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ENVIRONMENTALLY SUSTAINABLE USE OF ENERGY AND CHEMICAL POTENTIAL OF OIL SHALE

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ABSTRACT

The paper contains analysis of Estonian oil shale retorting processes in terms of Best Available Techniques (BAT) criteria. The different types of wastes of shale oil thermal treatment processes are described and analyzed some possibilities of their minimizing.

THE CRITERIA OF ENVIRONMEN-TAL SUSTAINABILITY

Negative environmental impacts of oil shale use, whether for electricity production in power plants or for oil producing, are well known.

One way to reduce possible environmental damages by shale oil producing should be using of best available techniques (BAT) criteria.(1-8) BAT term is defined in the EU Directive 96/61/EC concerning integrated pollution prevention and control (the IPPC Directive) as "the most effective and advanced stage in the development of activities and their methods of operation which indicate the practical suitability of particular techniques for providing in principle the basis for emission limit values designed to prevent and, where that is not practicable, generally to reduce emissions and the impact on the environment as a whole." The term "techniques" includes both the technology used and the way in which the installation is designed, built, maintained, operated and decommissioned. Those "available" techniques should allow implementation in the relevant industrial sector, under economically and technically viable conditions and "best" mean most effective in achieving a high general level of protection of the environment as a whole.

Information on each technique should preferably include the following elements :

1 Description
2 Main achieved environmental benefits:
3 Operational data: Actual performance data (including reference conditions and monitoring periods) on emissions / wastes and consumption (raw materials, water and energy).
4 Cross-media (whole environment) effects: Potential effects due to implementing the technique (advantages and disadvantages supported by data if available) in various environmental compartments such as :
  4.1 Energy consumption
  4.2 Acidification resulting from emissions to air
  4.3 Oxygen depletion potential in water
  4.4 Persistent /toxic/ bioaccumulable components in water or to land (incl metals)
  4.5 Creation or reduction in (waste) residues
  4.6 Ability to re-use or recycle (waste) residues
  4.7 Risk of accidents
  4.8 Consumption of raw materials and water.
5 Economics: Information on costs (investment and operating) and any savings (e.g. reduced raw material consumption, waste charges) where appropriate. Economic information relevant to new build and retrofit to existing installations will be included;

6 References to literature and example plants : Literature for more detailed information on the technique and examples of plants where the technique has been implemented. The degree to which the technique is in use in Europe or world-wide may be useful information.

The assessment of oil shale thermal treatment technologies to BAT means:

1. Identification of the key environmental issues for the technologies;
2. Identification of the best environmental performance levels, on the basis of the available data in the European Union and world-wide;
3. Examination of the conditions under which these performance levels were achieved.

RETORTING OF OIL SHALE

Retorting of oil shale is the main thermal process used in Estonia and worldwide for shale oil production. By-products of the process are gas, process water and solids: retorting residue and ash.

Retorting is accomplished in different forms (9). The principal methods of retorting are processing of lump oil shale (lumps 25 – 125 mm) with gaseous heat carrier (process "Kiviter" and processing of fines (less than 25 mm) with solid heat carrier (process "Galoter").

The principal differences of aforementioned processes are as follows:

1. Method of oil shale drying,
2. Use of different heat carriers,
3. Different processes concomitant with retorting (combustion, gasification),
4. Different handling of retorting residue and routs of utilization,
5. Different ways of using chemical and energy potentials of oil shale.

Differences in technology are accompanied by corresponding differences in process equipment.

Retorting with gaseous heat carrier ("Kiviter")

"Kiviter" technology is based on thermal treatment of lump oil shale with gaseous heat carrier. Oil shale is dried, thermal treated and the resulting retorting residue is cooled in a single apparatus – a vertical retort. The general scheme of process see Fig. 1.

Heat treatment of oil shale in the retort results in formation of oil, retorting gas and retorting water. Because of high temperature of gaseous heat carrier (800 – 850 ºC) thermal decomposition of organic matter of oil shale is accompanied by secondary process of partial cracking of oil that leads to diminished yield of oil and increased yield of gas, and by process of decomposition of carbonates that results in higher content of CO_2 in retorting gas. At the same time takes place partial gasification of carbon contained in retorting residue. Heat carrier with water vapor from oil shale drying, retorting gas, oil vapors, water vapor from organic matter decomposition, and gas of retorting residue cooling leave the upper part of the retort and enter the condensation system, where gas-vapor mixture is cooled, oil and water condensed and separated from gas. Heavy and middle-light oil flows are taken.

Retorting residue leaving hot zone of the retort at temperature above 650 ºC is cooled with return-gas. Thus retorting residue physical heat is utilized in the retorting process. Cooled retorting residue contains 6 – 7 % of total organic carbon (TOC). After contact with water in the discharging device the wet (30 – 35 % water) retorting residue is dumped.

