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REVIEW

OIL SHALE PROCESSING IN ESTONIA AND RUSSIA

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In the present paper historical review is given on the development of the oil shale processing industry in Estonia and Russia, including information on the use of different processing retorts for the production of shale oil and shale-derived domestic gas. Volumes of oil shale retorting and of the products manufactured are given. Technical potential for further development of commercially viable retorting technologies for low-temperature processing (semicoking) of large-particle and fine-grained oil shale is also shown. A practically ecologically clean technology of semicoking large-particle oil shale has been developed.

Oil shale is widely distributed in many parts of the world with known deposits in all continents. Although its extensive use has been delayed so far because preference was given to petroleum, coal and other traditional fuels, oil shale is regarded to date as an important alternative source of hydrocarbons and chemicals. The most thoroughly studied and in large-scale commercial use is the Baltic oil shale (kukersite) found in Estonia and Russia (Leningrad District). In 1998 mining of kukersite totalled 16 million tons (14 in Estonia and 2 in Russia). By 1981 the amount of mining reached 36 million tons (31 in Estonia and 5 in Russia). At present the major portion of the mined shale in Estonia is used as fuel for two large electric power plants having a capacity of 1,600 megawatts each, and excess of 3 million tons is retorted annually to produce shale oil and gas (including 2.5 million tons of large-particle shale and 0.5 million tons of shale fines).

However, kukersite as a feedstock for thermal processing possesses a number of specific properties complicating the semicoking process, such as a strong tendency to caking, i.e. transition into a plastic state by heating slowly at 350–400 °C, a high moisture content (8–10 %), a relatively low mechanical and thermal strength, and a high content of carbonates (40–50 %), the decomposition of which consumes some 20 % of the total heat required for the semicoking process. The decomposition of carbonates results in the formation of free calcium oxide which in contact with organic oxygen compounds in the volatile products has a negative effect on the yield and composition of the product shale oil.

One oil shale processing plant in Russia is located at Syzran (Samara District). Here very small amounts of shale from the Kashpir Deposit are processed (about 20 thousand tons per year); it is the only enterprise having any industrial experience in processing high-sulfur oil shales. The limited scale of processing of Volga Basin shales is due to a high content of sulfur in the product oil that makes it unusable as a liquid fuel. Only a limited assortment of products, including mainly those for medicinal use, such as sulfikhton, albikhtol, etc., is produced at this plant. These pharmaceuticals are extremely important in veterinary practice, but since they are needed only in negligible amounts, they cannot serve as justification for large-scale oil shale processing.

Typical properties of oil shale from Baltic and Volga basins are given in Table 1.

To obtain shale oil from the oil shale of the Baltic and Volga basins retorts of different design have been used at different periods since the start of commercial shale oil production (Tables 2 and 3). To date, thanks to the simplicity of design, high reliability in operation and relatively high performance data, the predominant type currently in commercial operation is continuous operating vertical retorts traditionally referred to as generators – the *Kiviter* process.

Table 1. **Properties of Oil Shale from Baltic and Volga Basins**

Indices	Oil shale deposits		
	Estonian, kukersite	Leningrad, kukersite	Kashpir
Moisture content, %	10	9	20
Content (dry basis), %:			
Carbon dioxide $(CO_2)^d{}_M$	18	20	8
Ash A^d	46	49	65
Organic matter*	36	31	27
Total sulfur $S^d{}_t$	1.80	1.50	3.70
Including:			
Sulfate	0.04	0.06	0.18
Pyrite	1.30	1.10	1.57
Organic (by difference)	0.46	0.34	1.95
Fischer assay oil yield, %	24.3	21.3	9.0
Heating value (bomb calorimeter), MJ/kg	13.8	12.0	8.5
Ash composition, %:			
SiO_2	30	26	38
Fe_2O_3	5	6	14
Al_2O_3	7	6	15
K_2O	2	2.5	3
Na_2O	0.5	0.5	2
MgO	4	3	1
CaO	45	48	20
SO_3	5.5	5	5
Total	99.0	97.0	98

*Here and hereinafter the organic matter content is equal to: $100 - (CO_2)^d{}_M - A^d$.

Table 2. **Start-up of Oil Shale Processing Units in Estonia**

Unit	Throughput rate, t/day	Number of retorts/ ovens	Start-up	Cease of operation
Kohtla-Järve, *Kiviter* AS*				
Experimental vertical retort (generator)	7	1	3.08.21	December, 1924
GGS-1	33	6	24.12.24	30.07.85
GGS-2	40	8	31.03.36	30.07.85
GGS-3	40	16	28.05.38	August, 1998
GGS-4	45	20	1943	
Commercial-scale experimental retort	100	1	1946	1955
GGS-5	100	12	22.07.51	
Chamber ovens	15	276	5.11.48	August, 1987
Tunnel ovens	400	2	1956	1968
First 1,000 ton-per-day retort	1,000	1	18.01.81	
GGS-6	1,000	2	18.01.87	
Kiviõli, *Kiviter* AS				
Experimental tunnel oven section		1	1926	In the 1930s
Commercial-scale experimental tunnel oven	75	1	1927	
Commercial tunnel oven	250	2	1931	The last oven was closed down in 1975
	350	2	1935	
GGS	100	4	Sept.–Oct., 1953	
		2	1954–1956	
		1	June, 1962	
		1	November, 1963	
Solid-heat-carrier units (SHC):				
SHC-200	200	1	29.10.53	1963
SHC-500	500	1	November, 1963	1.07.81
Sillamäe				
Commercial tunnel ovens	270	1	1928	Mostlikely during World War II
	500	1	1938	
Kohtla-Nõmme				
Davidson horizontal rotary retorts	25	4	1931	1961
		4	1934	1961
Narva, Estonian Power Plant				
SHC-3,000	3,000	2	30.06.80	

* *Kiviter* joint-stock company.

