

CURRENT STATUS OF OIL SHALE PROCESSING IN SOLID HEAT CARRIER UTT (GALOTER) RETORTS IN ESTONIA

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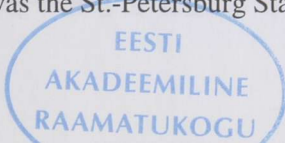
Thermal processing of oil shale in solid heat carrier unit grounds on the effective super-high-speed heat transfer between polydispersed fine-grained solid substances. Small size and large surface areas of the decomposable oil shale and heat carrier particles ensure their close contact in the mixing process in rotary drum reactor and high rate of heat transfer from heat carrier (ash residue of oil shale) to the shale feed resulting in rapid heating and decomposing of the latter in liquid and gaseous retorting products.

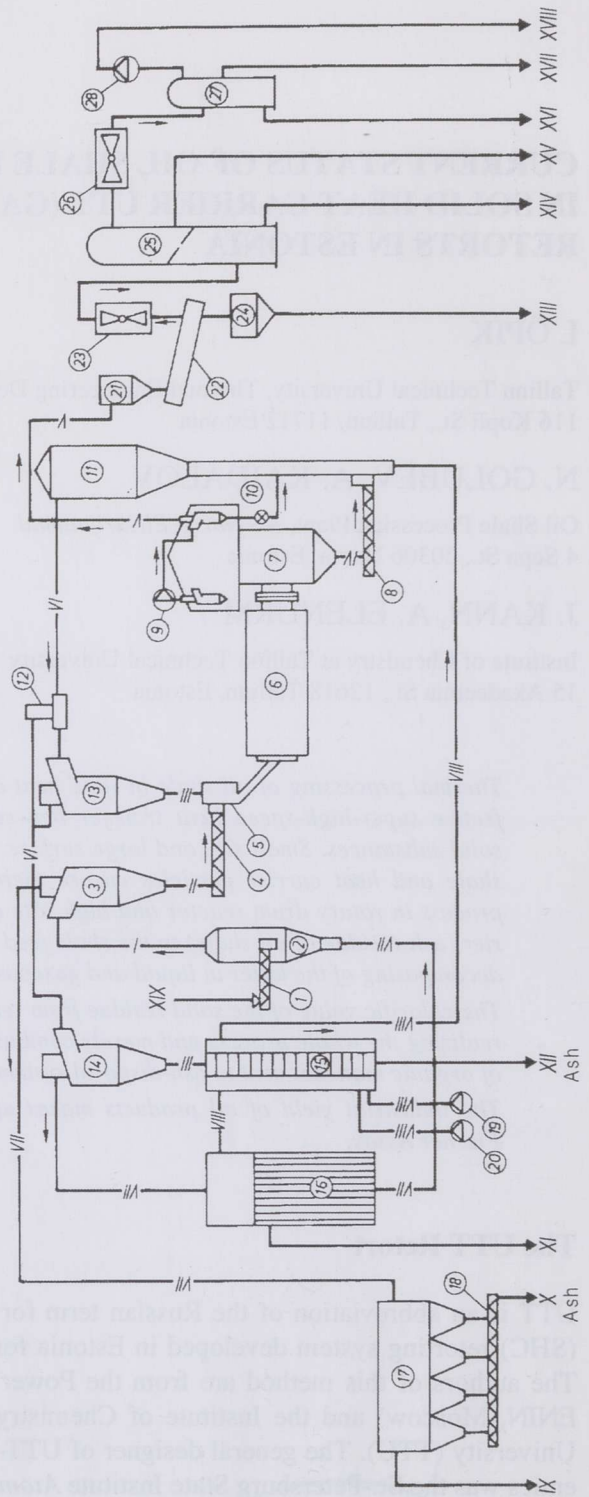
The calorific value of the solid residue from reactor – semi-coke – is used for realizing the whole process and merely combusted ash with minimum content of organic matter is sent to ash-disposal system.