Gaseous heat carrier is obtained by combustion of a fraction of retorting gas in retort furnaces.

The process equipment is relatively simple.

Retorting with solid heat carrier "Galoter"

Process with solid heat carrier in comparison with process using gaseous heat carrier is characterized by more complicated technology and equipment. The general scheme of process see Fig. 2.

Oil shale fines are dried in a separate drier with gaseous heat carrier. Heat carrier is produced by combustion of retorting residue and partly cooled with water. Drying is carried out in fluidized bed and oil shale is separated from gas in cyclones. Minute oil shale particles leaving the cyclones are

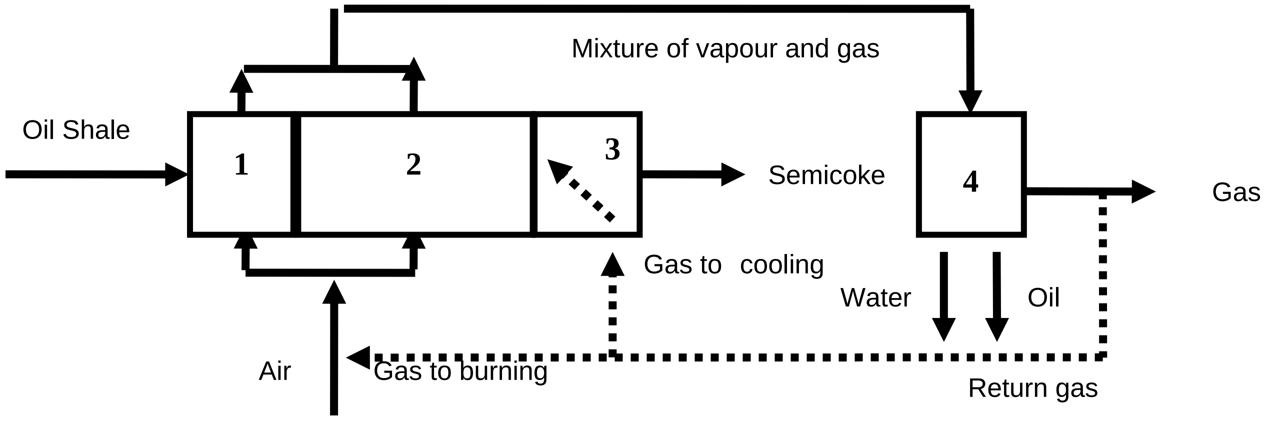

Fig.1 Common scheme of retorting with gaseous heat carrier (1 – Zone of Drying , 2 – Zone of retorting, 3 – Zone of cooling, 4 – Condensation.)

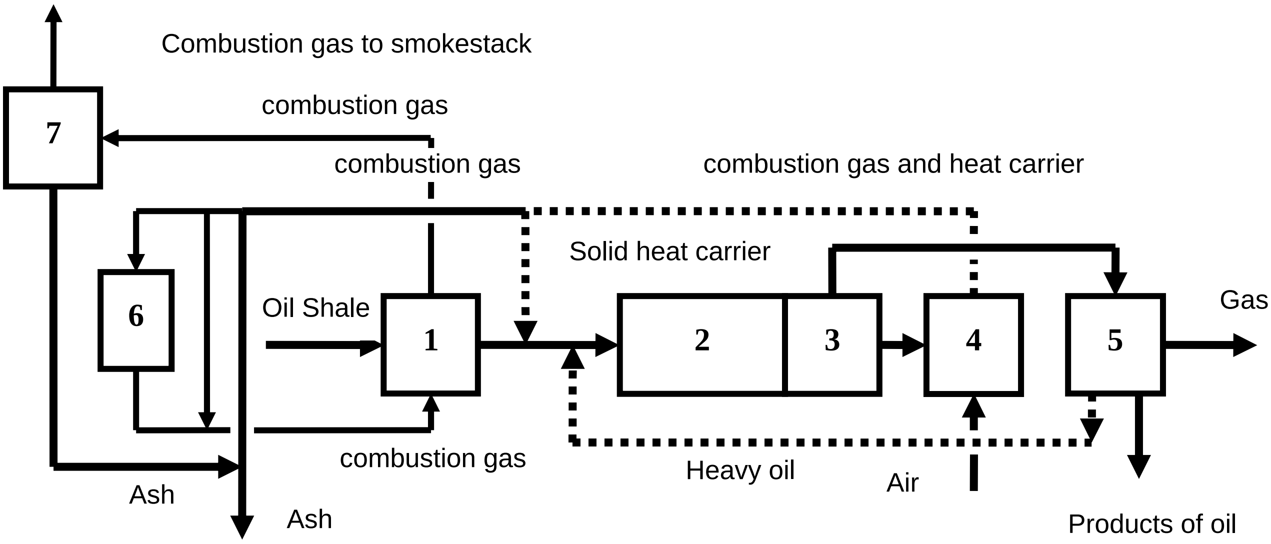

Fig.2 Common scheme of retorting with solid heat carrier (1 – Zone of drying, 2 – Zone of retorting, 3 – Separating of semicoke, 4 - Combustion of semicoke, 5– Condensation, 6 – Boiler, 7 – Electrostatic cleaner)

collected in electrostatic cleaner and dumped with ash.