Table 3. **Operational History of Oil Shale Processing Units in Russia**

Unit	Throughput rate, t/day	Number of retorts/ovens	Start-up	Cease of operation
		Slantsy, Leningrad District		
Vertical retorts (generators)	100	36	1952	
Chamber ovens	15	276	1951	January, 1997
		Syzran, Samara District		
Retort ovens	25	8	1932	1950
Vertical retorts (generators)	30–33	8	1942–1950	

The development of vertical retorts in Estonia has a comparatively long and most instructive history. The first attempts made in the 1920s to process kukersite in the *Rolle* retorts, the *Geissen* kilns, and the *Scottish* retorts, known for their efficient performance for a number of decades in the Scottish oil shale industry, were unsuccessful because of the caking properties of kukersite. On the other hand, test runs in *Pintsch*-designed experimental retort with a throughput of 7 tons per day erected at Kohtla-Järve in 1921 showed promising results. An oil yield of 18 % from the feed shale was attained. However, taking into account that at that period mostly high-organic oil shale was used for retorting (organic content 43–46 %, dry basis), the oil yield obtained could not be regarded as sufficiently high (77 % of Fischer assay oil).

Based on positive results obtained by testing the retort, already in 1921 *J. Pintsch A/G* began to design the first oil shale retorting plant at Kohtla-Järve which consisted of six retorts with a throughput of 33 t/day each (later named GGS-1: gas generator station). The *Pintsch*-type retorts where the retorting zone was separated from the gasifier by a narrowed shaft at the mid-height were selected for the first plant. The air needed for processing was drawn in through the lower part of the retort by vacuum maintained within the whole reaction volume [1, 2].

In December 1926, GGS-1 was commissioned into full commercial operation. A two-week balance test run gave the following results: average throughput of oil shale 33.4 t/day, plant oil yield 17.3 % from feed shale (68 % of Fischer assay oil), specific gas yield 690 m^3/t^* (incl. 20.6 g/m^3 C^+_5 hydrocarbons) with a calorific value of 4.86 MJ/m^3.

The demand for liquid fuels increased considerably in the early 1930s as a result of the beginning economic crisis. The state Oil Shale Works began to intensively search for opportunities of introducing new retorting capacities as fast and least expensive as possible. Under these circumstances local specialists led by K. Luts developed a new *Kohtla-Järve* design of a cylindrical retort without the narrowed shaft for an oil shale throughput rate of 37–38 t/day. The units GGS-2 and GGS-3 were equipped with such retorts [2, 3]. The construction of a new plant (GGS-4) was started in 1943;

* Here and hereinafter all characteristics of gas are given at 20 °C and 760 mm Hg.

the *Pintsch*-type retorts with a design capacity of 37–40 t/day were again selected for this purpose, but this time with more complete control of the process that enabled to obtain higher oil yields [3].

At the Kiviõli and Sillamäe plants tunnel ovens were selected for processing of oil shale, where the retorting process was carried out in steel oven-trucks. The tunnel ovens enabled to obtain oil with a higher content of gasoline fractions in the oil (up to 20 vol.%). Owing to the use of the gas and oil vapors formed in the tunnel oven process as circulating gaseous heat carrier heated in heat exchangers (superheaters) the plant oil yield reached that of the Fischer assay. In addition, about 1 % (on the initial feed shale) of light gasoline was recovered in a refrigerating plant. The calorific value of the product gas with a specific yield of 20–30 m^3/t was about 33.5 MJ/m^3 (excl. 20–25 g/m^3 of C^+_5 hydrocarbons that remained in the gas after light gasoline separation) [l, 4].

At Kohtla-Nõmme the low-capacity *Davidson* horizontal rotary retorts were operated for a relatively short period. The plant consisted of four rotating horizontal drums, heated externally with flue gases, generated by burning of their own semicoke. The oil vapors were withdrawn through offtake pipe. The oil yield was 19–20 % from the feed shale, i.e. about 90 % of Fischer assay oil. The gas yield was within a range of 80–120 m^3/t, its calorific value (excl. C^+_5 hydrocarbons) being about 14–15 MJ/m^3 [1].

After World War II, for the first time in worldwide practice synthetic domestic gas was produced from oil shale at the oil shale processing plant at Kohtla-Järve [5]. In November 1948, the first gas was supplied to St.-Petersburg, and some time later also to Tallinn. During this period, the amount of oil shale processed increased due to the introduction of chamber ovens and a number of vertical retorts. At Kohtla-Järve twelve vertical retorts were built (GGS-5), and eight retorts at Kiviõli. About one million tons of oil shale was retorted annually in pre-war Estonia. In 1965–1966, the maximum level of processing was reached – 4 million tons per year (in Russia – 3.2 million tons per year). A maximum of 500 million m^3 of domestic gas was produced per year in Estonia and 500 million m^3 in Russia. The gas yield was within a range of 300–350 m^3/t, its calorific value (excl. C^+_5 hydrocarbons) being about 15-17 MJ/m^3.

Later, relatively cheap natural gas was found to be more economical for meeting the needs of North-West Russia. The share of oil shale gas started decreasing rapidly. Since the 1970s the production of gas was gradually reduced and in 1987 the operation of chamber ovens was completely closed down.

