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REVIEW

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DEVELOPMENT OF THE OIL SHALE PROCESSING INDUSTRY IN ESTONIA AFTER WORLD WAR II

Before World War II, oil shale processing in Estonia was oriented predominantly to the production of liquid fuels [1]. The early post-war development was characterized by introduction of synthetic domestic gas production. This process utilized high temperature gasification of oil shale in chamber ovens of special design. The predominant production of liquid fuels was gradually replaced by non-fuel products and specialty chemicals derived from shale oil. As seen from Table 1, the physically and economically outdated units were gradually closed down and new ones were erected.

For the first time in worldwide practice, synthetic domestic gas was produced from oil shale at the oil shale processing plant at Kohtla-Järve (now a state joint-stock company, the RAS "Kiviter"). In November, 1948, the first gas was supplied to Leningrad (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 (formerly traditionally referred to as "oil shale generators"). At Kohtla-Järve 12 vertical retorts were built (GGS-5), and 8 retorts at Kiviõli (now the RAS "Eesti Kiviõli"). About one million tons of oil shale were retorted annually in pre-war Estonia. In 1965 - 1966, the maximum level of processing was reached - 4 million tons per year (Tables 2 and 3). A maximum of 500 million m^3 of domestic gas was produced per year.

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

The rapid development of the oil and gas industry in the Soviet Union in the 1960's forced the economic feasibility of orienting the Estonian oil shale industry from the production of fuels towards manufacturing value-added chemical products. This was accomplished with due consideration of the specific properties of kukersite shale oil. Since the early 1960's, the share of fuel products in the total value of production was gradually reduced to 10%, and even lower. At the same time, the manufacture of products based on phenols extracted from shale oil progressed rapidly [2].

The number of various products derived from oil shale totalled about 50. Besides fuel oils and synthetic domestic gas, the oil shale processing plants started manufacturing antiseptic oils for wood impregnation, electrode coke, roofing and construction mastics, a chemical soil conditioner "Nerosin", rubber softeners, casting binders, etc. The shale oil phenols (alkyl resorcinols) were used as feedstocks for epoxy and other adhesive resins and glueing compounds, synthetic tanning agents, plugging compounds, rubber modifiers, etc.

Table 1. **Start-up of Oil Shale Processing Units in Estonia**

Plant	Unit	Throughput rate, t/day	Number of retorts/ovens	Start-up	Cease of operation
Kohtla-Järve, RAS "Kiviter"	Experimental vertical retort (generator)	7-8	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	
	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 1000 TPD retort	1000	1	18.01.81	
	GGS-6	1000	2	18.01.87	
Kiviõli, RAS "Eesti Kiviõli"	Experimental tunnel oven section		1	1926	In the 1930's
	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	
		100	1	June, 1962	
		100	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
		25	4	1934	1961
Narva, Estonian Thermal Power Plant	SHC-3000	3000	2	30.06.80	

Table 2. **Oil Shale Processing at Retorting Plants in Estonia after World War II, thousand tonnes**

Year	RAS "Kiviter"					RAS "Eesti Kiviõli"				Total in vertical retorts	Estonian TPP, SHC-3000	Total volume of oil shale processed
	vertical retorts	chamber ovens	tunnel ovens	Davidson horizontal rotary retorts	total	vertical retorts	tunnel ovens	SHC-200 and SHC-500	total			
1955	1072	983	—	53	2108	167	372	—	539	1189	—	2647
1960	1284	1111	219	53	2667	244	444	13	701	1526	—	3368
1962	1480	1236	222	—	2938	309	467	26	802	1794	—	3740
1964	1628	1360	227	—	3215	361	444	86	891	1989	—	4106
1966	1691	1641	225	—	3557	375	445	122	942	2066	—	4499
1968	1699	1680	161	—	3540	381	446	111	938	2080	—	4478
1970	1697	1644	—	—	3341	363	372	127	862	2060	—	4203
1972	1748	1650	—	—	3398	405	410	134	949	2153	—	4347
1974	1720	1668	—	—	3388	439	210	145	794	2159	—	4182
1975	1708	1696	—	—	3404	448	52	135	635	2156	—	4039
1976	1764	1690	—	—	3454	459	—	130	589	2223	—	4043
1978	1748	1717	—	—	3465	475	—	105	580	2223	—	4045
1980	1653	1487	—	—	3140	485	—	94	579	2138	4	3723
1981	1721	1259	—	—	2980	478	—	53	531	2199	16	3527
1982	1743	1040	—	—	2783	479	—	—	479	2222	51	3313
1984	1813	788	—	—	2601	484	—	—	484	2300	77	3162
1986	1464	390	—	—	1854	496	—	—	496	1960	128	2478
1988	1915	—	—	—	1915	420	—	—	420	2335	311	2646
1990	1690	—	—	—	1690	387	—	—	387	2077	374	2451
1992	1443	—	—	—	1443	386	—	—	386	1829	309	2138
1993	1602	—	—	—	1602	391	—	—	391	1993	500	2493