Dry oil shale leaves the drier at temperature up to 135 ºC and then is mixed with solid heat carrier – hot ash (750 – 800 ºC) – at a ratio of 1,8/1. The ash is obtained by combustion of retorting residue in a separate furnace. Mixture of oil shale and heat carrier is fed into a horizontal rotating retort. Thermal treatment of oil shale starts in the mixer and proceeds in the retort. Solids leaving the retort at 460 ºC comprise a mixture of ash and retorting residue at a ratio of 2,4/1. Then the mixture enters the dust chamber to be separated from gas phase.

Investigations (10) has shown that aforementioned solid residue contains about 4 % of total organic carbon (TOC). Heat carrier contains 1 % of organic carbon. So, calculated content of TOC in retorting residue exceeds 11 %. Such a high level of TOC content might be explained by return of heavy shale oil after condensation and rectification into the mixer. Contact with hot heat carrier results in intensive heavy oil cracking with formation of gas, lighter oil fractions and coke. The amount of lighter oil fractions is substantially less than that of heavy oil.

Solid heat carrier contains free CaO, which binds oil shale phenols and thus diminishes their content in oil. That also reduces amount of oil and content of useful components in it.

THE GENERAL WASTE FLOWS OF OIL SHALE THERMAL TREATMENT PROCESSES

To evaluate environmental influence of the processes it is necessary to know flows of energy, materials and various kinds of waste in quantitative and qualitative terms. Those data are also needed to establish BAT criteria. The general material and waste flows of "Kiviter" and "Galoter" processes see Fig. 3 and 4 respectively. Investigations were carried out to have more accurate information about quantity and composition of different flows and to find ways to reduce formation of waste by technological means. Obtained results are classified according to waste types and are further discussed.

The influence of oil shale processing plants on environment is connected with a large amount of produced solid waste. The most harmful ingredients of the waste are bituminous substances that include polyaromatic hydrocarbons, phenols and others, and also minerals containing sulfides.

Solid waste of Kiviter process is formed mainly in the oil shale thermal treating operation. Processing of one tonne of oil shale results in formation of 480 – 490 kg of solid retorting waste that contains following amounts of substances mostly damaging the environment:

- Carcinogenic polyaromatic hydrocarbons – up to 5,3 g per tonne of solid residue;
- Sulfide sulfur (in aqueous extract) –200 to 400 g per tonne of solid residue;
- Volatile phenols*) (in aqueous extract) - up to 22 g per tonne of solid residue;
- Total organic carbon (TOC) – up to 14 % of solid residue (Inert carbon comprise 9 – 11%)

*) Permissible content of volatile phenols is established by regulations.

Galoter process produces 600 –650 kg of ash per one tonne of processed oil shale. Now ash is disposed by hydraulic transport; dry transportation is envisaged.

Ash main harmful components are as follows:

- Sulfide sulfur up to 11,7 kg per tonne of ash;
- Phenols (in aqueous extract) - up to 52,4 g per tonne of solid residue;
- Total organic carbon (TOC) – up to 1 %

Difference in TOC content in solid residues from Kiviter and Galoter processes is caused by additional combustion of retorting residue in a fountain furnace to produce heat carrier in case of Galoter process.

Different amounts of formed solid residues arise from different water content of starting oil shale (10 – 11 % in Kiviter process and virtually dry oil shale in Galoter process) and different organic matter content (heating value of oil shale used in Kiviter process is 3300 kcal./kg while in Galoter process it is 2300 kcal./kg).

The aforementioned shows that solid waste from oil shale processing contains environmentally hazardous substances in a large amount. Integer index of environmental pollution is total organic carbon content (TOC), which is determined in accordance with EVS EN 13137, and dissolved organic carbon, which is measured in aqueous extract in accordance with EN 1484.

According to European Union directives, permissible level of TOC in solid waste from technological processes is 6 %, and from combustion – 3 % (2000/76/EC).