The rapid development of the oil and gas industry in Russia in the 1960s forced the Estonian oil shale industry to change from producing predominantly liquid fuels towards manufacturing economically more feasible value-added chemical products. This was accomplished with due consideration of the specific properties of kukersite shale oil. Since the early 1960s, the share of fuel products in the total value of production was

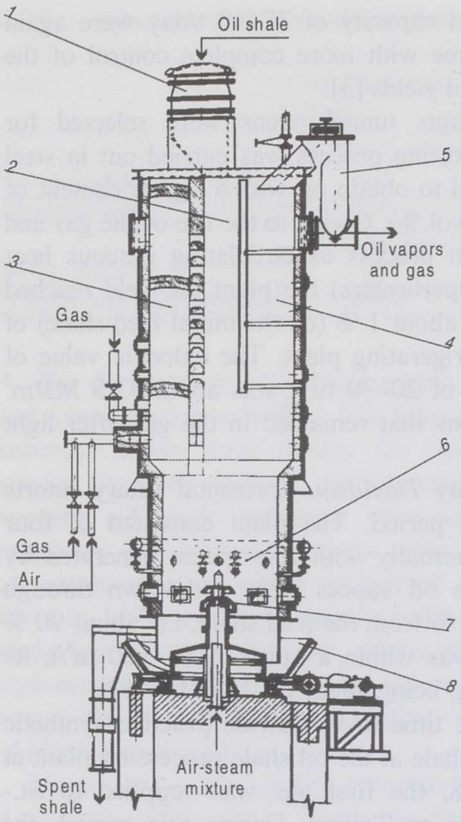

Fig. 1. Retort with cross-current flow of the heat-carrier gas: *1* – charging device, *2* – oil shale retorting chamber, *3* – heat carrier preparation and distribution chamber, *4* – oil vapors collecting and evacuation chamber, *5* – gas outlet, *6* – gasifier, *7* – gas blower, *8* – spent shale discharge device

gradually reduced to 10 %, and even lower. At the same time, the manufacture of products based on phenols extracted from shale oil progressed rapidly [6].

The number of various products derived from oil shale totalled about fifty. Besides fuel oils and synthetic domestic gas, the oil shale processing plants started manufacturing antiseptic oils for wood impregnation, electrode coke, roofing and constructions mastics, a chemical soil conditioner *Nerosin*, rubber softeners, casting binders, etc. The shale oil phenols (alkyl resorcinols) were used as feedstock for epoxy and other adhesive resins and glueing compounds, synthetic tanning agents, plugging compounds, rubber modifiers, etc. [7].

Since the 1990s the assortment of oil shale-derived products, which could be marketed under new economic conditions diminished considerably; at present the number of marketable shale oil products does not exceed ten.

During the entire post-war period, the vertical retorts underwent a long process of development. As a result of several reconstructions the daily throughput of the retorts at GGS-5 (Kohtla-Järve) and GGS (Kiviõli) was increased from 90–100 tons to 180–200 tons of oil shale (Fig. 1) [8]. The outer diameter of the cylindrical retort vessel is 4.4 m, its height is 11.8 m. The overall height of the retort is 17 m.

The throughput rate of the retorts at GGS-3 and GGS-4 was also almost doubled. In the early reconstructions the concept of central inlet of the heat carrier [3] was used followed by a new concept of heat-carrier gas cross-flow in the retort (the *Kiviter* process). The significant increase in retort throughput rate was accompanied by an increase in the shale oil yield from 65–70 to 75–80 % of the Fischer assay oil.

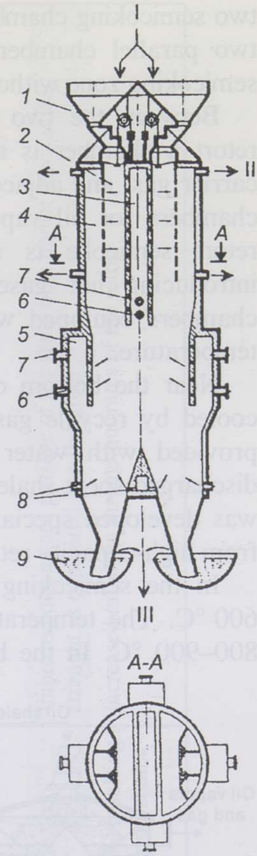

Fig. 2. 1,000 ton-per-day retort: *1* – charging device, *2* – oil shale retorting chamber, *3* – central heat carrier preparation and distribution chamber, *4* – oil vapors collecting and evacuation chamber, *5* – side chambers for oxidizing agent inlet, *6* – gas burners, *7* – recycle gas inlets for heat carrier preparation, *8* – recycle gas inlets for cooling spent shale, *9* – spent shale discharge device; I – oil shale, II – oil vapors and gas, III – spent shale

In the mid-1970s, it was planned to build oil shale processing plants of high capacity for an annual throughput of 5 million tons of oil shale. However, this goal could not be achieved using retorts of low unit capacity. Therefore, a compelling need arose for developing large-capacity retorts providing high productivity combined with significantly lower processing costs. As a result of a joint effort by science and industry (Oil Shale Research Institute and RAS *Kiviter* (now *Viru Chemistry Group* AS), Kohtla-Järve, Estonia, together with *Lengipronef-tekhim*, St.-Petersburg, Russia) a prototype 1,000 ton-per-day retort was developed (Figs. 2 and 3) and started operation at *Kiviter* AS followed later by two similar retorts (GGS-6) [8].