Table 3. **Shale Oil Produced at Retorting Plants in Estonia after World War II, thousand tonnes**

Year	RAS "Kiviter"					RAS "Eesti Kiviõli"				Total in vertical retorts	Estonian TPP, SHC-3000	Total volume of shale oil produced
	vertical retorts	chamber ovens	tunnel ovens	Davidson horizontal rotary retorts	total	vertical retorts	tunnel ovens	SHC-200 and SHC-500	total			
1955	165	59	—	10	204	20	74	—	94	185	—	328
1960	191	67	45	10	313	27	84	2	113	218	—	426
1962	221	73	45	—	339	31	83	3	117	252	—	456
1964	245	83	46	—	374	40	87	11	138	285	—	512
1966	260	97	45	—	402	43	87	16	146	303	—	548
1968	269	101	32	—	402	44	90	14	148	313	—	550
1970	274	104	—	—	378	41	74	17	132	315	—	510
1972	282	102	—	—	384	45	80	18	143	327	—	527
1974	281	98	—	—	379	48	41	20	109	329	—	488
1975	279	102	—	—	381	51	—	18	69	330	—	450
1976	293	104	—	—	397	51	—	18	69	344	—	466
1978	278	101	—	—	379	52	—	14	66	330	—	445
1980	262	80	—	—	342	54	—	13	67	316	0.3	409.3
1981	269	69	—	—	338	52	—	7	59	321	1.4	398.4
1982	283	56	—	—	339	52	—	—	52	335	6	397
1984	290	46	—	—	336	52	—	—	52	342	10	399
1986	233	20	—	—	253	63	—	—	63	296	15	331
1988	310	—	—	—	310	63	—	—	63	373	36	409
1990	266	—	—	—	266	64	—	—	64	330	43	373
1992	224	—	—	—	224	64	—	—	64	288	39	327
1993	237	—	—	—	237	64	—	—	64	301	65	366

Under the economic conditions of that time, making effective use of the unique properties of kukersite provided not only economic stability for the Estonian oil shale industry, but even allowed for its successful expansion. This was based on manufacture of non-fuel products not easily obtainable from petroleum, coal or oil shales other than kukersite. At that time, the production of shale oil gasoline lost its viability. Cheap, better quality, petroleum-derived motor fuels appeared on the market. This was one of the reasons why tunnel ovens for retorting kukersite were finally closed. These were characterized by high labour and energy consumption as well as difficult and unhealthy working conditions.

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. 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 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.

In the mid-1970's, it was planned to build oil shale processing plants of high capacity for an annual throughput of 5 million tons of oil shale. This goal, however, 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", Kohtla-Järve, together with Lengiproneftekhim, St. Petersburg) a prototype 1000 ton-per-day Kiviter retort was developed and started operation at RAS "Kiviter" followed later by two similar retorts (GGS-6).

In the 1980's, at RAS "Kiviter", the construction was started on a new oil shale processing plant (GGS-7) consisting of four high capacity modified Kiviter retorts. This also included gas cleaning and utilization, waste water purification facilities, and the spent shale hydrotransport disposal system. Simultaneously, it was decided to gradually close down the retort plants GGS-3, 4, and 5. In 1990, however, the construction of GGS-7 was suspended due to investment problems. By that time, the annual amount of processed oil shale had fallen to a level of 2 million tons. This was due to the worn-out condition of the old retorts and difficulties in marketing shale oil products in 1991-1992.

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 period of many years by different research organisations both in Estonia and abroad.

The method of retorting shale fines with a solid heat carrier (the Galoter process) was developed by the Moscow G. M. Krzhizhanovski Institute of Energetics (ENIN). This was tested in 1953-1981 in several stages at RAS "Eesti Kiviõli", in 200 and 500 ton-per-day experimental retorts (UTT-200 and UTT-500, respectively). Based on data and experience obtained from these tests, two commercial Galoter retorts, each with a design capacity of 3000 tons per day (UTT-3000), were erected and put into operation on the site of the Estonian Power Plant near Narva.

