage thermal processing leads to formation of more aromatic oil.

Conclusion

Estonian oil shale decomposition through the bitumen stage could be a process by which the liquefaction of organic matter in the low temperature range obtains a higher yield of liquid products compared to existing technology. Comparison of oil shale retorting and thermal treatment through the bitumen stage shows that organic matter is transferred at relatively low temperatures to soluble formation in organic solvents. It gives the chance to separate the organic part from the mineral part and prepare organic matter of oil shale for a hydrogenation process. The yield of liquid products could be up to 90%.