As can be seen in Fig. 2, the new retort employs the concept of cross-current flow of heat-carrier gas through the fuel bed with the supply of additional heat into the semicoking chamber. A portion of the heat carrier is prepared by burning recycle gas, ensuring thus the stability of the process and avoiding the melting of ash. Raw shale is fed through a charging device into

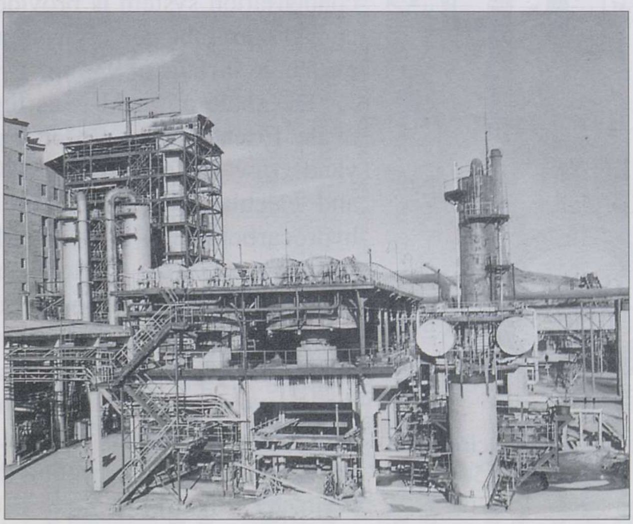

Fig. 3. General view of 1,000 ton-per-day retort with condensation system

two semicoking chambers arranged in the upper part of the retort. The use of two parallel chambers enables to provide a larger useful volume of the semicoking zone without increasing the thickness of the fuel bed.

Between the two semicoking chambers along the vertical axis of the retort a chamber is arranged for the preparation and distribution of heat-carrier gas, and adjacent to the semicoking chambers from the outer side are chambers for oil vapors collecting and evacuation. In the mid-part of the retort semicoke is subjected to additional heating or gasification by introducing hot gases or an oxidizing agent through side combustion chambers equipped with gas burners and recycle gas inlets to control the temperature.

Near the bottom of the retort is cooling zone where the spent shale is cooled by recycle gas and removed from the retort via a discharge device provided with water seal (9.8 kPa or 1,000 mm water column). The discharged spent shale has a water content of 30–35 %. The discharge device was developed specially to ensure even and reliable removal of spent shale from high-capacity retorts.

In the semicoking chamber the oil shale is dried and heated to 500–600 °C. The temperature of the heat carrier is maintained in the range of 800–900 °C. In the bottom of the retort the spent shale is cooled to 200–250 °C. Oil vapors are withdrawn from the retort at 200–250 °C to a condensing system equipped with air coolers.

The 1,000 ton-per-day retort is erected on an open site. The outer diameter of the cylindrical retort vessel is 9.6 m, its height is 21 m. The overall height of the retort including the oil shale bin is 35 m. To cool the oil vapors and off-gas the condensation system is provided with air-cooled bare tube coolers with a total heat-exchange surface of 930 m^2.

The shale oil yield is as high as 80 % of the Fischer assay. Specific product gas yield (raw shale basis) is 420–440 m^3/t and calculated heating value (excl. C^+_5 hydrocarbons) is 3.5–3.8 MJ/m^3. The 1,000 ton-per-day retort has shown continuous on-stream operation as high as 85–90 % of the calendar time. Further research on the *Kiviter* process resulted in the development of another design modification employing a circular retorting chamber, encircling the retort by perimeter (Fig. 4) [9].

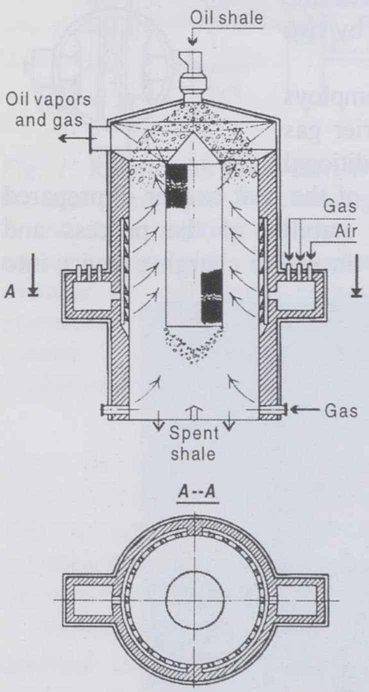

Fig. 4. Retort with a circular retorting chamber (250–300 ton-per-day)

Table 4. **Advantages of the Retorts with a Circular Semicoking Chamber in Comparison with Retorts Using Cross-Current Flow of the Heat-Carrier Gas**