The industrial yield of oil products makes up 85-90 % from the standard Fischer Assay.

The UTT Retort

UTT is an abbreviation of the Russian term for Galoter Solid Heat Carrier (SHC) retorting system developed in Estonia for processing oil shale fines. The authors of this method are from the Power Engineering Institute (JSC ENIN, Moscow) and the Institute of Chemistry (IC) of Tallinn Technical University (TTU). The general designer of UTT-3000 retorts at the late seventies was the St.-Petersburg State Institute *Atomenergoproekt* [1].





Schematic diagram of an UTT-3000 unit (E. Volkov, G. Stelmakh [1], Fig. 3, P. 17):

1 – oil shale feed conveyor; *2* – drier; *3* – dry shale cyclone; *4* – conveyor; *5* – mixer; *6* – rotary drum reactor $\varnothing = 5,0/4,38$ and $L = 14$ m, 0,94 rpm; *7* – chamber for dust removal from retort vapors and gas with built-in cyclones; *8* – semicoke conveyor; *9* – ejector; *10* – dust recovery system; *11* – aerofountain furnace for combustion of semicoke; *12* – splitter to heat carrier by-pass; *13* – heat carrier cyclone; *14* – hot ash cyclone; *15* – ash heat exchanger; *16* – heat recovery boiler; *17* – electric precipitator; *18* – conveyor; *19*, *20* – air blowers; *21* – heavy oil washing tower; *22* – gas collector; *23* – heavy oil cooler-condenser; *24* – heavy oil tank, *25* – rectification tower, *26* – cooler-condenser for gas-naphtha and tar water; *27* – separator; *28* – gas blower.

Flows: *I* – oil shale mixed with flue gas; *II* – dry shale; *III* – heat carrier (ash); *IV* – semicoke and heat carrier; *V* – oil vapors and retort gas; *VI* – hot ash in flue gas flow; *VII* – flue gas, heavy oil; *VIII* – air; *IX* – stack gas; *X* – ash; *XI* – steam; *XII* – ash; *XIII* – heavy oil; *XIV* – heavy and middle oil mixture; *XV* – gas turbine oil fraction; *XVI* – tar water; *XVII* – naphtha; *XVIII* – retort gas and gas naphtha; *XIX* – oil shale feed

Ash of semicoke separated from oil vapours and gas leaving the reactor and burnt in aerofountain furnace is the heat carrier in UTT retorts.

The production capacity of UTT-3000 retorts has been as planned – 3,000 t per calendar day (125 t/h) of feed shale. The rotary drum reactor (pyrolyzer) itself had no operating problems. However, limited by fouling hydrocarbon vapour and retort gas cleaning cyclones with coke sediments and combustion gas cyclones with ash sediments, the non-stop run of the retort was very short. During the first 6-7 years the maximum non-stop run was 6 days being usually only 2-3 days. For a cleaning operation 3-4 and even more days were needed. The content of solid particles in heavy oil rose to 10 wt%. The operation results in 1981–1987 (Table 1) gave rise to proposals to shut down the processing plant altogether. A state commission, in whose work some authors of this paper participated, studied the UTT retort in 1988 and recommended to improve its operation according to the conclusions reached at discussions.

Table 1. Calculated (Designed) and Actual Production Capacity of a Single UTT-3000 Retort in 1980–1986

Year	Annual operating time		Processed shale		Produced oil, $t \times 10^3$	Oil yield, wt%
	h	% from 8,760 h	$t \times 10^3$	t/h		
As designed	6,800	78	850	125	105	12.4
1980	61	0.7	4	66	0.3	7.5
1981	130	1.5	16	123	1.4	8.8
1982	379	4.3	51	135	5.7	11.2
1983	172	2.0	25	146	3.0	12.0
1984	634	7.2	77	121	9.7	12.6
1985	762	8.7	87	114	11.0	12.6
1986	1,036	11.8	128	124	15.2	11.9