Directive 2033/33/ states that determination of DOC in aqueous extract is compulsory

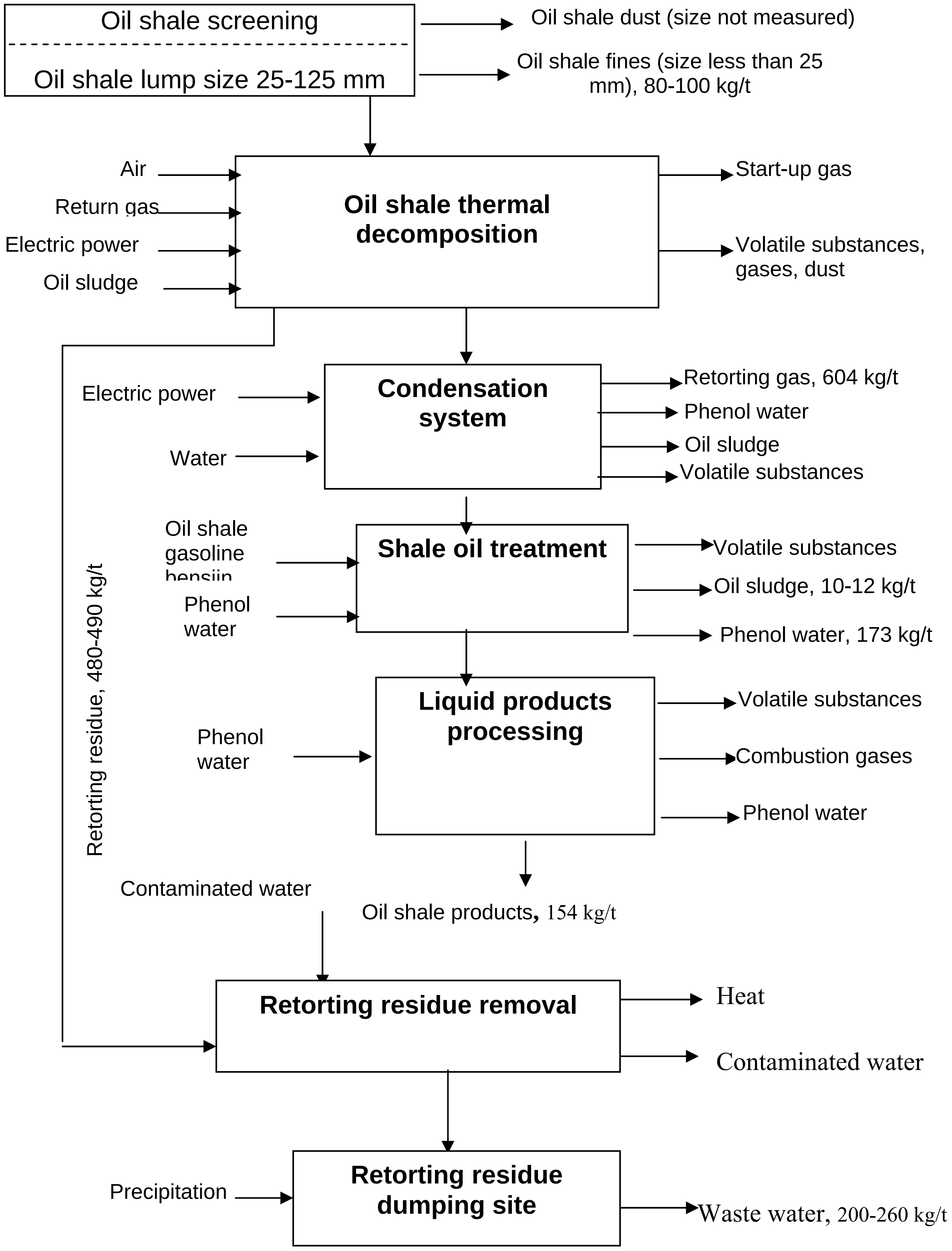

Fig. 3 The general waste flows of oil shale retorting with gaseous heat carrier

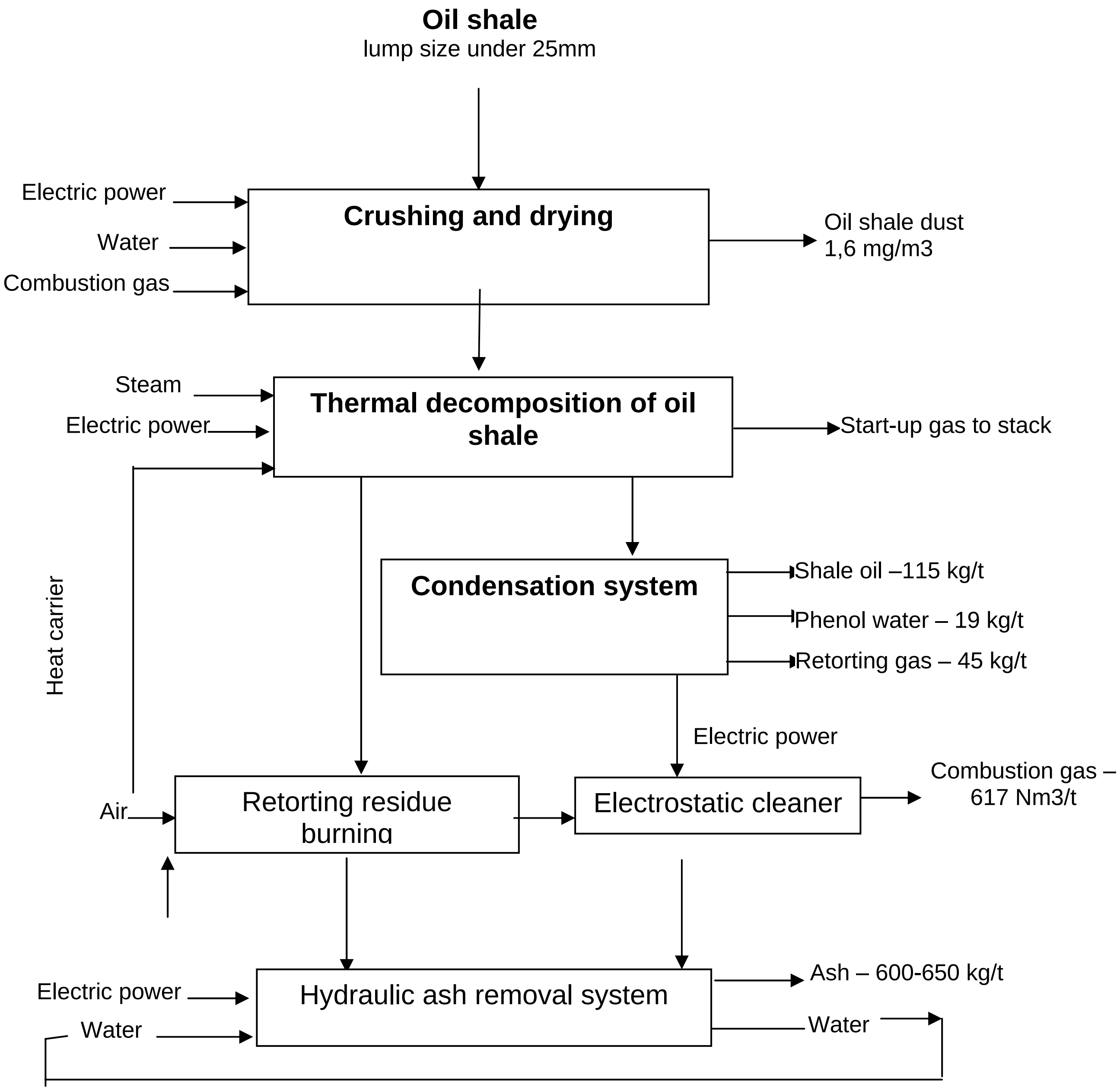

Fig. 4 The general waste flows of oil shale retorting with solid heat carrier

for decision-making on suitability of waste for dumping.

Preliminary comparative analysis of data on TOC and DOC reveals that there is no direct link between them, but they are related to process variables of oil shale processing. Data on ash produced in Galoter process show that low content of TOC does not always prevent from exceeding permissible level of DOC required by 2003/33/EC directive. To evaluate the danger that solid waste presents and to find ways of its dumping it is necessary to carry out additional work on analyses of TOC and DOC together with determination of waste composition at different process variables.

Content of TOC in solid retorting waste from Kiviter process may reach 14 %. TOC consists of inert carbon formed during decomposition of kerogen, and carbon contained in bituminous and tar substances.

Carbon content in retorting residue of lump oil shale thermal treatment

Because retorting residue is mainly dumped, investigations were carried out to establish factors influencing TOC and DOS content and the possible ways of bringing these properties in accordance with existing norms by changing process variables

Description of TOC and DOC formation in retorting residue