Important design and process features	Advantages
1. Absence of cold-side walls of the retorting chamber	Elimination of problems related to the "wall effect" and to the phenomenon of the heat-carrier gas passing predominantly along the side walls, and to nonuniform downward passage of the shale bed
2. Flow of the heat-carrier gas from the periphery of the circular retorting chamber towards its centre	Improved heat transfer across the whole shale bed, as the gas has higher temperatures and lower velocities at the inlet, and lower temperatures and higher velocities at the outlet
3. Useful effect of segregation of oil shale particles according to their size at the charge: larger particles move to the periphery of the chamber towards the hotter zone, smaller ones – towards the centre into the zone of lower temperatures	Favourable conditions for uniform heating of both large and small oil shale particles
4. The bulk of oil shale rock moves through the high-temperature zone	Intensified retorting process and increased throughput rates
5. Lower temperatures of the gas outlet resulting from improved heat transfer in the shale bed (e.g. from 200–250 to 140–160 °C on retorting kukersite)	Lower specific heat consumption and, consequently, that of heat-carrier gas and air (e.g., 1.5 times lower on retorting kukersite); improved conditions for lower solids carry-over
6. No definite correlation between the oil shale throughput rate and the velocity of heat-carrier gas in the shale bed	Easier scale-up of the retort capacity
7. Gradual downward increase in diameter of the retorting chamber; the "cool" grate has the form of a cylinder	Improved downward passage of the shale bed; higher mechanical strenght as compared to a flat grate
8. Increase of the useful retorting shaft volume (from 30–45 to 60–70 %) resulting from its arrangement along the perimeter of the retort (especially for oil shales bituminizing on heating, e.g. kukersite)	Increased oil shale throughput rates of the retort

This concept provides a 1.5–fold increase of the net volume of the retorting shaft with no change in the thickness of the shale bed that is of particular importance for normal retorting of kukersite. Moreover, this design eliminates the side walls of the retorting chamber responsible for an uneven distribution of the heat carrier in the fuel bed, as well as difficulties in uniform oil shale downward passage in the retort, and other negative phenomena (Table 4).

Owing to the specific features of the retorts with a circular semicoking chamber, the air consumption for the retorting process in commercial-size experimental retorts was reduced from 340–360 to 240–260 m^3, and that of the recycle gas from 600–670 to 400–450 m^3 per ton of feed shale. At the same time it led to increased oil shale throughput rates from 180–200 to 250–300 tons per day with a simultaneous reduction in the residual oil yield of the semicoke from 2–3 to 0.5–1.0 % (Fischer assay oil). Quite naturally, there was an increase also in the plant oil yield and a decrease in the gas yield, but it could not be measured, because no separate condensation system was available at the plant.

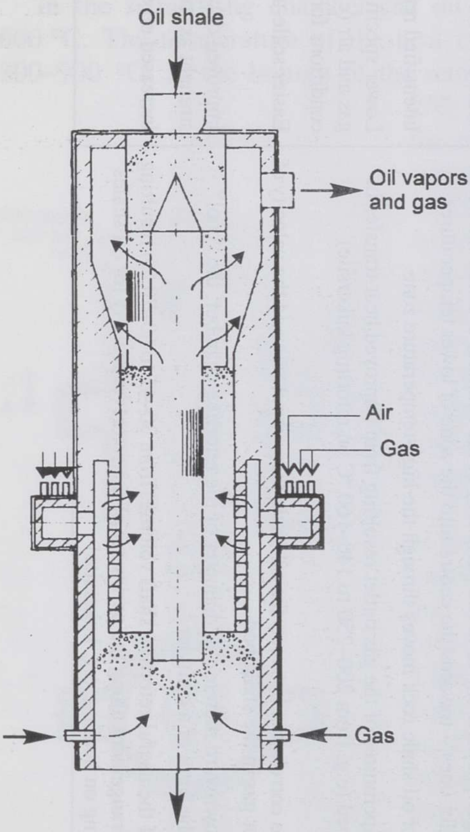

Fig. 5. Retort with a circular retorting chamber (1,500 ton-per-day)

However, the experience also indicated that the retorts with a circular retorting chamber could be operated efficiently only for processing oil shales with a maximum Fischer assay oil yield as high as 18–22 %. In case of richer oil shales, the cylindrical metal grate in the centre of the retort tends to get quickly jammed with thermobitumen, and the retort has to be frequently stopped for cleaning.

As a rule, the majority of the world's oil shale deposits are represented by leaner shales that can be retorted without technological difficulties characteristic to kukersite. This is confirmed by rather short experience gained in China so far. Since mid-1991 a small-capacity retort is in operation at a plant of the Maoming Petroleum Chemical Company to process the local oil shale in a circular retorting chamber. The reconstructed retort has a throughput of 150 tons per day. Since the retort is connected to a separate condensation system, for the first time it has become possible to directly measure the yield of oil from a circular retorting chamber and thus evaluate the effectiveness of this design. The plant yield of oil increased from 60–65 to 75–80 % of Fischer assay oil, at times reaching 83–85 % [10].

The problems of creating high unit-capacity retorts are much simpler because of large dimensions of the retort. With due consideration of the operational experience of the 1,000 ton-per-day retorts and the earliest commercial-scale retorts with a circular chamber, high-capacity retorts of the latter type were designed for GGS-7 of the *Kiviter* AS. The installation includes four retorts with a throughput rate of 1,500 t/day each (Fig. 5) [8, 11]. A number of novel design features were introduced to improve the efficiency of oil shale processing in these retorts. For example, to ensure uniform and stable passage of the shale through the retort, its inner diameter gradually increases downward. This simple idea had never been realized in oil shale retorts so far [11].

It is shown that high unit-capacity retorts are more "sensitive" to changes of design features than small low-capacity retorts. Therefore, with skilful and competent use of the specific features of large-size retorts, efficient conditions are created for retorting large-particle oil shale, which, as a result, leads to higher performance data of the retorts.

The construction of the 1,500 ton-per-day retorts according to a design including several novel technical concepts was started in 1988 (Fig. 6).