Table 2. Production of the UTT-3000 Retort (Eesti Elektriiaam) Operated Only One at the Same Time in 1982–2000

Year	Processed oil shale, $t \times 10^3$	Processed waste, $t \times 10^3$	Produced oil, $t \times 10^3$	Produced retort gas, million m^3	Total oil yield, %	In operating time, h
1992	309	Not	38.5	Not utilized	12.5	2982
1993	503	Not	65.9	Not utilized	13.1	4433
1994	564	Not	71.3	19.2	12.6	5445
1995	511	5	62.1	19.1	12.2	4962
1996	546	15.4	69.9	21	12.8	5197
1997	609	9.6	78.9	22.2	13.0	5651
1998	509	11.5	65.3	19.5	12.8	5000
1999	488	9.7	59.9	16.6	12.3	4370
2000	687	6	77.5	22	11.3	5887

After partly reconstruction and technological corrections during early nineties the production quantity (Table 2) and quality of a UTT retort have raised essentially. The most important changes made were reduction of heat carrier temperature below 800 °C, reconstruction of the system of dust recovery cyclones, and recycling of heavy oil for secondary processing in the reactor.

The shale from the neighborhood *Narva* and *Sirgala* open pits, where the layers B-C + E-F2 are mined, is used as feed for UTT-3000. The average mineral content of dry feed is 72 wt% (49.6 t% ash + 22.4 wt% mineral CO₂). Sulfur content of dry feed is 1.6 wt%, included 0.46 wt% organic sulfur.

The yield of Fischer Assay oil from dry feed for UTT-3000 in the years 1995–1997 was 18–19 %. The industrial oil output was 129–139 kg (~ 0.85–0.9 bbl) and the retort gas output 36 cubic meters per tonne of raw oil shale feed.

The particle size of the shale feed is <25 mm.

The residence time in drum reactor is 0.25–0.35 h for solids and ~20 s for hydrocarbon vapors and gases.

Table 3. UTT-3000 Oil Fractions, wt%

Oil fraction	Outflow, position in the Figure	Value
Heavy oil (S = 0.54 wt%)	XIII	<25
Heavy and middle oil mixture (S = 0.56–0.58 wt%)	XIV	75–50
Gas turbine fuel (S = 0.72 wt%)	XV	11
Naphtha (S = 0.8 wt%)	XVII + XVIII	14
Total oil	–	100

The average HHV value for UTT-3000 water-free oil is 39.6 GJ/t and density 0.96 t/nm³. The same parameters for retort gas are 46.4 MJ/nm³ and 1.165 kg/nm³. Oil characteristics are given in Tables 3 and 4 [2, 10].

Dust separation after reactor from oil vapors and retort gas takes place in the built-in cyclones of dust removal chamber. After equipping the dust recovery system with ejector from the 2nd stage cyclone (the Figure (reproduced from [1]) pos. 9), the content of mechanical impurities estimated in ~75 wt% of oil is between 0.015–

Table 4. UTT-3000 Total Oil Characteristics

Parameter	Value
Total oil characteristics, wt%:	
C	82.3
H	10.0
S	0.7
N	<0.3
Cl	<0.1
O (from difference)	6.7
Total	100.0
Density g/cm ³	0.96
Viscosity at 80 °C, cSt	6.4
Flash point (open-cup), °C	48
Solidification point, °C	–27
Calorific value, MJ/kg	39.6

0.1 wt%, while ~25 wt% of heavy oil containing 1.5–3 wt% ash is recycled to the retort for secondary pyrolysis together with oil shale, when not sold as road bitumen. Some typical operating data of UTT-3000 characteristic for last years are presented in Table 5.