Retorting of oil shale lumps 25 – 125 mm proceeds in vertical retorts with cross-flow of gaseous heat carrier, which is produced by combustion of return gas in furnaces built in the retort and mixing the combustion gases with cold return gas. Heat carrier temperature is up to 800 ºC.

Use of cross-flow of heat carrier resulted in significantly increased yield of oil products, but some technological, e.g. heating problems emerged. First of all, it had an impact on secondary processes as pyrolysis and gasification. Mineral matter of kukersite oil shale is distinguished by high content of carbonates (40–50 %). Their decomposition starts at 650 ºC and makes inevitable formation of free calcium oxide at temperatures of heat carrier and retorting process. Some oil components possibly react with the oxide to form deposits of reaction products on the oxide surface.

Previous investigations have shown that heat carrier cross-flow creates a diagonal pattern of temperature distribution field (Fig 5). So, conditions of heat transfer from flow heat carrier to oil shale are uneven along the retorting chamber, and the lower part on the hot side is overheated while material adjacent to the cold side is underheated. The result is that thermal decomposition of oil shale organic matter could be incomplete. That is especially true if retort capacity is increased, flow of heat carrier reduced and heat carrier temperature diminished. Hence, there is a possibility of not completely processed material leaving the retorting chamber and entering the cooling zone. Such material is removed from the retort alongside with normally processed retorting residue and causes increase in carbon remaining in the residue.