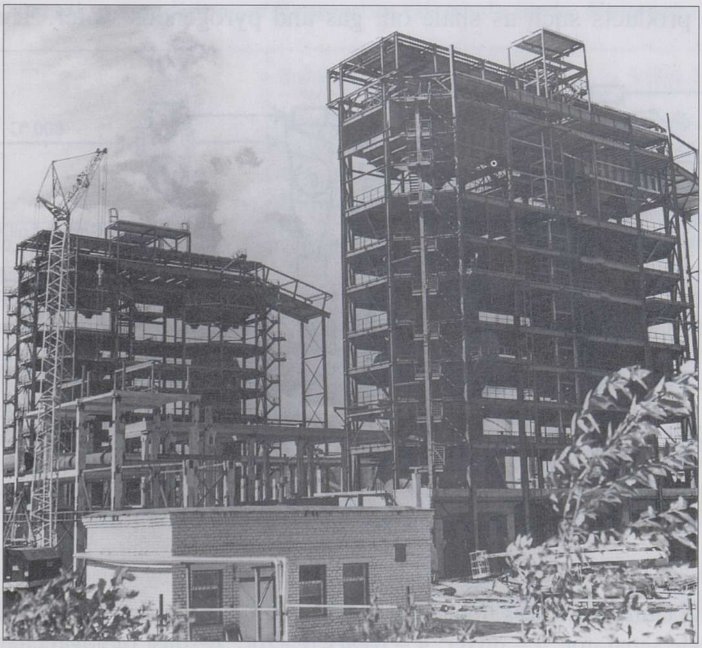

Fig. 6. General view of the retorting station (GGS-7) comprising four 1,500 ton-per-day retorts while under construction

Unfortunately, in 1991–1992 the construction was stopped because of lack financing, and in 1997 the unit was totally dismantled. Nevertheless, the above design developed for high-capacity oil shale retorts is of significant interest for the development of technologies for retorting relatively low-organic oil shales occurring predominantly all over the world. For such lean shales the throughput rate of the circular retorting chamber retorts can be brought up to 5,000–6,000 tons per day.

To ensure further development of oil shale processing, technologies must be available not only for retorting lump shale, but also shale fines. Methods for retorting shale fines have been developed over a long-term period by different research organizations both in Estonia and abroad.

A method of retorting shale fines with a solid heat carrier (the *Galoter* process) was tested in 1953–1981 in several stages at Kiviõli, in 200 ton-per-day and 500 ton-per-day experimental retorts (SHC-200 and SHC-500, respectively). Based on data and experience obtained from these tests, two commercial *Galoter* retorts, each with a design capacity of 3,000 ton-per-day (SHC-3000), were erected and put into operation on the site of the Estonian Power Plant near the town of Narva [12, 13].

As can be seen in Fig. 7, fine oil shale is dried in the aerofountain dryer *1* by heat of combustion gas. Then it is separated from gases in the dry oil shale separator *2* and dry oil shale is supplied to the mixer *3* and so forth to the rotary reactor *4* where the heat carrier as ash of the processed oil shale heated to the required temperature comes from the heat-carrier separator *8*. In the reactor *4* oil shale is heated by the heat carrier mixed with oil shale to yield the products such as shale oil, gas and pyrogenous water. The vapor-

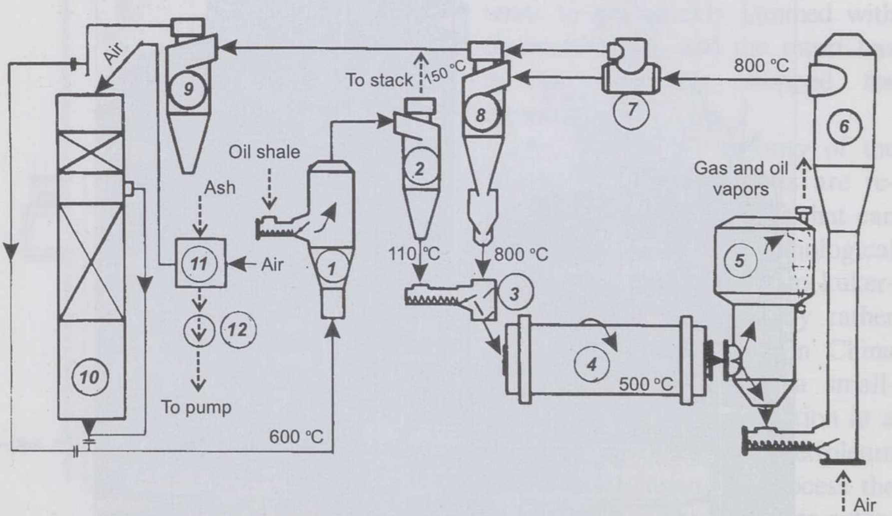

Fig. 7. The *Galoter* process flow diagram (SHC-3,000): *1* – aerofountain dryer, *2* – dry oil shale separator, *3* – mixer, *4* – rotary reactor, *5* – dust removal chamber, *6* – aerofountain furnace-combustor, *7* – by-pass, *8* – heat-carrier separator, *9* – ash separator, *10* – waste heat boiler, *11* – ash heat exchanger, *12* – dredger pump

gas mixture of these products is cleaned from dust in the dust removal chamber *5* providing proper cleaning. It is then cooled in the condensation system where shale oil and pyrogenous water are separated (the condensation system is not shown in Fig. 7).

The mixture of shale semicoke and ash is supplied to the combustor *6* where combustible components of semicoke are burnt generating heat required for heating the circulating heat carrier. The latter is then separated from the combustion products in the separator *8*. The combustion gases are separated from ash and removed from the process via the ash separator *9* and directed to the dryer *1*. The excess potential heat in shale semicoke and, respectively, in the combustion gas is used for generating steam in the waste heat boiler *10* arranged in front of the dryer *1*.