Table 4. **Properties of Feed Shale and Basic Operational Data for Semicoking in Retorts of Different Design***

Characteristics	RAS "Kiviter"			RAS "Eesti Kiviõli"		Estonian TPP
	Chamber ovens	Kiviter process			Galoter process	
		GGS-5	GGS-6	GGS	SHC-500	SHC-3000
Test number	1	2	3	4	5	6
Oil shale:						
Moisture, %	8.5	8.7	8.9	8.0	17.6	12.0
Conventional organic matter (dry basis), %	35.4	33.5	36.6	27.2	32.0	29.0
Fischer assay oil yield, %	23.8	23.0	24.3	18.1	21.4	19.1
Calorific value (bomb calorimeter), MJ/kg	13.52	13.06	16.86	9.80	12.10	10.88
Yield of products:						
Shale oil, %:						
Plant yield (raw shale basis)	4.9	16.4	16.4	11.2	13.6	12.0
Yield of Fischer assay oil	22.7	78.3	74.0	67.2	77.3	72.0
Specific gas yield, m^3/t	348	507	434	370	40	50
C_5 hydrocarbons in product gas, g/m^3	65	24	24	20	376	240
Operational data:						
Feed shale throughput rate, t/day	17.5	182	927	174	463	3000
Temperature, °C:						
of heat carrier	—	969	850	850	795	800
in heating chambers	1244	—	—	—	—	—
of oil vapours at the retort offtake	700	226	225	152	485	480
after condensation system	24	44	31	56	25	50

*SHC — solid heat-carrier; TPP — Thermal Power Plant.

Table 5. **Properties of Oil Produced by Semicoking Oil Shale**

Properties	Test number (see Table 4)					
	1	2	3	4	5	6
Density at 20 °C, g/cm³	1.073	0.9998	1.013	1.0132	0.9685	0.978
Viscosity at 75 °C, °E	1.74	2.8	3.3	3.3	1.3	1.4
Flash point, °C	98	104	100	114	2.8	55
Initial boiling point, °C:	180	170	195	180	80	92
Distillation, Vol. %, at:						
100 °C	—	—	—	—	3	1
120 °C	—	—	—	—	5	2
140 °C	—	—	—	—	6	6
160 °C	—	—	—	—	12	9
180 °C	—	1	—	—	16	15
200 °C	2	2	1	1	20	20
220 °C	5	4	4	4	24	24
240 °C	10	6	11	6	29	29
260 °C	16	8	16	11	33	36
280 °C	25	12	23	17	37	45
300 °C	30	19	28	29	43	—
320 °C	39	24	36	37	51	—
340 °C	44	35	46	54	61	—
360 °C	59	60	76	75	82	—
Calorific value (bomb calorimeter), MJ/kg	38.6	39.4	39.6	39.5	40.4	39.8
Phenolic compounds, %	19.4	28.1	23.4	24.6	11.5	15.0
Molecular mass, M	235	287	278	302	275	—
Elemental composition, %:						
C	86.7	83.5	83.3	81.6	83.0	83.6
H	7.7	10.1	9.3	9.4	10.1	10.1
S	0.7	0.7	0.7	0.7	0.8	0.9
O+N (by difference)	4.9	5.7	6.7	8.3	6.1	5.4

Table 6. **Chemical Group Composition of Light-middle Fractions of Shale Oil, wt. %**

Fractions and compounds	Test number (see Table 4)			
	1	2	4	5
Fraction boiling up to 200 °C:				
Alkanes and cycloalkanes	8	14	15	15
Alkenes	15	41	31	52
Aromatic hydrocarbons	56	22	31	21
Neutral oxygen compounds	16	16	19	11
Phenols	5	7	4	1
Fraction yield, %	4.5	3.88	2.6	15.7
Fraction boiling at 200-350 °C:				
Alkanes and cycloalkanes	5	8	9	6
Alkenes	2	13	10	12
Aromatic hydrocarbons	58	30	33	35
Neutral oxygen compounds	12	22	21	27
Phenols	23	27	27	20
Fraction yield, %	42.70	28.25	33.70	39.30

Table 7. **Characteristics of Retort Gas**

Indices	Test number (see Table 4)					
	1	2	3	4	5	6
Content of components, Vol. %						
CO_2	15.9	21.8	14.2	16.0	1.7	Traces
H_2S	0.8	0.6	0.6	0.6	Traces	Traces
C_nH_m	6.6	1.0	0.8	0.9	26.3	36.2
Including: C_2H_4	5.0	0.6	0.5	0.5	12.0	18.4
C_3H_6	1.2	0.3	0.2	0.3	8.9	8.7
C_4H_8	0.4	0.1	0.1	0.1	5.4	9.1
O_2	1.1	0.6	1.0	1.0	0.8	0.2
CO	12.5	3.9	7.3	4.7	8.6	8.6
H_2	26.0	5.5	7.6	9.0	14.5	14.4
C_nH_{2n+2}	17.2	2.8	1.95	2.4	24.1	38.4
Including: CH_4	14.1	1.4	1.5	1.7	14.4	19.8
C_2H_6	2.8	0.9	0.3	0.4	6.3	11.2
C_3H_8	0.2	0.3	0.1	0.2	2.2	5.4
C_4H_{10}	0.1	0.2	0.05	0.1	1.2	2.0
N_2	19.9	63.8	66.55	65.4	24.0	2.2
Content of H_2S, g/m^3	11	8	8	8	Traces	Traces
Calculated gross calorific value (without C_5^+ hydrocarbons), MJ/m^3	16.7	3.6	3.6	3.0	46.0	53.9