As industrially processed lumps of oil shale are of different size (25 – 125 mm), the largest exceed 5 times the size of the smallest ones; there is another cause for influence on decomposition process.

If decomposition products leave lumps and the void space between the lumps relatively quickly in case of smaller lumps, then in case of larger lumps volatile products are subjected partly to secondary pyrolysis Also was established the fact that in retorting process volatile substances disengage from the surface of oil shale pieces at a maximum speed of 0,27 mm/s and thus time of their stay inside the piece exceeds quite significantly their retention time in the void space. The larger the lump, the more influence is exerted by secondary processes on properties of retorting products, the solid residue included.

Secondary reactions of pyrolysis and cracking are most intensive at higher temperatures in the overheated zone inside the lumps as well as in the void space. They produce additional to normally formed in the course of organic matter decomposition amount of coke, and thus increase in content of total organic carbon (TOC) in the retorting residue.

On the other hand, gasification of carbon present in the retorting residue is also possible ($CO_2 + C = 2CO$), thus decreasing TOC content.

Decomposition of carbonates diminishes the total amount of retorting residue. So, carbon in the retorting residue becomes more concentrated and TOC content is increased. Another factor contributing to TOC increase and connected to decomposition of carbonates is binding of shale oil components by newly formed calcium oxide.

Evaluation of effects of each abovementioned secondary process on TOC content in retorting residue requires further investigations and is out of scope of
the present article.

Table 1

Influence of side furnace and furnace temperature on retorting residue properties

Test no.	Side furnace temperature, °C	Retorting residue properties		
		TOC content, %	DOC content, mg/kg	Oil content, %:
1		15,4	901	7,3
2		9,7	138	2,1
3		8,7	817	2,6
4	845	9,4	291	1,4
5	848	7,1	312	0,9
6	848	6,8	787	0,8
7	850	9,6	853	0,7
8	950	8,2	733	0,5
9	950	9,5	571	1,11
10	988	8,6	673	0,4
11	1000	7,4	126	0,4
12	1000	8,8	694	0,9
Analisis of results without side furnace				
Average content		11,3	619	4
Maximum content		15,4	901	7,3
Minimum content		8,7	138	2,1
Difference of boundary values		6,7	763	5,2
Analisis of results with side furnace				
Average content		8,4	560	0,79
Maximum content	1000	9,6	853	1,4
Minimum content	845	6,8	126	0,4
Difference of boundary values	155	2,8	727	1
Comparison of results (without side furnace - with side furnace)				
Average content		2,9	58,7	3,21
Maximum content		5,8	48	5,9
Minimum content		1,9	12	1,7

But two main conclusions are possible. First, it is necessary to find out means for more even temperature distribution of heat carrier cross-flows in retorts to achieve relative reduction in TOC content in retorting residue before dumping and secondly to make possible further processing of retorting residue.

Possibilities of structural supplements in retort design

As was stated afore, temperature distribution in retorting chamber of the present retort design is very uneven. At the hot side of the chamber retorting products are subjected to partial coking while at the cold side thermal decomposition of oil shale organic matter is incomplete. Addition of return gas or heat carrier from a side furnace should decrease TOC and DOC content in retorting residue because of more even temperature distribution in cross-flows.

To prove that assumption industrial scale tests were carried out in a retort equipped with a side furnace at different furnace temperatures. The side furnaces temperatures and results of retorting residue analyses are give in Table 1. Samples of retorting residue were taken