The boiler-utilizer operation is controlled so that the inlet temperature to the dryer *1* makes it possible to attain complete drying and heating of oil shale up to 120–150 °C at the inlet to the reactor. Ash from the separator *9* is fed to the ash heat exchanger *11* and is then with the dredger pump *12* evacuated through the ash removal hydraulic system.

Technical data on the performance of the oil shale retorts erected in the post-war period, as well as physical and chemical properties of the relating products are given in Tables 5–11. As can be seen in Fig. 8, in recent years the Institute of Oil Shale at Tallinn Technical University has developed a practically ecologically clean technology of semicoking large-particle oil shale in vertical retorts [14, 15].

Table 5. **Operating Conditions of Processing Oil Shale in the Retorts***

Indices	Baltic Basin (kukersite)		Volga Basin
	Vertical retorts, Kohtla-Järve, *Kiviter* AS	Solid-heat-carrier units, Narva, Estonian Power Plant	Vertical retorts, Syzran, Samara District
Feed shale throughput rate, t/day	150–1,000	3,000	40–60
Temperature,°C:			
Oil vapors from the retorting zone	200–230	480	130–140
Heat carrier into retorting zone	850–950	700–800	850–950
After condensation system	40–50	20–30	30–40
Specific combustion air, m^3/t	350–400	–	350–400
Specific consumption of recycle gas, m^3/t:			
For heat carrier preparation	450–500	–	450–500
Into cooling zone	150–200	–	150–200
Electric energy consumption for 1 ton of oil shale, kWh/t	14–16	20–25	8–10
Steam (5–8 at) consumption for 1 ton of oil shale, kg/t	40–50	8–12	130–145
On-stream time, %	85–90	70–80	80–90

* Process chemical efficiency 70–72 %.

Table 6. **Yield and Properties of Oil Produced by Retorting Oil Shale**

Properties	Baltic Basin (kukersite)		Volga Basin
	Vertical retorts, Kohtla-Järve, *Kiviter* AS	Solid-heat-carrier units, Narva, Estonian Power Plant	Vertical retorts, Syzran, Samara District
Yield of shale oil, %:			
Plant yield (raw shale basis)	16.5–17.5	13	6–7
Plant yield of Fischer assay oil	75–80	75	70–75
Density at 20 °C, kg/m^3	1,000	975	1,037
Water, %	2	1	2
Entrained solids, %	1.3	1.0	0.6
Ash, %	0.9	0.2	0.2
Viscosity at 75 °C, $10^{-6} \cdot m^2/s$	18.7	6.9	11.4
Flash point, °C	104	9	112
Pour point, °C	–22	–25	–7
Molecular mass	285	275	250
Phenolic compounds, %	28	15	1.8
Heating value (bomb calorimeter), MJ/kg	39.40	39.77	39.42
Initial boiling point, °C:	170	80	184
Distillation, vol.%, at:			
100 °C	–	3	–
150 °C	–	11	–
200 °C	2	21	2
250 °C	7	30	7
300 °C	19	41	26
350 °C	48	62	55
Elemental composition (dry basis), %:			
C	83.5	83.6	79.6
H	10.1	10.1	9.9
S	0.7	0.9	7.2
0 + N (by difference)	5.7	5.4	3.4

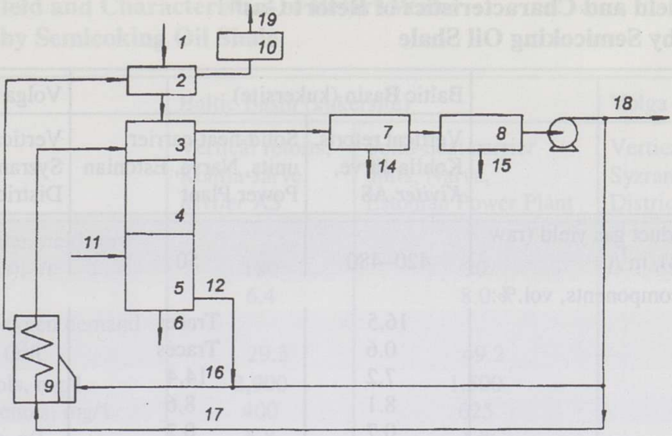

Fig. 8. Principal flow diagram of processing oil shale in retorts with separate take-off of the oil vapors and the gasification gases: *1* – oil shale, *2* – drying zone, *3* – semicoking zone, *4* – separation zone, *5* – gasification and cooling zone, *6* – spent shale, *7* – condensation and recovery system, *8* – desulfurization, *9* – gas heater, *10* – dust removal and desulfurization system, *11* – oxidizing agent, *12* – gasification gas to burner, *13* – oil vapors and gas, *14* – crude shale oil, *15* – sulfur, *16* – make-up recycle gas to burner, *17* – recycle gas, *18* – product gas, *19* – flue gas

Table 7. **Chemical Group Composition of Light-Middle Fractions of Oil Obtained by Semicoking Oil Shale from Baltic and Volga Basins, wt.%**