Table 8. **Properties of C_5^+ Light Gasoline Recovered from Gas**

Indices	Test number (see Table 4)			
	1	2	4	5
Density at 20 °C, g/cm³	0.823	0.7235	0.7183	0.6771
Refraction index, n_D^{20}	1.468	1.4200	1.4183	1.398
Molecular mass, M	86	89	—	—
Initial boiling point, °C:	50	36	—	25
Distillation, Vol. %, at:				
30 °C	—	—	—	9
40 °C	—	2	—	32
50 °C	—	8	—	50
60 °C	—	16	—	69
70 °C	—	25	—	78
80 °C	10	36	—	84
90 °C	—	48	—	88
100 °C	50	59	—	90
110 °C	—	70	—	—
120 °C	—	79	—	—
130 °C	—	86	—	—
140 °C	—	92	—	—
150 °C	87	93	—	—
200 °C	93	—	—	—
Elemental composition, %:				
C	88.2	—	—	—
H	9.0	—	—	—
S	1.3	—	—	—
O+N	1.5	—	—	—

Table 9. **Chemical Composition of C_5^+ Light Gasoline Fraction Recovered from Gas, wt. %**

Hydrocarbons	Test number (see Table 4)			
	1	2	4	5
Alkanes:				
n-propane	0.1	—	—	—
n-butane	0.2	2.9	—	4.1
n-pentane	1.1	7.5	—	8.7
n-hexane	1.2	8.4	—	5.0
n-heptane	2.3	6.8	—	3.1
n-octane	1.7	5.9	—	0.8
higher paraffins	4.1	—	—	—
Total	10.7	31.5	19.3	21.7
Alkenes:				
propene-1	0.2	—	—	—
butene-1	0.4	2.9	—	6.6
trans-butene-2	0.4	1.3	—	4.0
cis-butene-2	0.3	1.0	—	2.8
1,3-butadiene	—	1.5	—	3.6
pentene-1	1.3	5.6	—	11.4
trans-pentene-2	0.5	2.9	—	6.2
cis-pentene-2	0.3	1.7	—	3.2
2-methylbutene-2	—	0.7	—	2.5
cyclopentene	—	1.9	—	4.1
trans+*cis*-1,3-pentadiene	—	5.8	—	8.4
hexene-1	1.5	10.7	—	10.7
hexene-2	0.6	3.5	—	2.3
heptenes	3.7	9.6	—	5.7
octenes	2.6	6.1	—	0.5
nonenes	1.1	—	—	—
isoolefins	0.3	—	—	—
diolefins	3.4	—	—	—
cycloolefins	1.5	—	—	—
higher alkenes	0.5	—	—	—
Total	18.6	55.2	57.6	72.0
Aromatics:				
benzene	39.4	7.3	13.7	3.3
toluene	14.4	1.9	4.0	0.8
ethylbenzene	1.4	—	—	—
higher aromatics	7.5	—	—	—
Total	62.7	9.2	17.7	4.1
Identified	92.0	95.9	94.6	97.8
Not identified	8.0	4.1	5.4	2.2

In the middle of the 1980's a method for retorting fine-grained oil shale (1-5 mm) in fluidized bed was developed by the Oil Shale Research Institute. An experimental retort was built at RAS "Eesti Kiviõli" with a design capacity of 25 tons of oil shale per day. The retort has a simple design, and as the first test runs have shown, is easily operated and controlled. The yield of shale oil was as high as 90% of the Fischer Assay. Further testing and improvement of this retort, however, was suspended because of financial problems.

Technical and economic data on the performance of the retorts erected in the post-war period, as well as physical and chemical properties of the oil shale products, are given in Tables 4-9.

In conclusion, it is pertinent to note that in the 1970's and 1980's technologies were introduced at the Estonian oil shale processing plants for processing imported raw materials other than oil shale. For example, at the RAS "Kiviter" the synthesis of ammonia and urea was introduced based on natural gas as a feedstock. This was followed by the production of sulphuric acid from lump sulphur. Pyrolysis oil (a liquid by-product of ethylene production) was imported to produce aromatic hydrocarbons and various synthetic resins. The production of benzoic acid was started based on liquid-phase oxidation of toluene by proprietary Corporate technology. At the same time, the manufacture of synthetic detergents and formalin was introduced at RAS "Eesti Kiviõli".

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