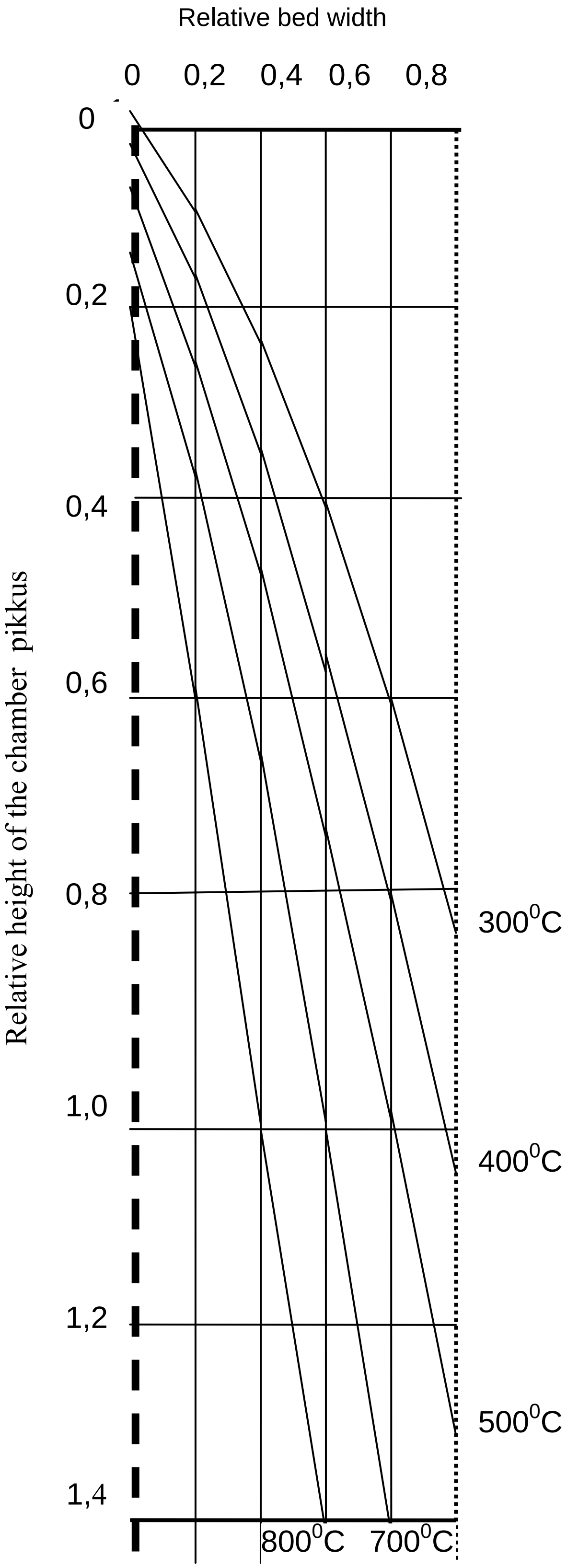

Fig 5. Distribution of solid material temperature inside the retorting chamber

before dumping and all results were calculated on dry basis. As could be seen from the data, there are two main variables: work with the side furnace or without, and temperature in the furnace. So, properties of retorting residue were analyzed in relation to these factors (see Table 1).

The first conclusion is that properties of retorting residue are generally much more stable in case of work with a side furnace, especially concerning data on TOC and oil content. The conclusion is that use of a side furnace significantly levels off temperature conditions of retorting process.

As furnace temperature is raised, oil content is clearly diminishing (2 – 3 times). But there is no clear correlation between TOC content and furnace temperature. Evidently, abovementioned secondary processes are more active at higher temperatures.

DOC content varies widely and is not dependant on use of a side furnace and furnace temperature. One of the possible explanations is that content of soluble carbon in retorting residue is determined by process variables acting beyond the retorting chamber.

Partial gasification of retorting residue

Design of some retorts makes possible to treat retorting residue with mixture of air and steam before the residue is removed. Under these conditions residue carbon is partly gasified and gaseous products are moved away with heat carrier flow.

To establish possible influence of the operation on content of DOC and TOC, two sets of samples of residue from retorts of that design were taken, with and without gasification. Results of analyses were compared with similar results obtained from tests with side chamber retort.

As was expected, gasification under these conditions reduces average TOC content in retorting residue, but only in part. In essence, energy potential of retorting residue remains untapped and problem of more complete gasification should be dealt with in the future,

Determination of DOC in these samples led to irregular results. In one case DOC content was 756,7 mg/kg, and in another – 138,1 mg/kg. The same phenomenon was mentioned above.

WASTEWATER

In Kiviter process about 1 m3 of wastewater is formed per 1 tonne of oil shale (including industrial water and precipitation, and water from solid retorting waste dumping).

In Galoter process phenol water is fed into big boilers for combustion. Treatment of wastewater from Kiviter process is accomplished in standard biological treatment plants.

The influence of phenols and other organic impurities on chemical oxygen demand (COD) of phenol waters

COD (chemical oxygen demand) is one of the most significant characteristics, connected with ecological danger of wastewater. Under conditions of joint discharge of municipal and industrial wastewater, the COD value of biologically treated water should not exceed 125 mg/l, and, in case of industrial water only, the limit is 250 mg/l. Maximum permissible concentration (MPC) of monobasic phenols in the effluent discharge is 0,1 mg/l, and of dibasic phenols – 15 mg/l

In connection with increasing demand for oil shale phenols, joint processing of Kiviter shale oil with fuel oil fractions from Galoter process has started. But that has created some problems because of increasing the COD value in phenol water from shale oil treatment operation and in dephenolized water. The composition of chemical compounds, transferred into phenol water at shale oil treatment operation in joint processing of Kiviter and Galoter shale oils, and, the influence of phenols and other organic impurities on COD of phenol and dephenolized waters was studied using as model laboratory samples as samples, taken at different stages of industrial process of water dephenolation.