In 1995 processing of scrap automobile tires, rubber waste, oily soils, and oil sediments from tank wagons, all added to oil shale feed in the amount up to 10 wt.% was started [3, 4]. During six years since 1995, 50,000 t of crushed tires and 11,000 t of oil wastes have been processed with total oil yield approximately 30,000 t (see Table 2). Somewhat elevated carbon content in the UTT ash may be a result of oxygen deficit as well as caused by the structure of the tires coke [5].

Table 5. Ordinary Technological Data of the UTT-3000 No. 1 (2000) and No. 2 (1999)

	Retort No. 1, January, 2000	Retort No. 2, July, 1999
Temperature, °C:		
Solid heat carrier, t_{AFF}	790–810	750–780
Retort output	465–475	470–480
Output of dry shale cyclones	125–165	140–195
Pressure, bar:		
Furnace air inlet	0.36–0.38	0.3–0.33
Reactor	0.21–0.24	0.21–0.23
Solid impurities in oil, wt%:		
Heavy recycle oil	1.2–1.7	2.4–3.0
Heavy and middle oil mixture	0.06–0.09	0.02–0.09

Environmental Hazards

The main environmental hazards are the chemical composition of ash used for landfill and harmfulness of stack emissions.

The adequacy of these wastes to the criteria of European Union Council Directives is not specified, and its determination must be a primary task for the Processing Plant of *AS Narva Elektriijaamad*.

At present there are only three different environmental taxes in Estonia for oil shale wastes as landfill: for shale waste concentration at mines, for the fly and bottom ashes equally and for semicoke (= residue of low-temperature coking). The taxes are corrected only on the basis of the quality and distance of settlements from the waste disposal. There is no correction on the different hazardous ranges of ash or semicoke. It is proposed to raise the taxes for ashes by 5 and for semicoke by 20 % annually during 15 years. At present the UTT ash, residue of semicoke combustion, is taxed not as ash but as semicoke.

Hazardous components of UTT stack gases subjected to environmental taxation are CO, hydrocarbons and fly ash. The taxes for the first two rise by 20 % and for ash by 5 % annually.

Ash or Semicoke?

It is an incomprehensibility to qualify the UTT-3000 ash as semicoke, resulting from very low environmental taxes in the eighties. Usually the content of unburned organic matter in ash does not exceed 0.5 wt% while, for instance, the limit of organic matter in ashes by German standards is 3 or 5 wt%, according to the quality of a disposal [6]. The criteria of EC do not limit the content of organic matter, there are only criteria based on eluate (water leaching) tests [7] needed to carry out with the UTT ash.

The ash quality depends on two main operating factors – the temperature of the heat carrier at the outlet of the aerofountain furnace t_{AFF} and the air excess (sufficiency) factor α .

Due to the presence of some amounts of oxygen (0–1 vol.%), the air factor α is interpreted inexactly as approximately $\alpha \approx 1$ [2]. Taking into account the simultaneous content of CO, H₂ and hydrocarbons in stack gases and unburned carbon and sulfur in ash, it was found that there has never been enough oxygen (?) for complete combustion of semicoke in the furnace (Table 6).

Table 6. UTT-3000 Stack Gas Analyses

	1999, 23 Sept.	1999, 26-29 Dec.	2000, 1 Dec.	2001, 1 Feb.	1999–2001, statistical data
Components, vol. %:					
O ₂	0.2	1.0	?	?	–
CO ₂	19.8	–	–	–	–
CO	2.1	2.2	1.9	1.3	0.2–3.8
H ₂	?	?	1.17	0.64	–
Hydrocarbons as CH ₄	0.6	0.6	0.2	0.12	0.3–1.0
Air excess rate α^*	<0.92	<0.94	?	?	–
SO ₂ , ppm	<200	–	–	–	30–140
NO _x , ppm	<30	–	–	–	3–17
HCl, ppm	<100	–	–	–	4–33
Phenols, mg/nm ³	–	–	–	–	0.3–0.7
Solid particles, mg/nm ³	540	–	–	–	–

* The unburned carbon and sulfur in ash complementarily reducing α have not been taken into account.