Fractions	Compounds					
	Alkanes and cycloalkanes	Alkenes	Aromatic hydrocarbons	Neutral heteroatomic compounds	Phenols	Fraction yield from total shale oil
Vertical retorts (Kohtla-Järve, *Kiviter* AS)						
IBP-200 °C	14	41	22	16	7	3.9
200-300 °C	12	20	30	19	19	16.1
300-350 °C	3	3	30	36	38	12.1
IBP-350 °C	8	16	29	22	25	32.1
Solid-heat-carrier units (Narva, Estonian Power Plant)						
IBP-200 °C	15	49	22	13	1	19.8
200-300 °C	8	15	38	23	16	16.9
300-350 °C	3	2	32	34	29	13.2
IBP-350 °C	9	25	30	22	14	49.8
Vertical retorts (Syzran, Samara District)						
IBP-200 °C	5	13	52	28	2	2.6
200-300 °C	4	5	52	32	7	20.9
300-350 °C	4	1	48	40	7	18.5
IBP-350 °C	4	4	50	35	7	42.0

Table 8. **Yield and Characteristics of Retort Gas* Obtained by Semicoking Oil Shale**

Indices	Baltic Basin (kukersite)		Volga Basin
	Vertical retorts, Kohtla-Järve, *Kiviter* AS	Solid-heat-carrier units, Narva, Estonian Power Plant	Vertical retorts, Syzran, Samara District
Specific product gas yield (raw shale basis), m^3/t	420–480	50	750
Content of components, vol.%:			
CO_2	16.5	Traces	19.4
H_2S	0.6	Traces	2.7
H_2	7.2	14.4	6.1
CO	8.1	8.6	3.5
O_2	0.7	0.2	0.3
C_nH_{2n+2}	2.0	38.4	2.0
Including:			
CH_4	1.5	19.8	1.2
C_2H_6	0.3	11.2	0.4
C_3H_8	0.1	5.4	0.3
C_4H_{10}	0.1	2.0	0.1
C_nH_m	1.0	36.2	0.6
Including:			
C_2H_4	0.6	18.4	0.4
C_3H_6	0.3	8.7	0.1
C_4H_8	0.1	9.1	0.1
N_2	63.9	2.2	65.4
Calculated heating value (excl. C^+_5 hydrocarbons), MJ/m^3:			
High	3.66	54.00	3.33
Low	3.38	49.87	3.04
Content of C^+_5 hydrocarbons in product gas, g/m^3	25	240	7
Content of H_2S, g/m^3	9	Traces	42
Density, kg/m^3	1,349	1,226	1,352

*Here and hereinafter all characteristics of gas are given at 20 °C and 760 mm Hg.

Table 9. **Yield and Characteristics of Retort Water Obtained by Semicoking Oil Shale**

Indices	Baltic Basin (kukersite)		Volga Basin
	Vertical retorts, Kohtla-Järve, *Kiviter* AS	Solid-heat-carrier units, Narva, Estonian Power Plant	Vertical retorts, Syzran, Samara District
Specific water yield (raw shale basis), l/t	180	30	230
pH	6.4	8.0	8.2
Chemical oxygen demand (COD), g O^2/l	29.3	49.2	–
Total phenols, mg/l	3,900	1,500	600
Volatile phenols, mg/l	400	625	600
Dry residue, g/l	6.8	1.8	24.0
Chloride (Cl^-), mg/l	248	3.3	–
Total sulfur, mg/l	420	187	6,500
Volatile ammonia, mg/l	765	1,800	4,600
Volatile acetic acid, mg/l	480	6,720	4,000

Table 10. **Yield and Characteristics of Retort Ash and Semicoke Obtained by Semicoking Oil Shale**

Indices	Baltic Basin (kukersite)			Volga Basin
	Vertical retorts, Kohtla-Järve, *Kiviter* AS		Solid-heat-carrier units, Narva, Estonian Power Plant	Vertical retorts, Syzran, Samara District
	Ash	Semicoke		
Specific ash yield (raw shale basis), kg/t	510	550	490	560
Moisture content, %	35	28	Dry	30
Content (dry basis),%:				
Carbon dioxide $(CO_2)^d{}_M$	9	12	3	6
Ash A^d	82	76	94	89
Organic matter	9	12	3	5
Carbon C^d	6	9	2	3
Total sulfur $S^d{}_t$	1.8	2.2	2.9	3.5
Fischer assay oil yield, %	None	1.5	None	None
Heating value (bomb calorimeter), MJ/kg	2.50	3.77	–	2.10

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Table 11. **Composition of Water-Soluble Phenols Obtained by Semicoking Oil Shale from Baltic Basin (Kukersite)*, %**

Indices	From water	From shale oil	
	Solid-heat-carrier units, Narva, Estonian Power Plant		Vertical retorts, Kohtla-Järve, *Kiviter* AS
Monohydric phenols	20.0	3.5	7.3
Including:			
Phenol	10.6	1.0	–
Methyl phenols	7.4	1.7	–
Dimethyl-ethyl phenols	2.0	0.8	–
Dihydric phenols	80.0	96.5	92.7
Including:			
Resorcinol	1.5	0.9	2.5
2-Methyl resorcinol	1.5	1.1	1.5
4-Methyl resorcinol	0.8	1.0	
5-Methyl resorcinol	32.7	31.0	30.7
5-Ethyl resorcinol	8.1	8.5	8.1
2,5-Dimethyl resorcinol	15.2	19.8	6.5
4,5-Dimethyl resorcinol	7.0	10.3	8.2
The highest phenols	13.2	23.9	35.2
Total	100.0	100.0	100.0
Including:			
5-Alkyl resorcinols	40.8	39.5	41.1
Dimethyl resorcinols	22.2	30.1	17.9

* Total yield of water-soluble phenols (shale oil basis), %: vertical retorts 1.5, solid-heat-carrier units 0.5.

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