The data in Table 6 demonstrate the need on supplementary measurements to determine the air balance of the UTT-3000, including an analysis of semicoke from the conveyer (Figure, pos. 8) and stack gas for hydrocar-

bons (CH₄) a. o. before the drier (Figure, pos. 2). The quality of ash must be investigated on combustion with real air excess.

At present the t_{AFF} exerts a more direct influence on the ash quality as the air factor. Operating statistics from the years 1996–2000 demonstrate an expressive correlation between the hydrogen sulfide H₂S content of retort gas and the final temperature of semicoke combustion t_{AFF} in the aerofountain furnace measured between $t_{\text{AFF}} = 720\text{--}820$ °C (Table 7). That is the region of starting the dissociation of oil shale mineral carbonates in the aerofountain furnace. Calculations demonstrate that at temperatures 700–750 °C the destruction of dolomite takes place, and at 750 °C the destruction of calcite starts. In Table 7 approximate data on the efficiency of carbonate dissociation (wt.% from CO₂ of total carbonates calculated according to [8, 9]) are presented.

Table 7. H₂S Content of Retort Gas (Operating Data, 1996–1998) and Calculated Rate of Decomposition of Carbonates in the UTT Furnace for Oil Shale with 31.5 wt% Calcite and 13.5 wt% Dolomite in Dry Matter

t_{AFF} , °C	H ₂ S in retort gas, vol.%	Calculated thermal decomposition of oil shale carbonates (calculated dispersion $\pm 50\%$), wt%			
		Decomposition rate of carbonate CO ₂	Individual compounds, dry shale basis		
			CaO	MgO	carb. CO ₂
720	5–7	1.5	0.0	0.3	0.3
740	4–6	–	0.0	–	–
760	2.7–4.4	2	0.2	0.4	0.4
780	1.3–3	3	–	–	0.6
800	0.4–1.6	5	0.7	0.5	1
820	< 0.4	8	1.0	0.7	1.6
850	–	15	1.4	1.1	3

H₂S content of retort gas 5–7 vol.% made up 76–106 g/nm³ or approximately 65–90 g per kg of gas – 6.5–9 wt%. Taking into account the average yield of retort gas from organic matter – 15 wt.%, at low temperatures of the heat carrier nearly all the organic sulfur goes into oil and as H₂S into retort gas.

At high temperatures of solid heat carrier ($t_{\text{AFF}} > 800$ °C) the rest of organic sulfur not bounded in shale oil goes into stack gas as SO₂ (by $\alpha \gg 1$) or into ash as CaS (by $\alpha \ll 1$).

The forms of sulfur in ash as well as their environmental quality investigated by A. Elenurm gave no reason to be pessimistic [2, 10]. During long-term investigations and analyses of the ash-disposal-system circulating wa-

ter, it was established that processing of Estonian oil shale in an UTT-3000 unit has caused no accumulation of environmentally harmful sulfide sulfur in the circulating water. The content of sulfide S in water tends to decrease in spite of the raise in the annual production (Table 2), the monthly average remaining below 0.6 mg/l (average from twelve tests in 1999 – 0.8, and in 2000 – 0.4 mg/l).

The SHC processing has no influence on the low benzo(a)pyrene content of the water circulating in the ash disposal system (2×10^{-9} g/l).

The Drier

High content of hydrocarbons (measured as CH₄) in stack gas (Table 6) makes it necessary to test the raw oil shale feed drier (Figure, pos. 2). As a result of overheating of oil shale finest particles, generation of hydrocarbons may occur.

Conclusions

During 20 years of operating and developing of the UTT-3000 technology, no complete testing of this retorting system has been carried out. As discussed above operating parameters – temperature of the heat carrier, as well as the semicoke combustion air factor – are presented having an essential effect upon the environmental qualities of UTT ash and gaseous emissions. Estimation of the optimum operating data should be the goal of a complete testing of the UTT-3000 retorts.

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