Table 2 – Properties of investigated shale oils

Item	Total retorting oil		Shale oil fuel	
	Prepared sample	Initial sample	Grade A	Grade B
Dencity at 20 °C, kg/m^3	915	943	1020	970
Kinematic viscosity at 50 °C, mm^2/s	5,8	6,3	73	16,7
Solids, mass %	0,04	1,27	0,19	0,08
Ash, mass %	0,02	0,55	0,12	0,06
Water, mass %	1,7	0,5	0,2	0,2
Elements, %				
C	81,4*		83,1	81,8
H	10,1*		9,7	9,6
S	0,8*		0,5	0,6
O + N	7,9*		6,7	8,0

Table the number of shale oil sample).
Concentration of phenols in laboratory samples of phenol water, obtained by washing model samples of shale oil and gasoline fraction, varied from 1 g/l to 8 g/l, concentration of impurities (volatile acids and bases in total) is less than 90 mg/l in water from shale oil washing, and less than 160 mg/l from gasoline fraction washing So, concentration of impurities is one order of magnitude less than minimal

Model shale oil samples and their washing with water

The initial sample for investigations is total retorting shale oil from Kiviter process consisting of:

Light-middle oil	48 mass %
Heavy oil	26 mass %
Gasoline fraction (diluent)	26 mass %

Properties of investigated shale oils are presented in Table 2.
Test samples of grade A and B shale oil fuel have complied with local standard EE 10579981 – NJ ST 9 : 2005.
The compositions of shale oil samples used in water-washing tests, are presented in Table 2.
Samples of oil shale were subjected to water extraction in separating funnels. Heated to 65 °C, distilled water was added to oil test sample (ratio of oil to water 1 : 1), the composite was mixed for 30 min, then settled for one hour at 50 - 55 °C and after that the phenol water was separated.
In obtained water samples, phenols were determined using differential ultraviolet spectroscopy and carbonyl compounds by measuring consumption of hydroxylamine chloride (oxymation reaction). For determining volatile acids and bases, the water samples were distilled and the distillates were titrated to pH 9 by determining of bases, and to pH 1 - 2 in case of acids. Ammonium nitrogen was determined by standard method (ISO 5664). Analyses of phenol water laboratory samples are presented in Table 3 (the number of water sample corresponds with on linear dependence between COD and phenol concentration (R2 = 0,9904)

Table 3 – Characteristics of industrial phenol water samples

Item	**Samples of phenol water**						
	From storage plant	**From oil treating plant**		**To dephenolation plant**		**Dephenolized water**	
	27.04.05	27.04.05	24.05.05	27.04.05	24.05.05	27.04.05	24.05.05
pH	4,90	5,13	5,01	4,93	5,13	5,12	5,25
Concentration:							
- phenols, g/l	12,0	14,0	10,0	12,9	11,5	0,20	0,15
- volatile bases expressed as ammonium ion, mg/l	626,4	590,4	482,4	580,0	482,4	189,0	396,0
- volatile acids expressed as acetic acid, mg/l	768,0	912,0	864,0	912,0	744,0	606,0	732,0
- ammonium nitrogen, mg/l	734,3	704,8	581,3	734,3	631,8	655,0	581,3
Quantity of 0,5 N solution of NaOH equivalent to 0,5 N solution of $NH_2OH \cdot HCl$ consumed in oxymation reaction, ml per 50 ml of sample	2,7	3,3	2,7	2,6	3,25	2,3	2,8
COD, g/l	38,6	40,7	36,6	37,9	38,2	4,55	4,61

As shown in Table 3, the washing of grade A and/or B fuel oils, and retorting oils with their admixture with water, results in increased concentration of phenols. In comparison with washing of retorting oil only, phenol concentration grows from 4,6 g/l to 8,0 g/l. Phenol water pH changed from 4,35 to 5,53 in that case. Full substitution of light-middle oil with grade B fuel oil or heavy oil with grade A fuel oil follows by pH increase up to 4,92.

Sulfur compounds are presumably present in phenol waters as hydrosulfides and mercaptides.

Concentration of volatile bases in phenol water from washing of retorting oil is about twice as much as that from washing of grade A and/or B fuel oils. Changes in concentration of volatile acids (from 40 to 60 mg/l in average) in phenol water samples are connected with variations in gasoline fraction content in oil samples, and in all cases exceed concentration of volatile bases 2 – 3-fold. That gives ground to assumption, that different nitrogen compounds are present in phenol water like amino acids, ammonium salts, amino hydroxides.

. Investigations of industrial phenol waters

Characteristics of industrial samples of phenol and dephenolized waters from oil treatment and dephenolation plants in the period of joint processing of retorting oils and grade A and/or B fuel oils are presented in table 4

In industrial samples of phenol water, the range of phenol concentration is wider – from 0,15 to 14 g/l (Table 3), and total content of impurities is about ten-fold that of laboratory samples. Concentration of volatile bases is 432 – 580 mg/l, and of volatile acids 744 – 912 mg/l. Concentration of these impurities changes very little in the course of dephenolation process, but concentration of phenols decreases from 10 – 14 g/l to 0,2 g/l. There is a linear dependence between COD of industrial water samples and phenol concentration (R2 =0,9783)

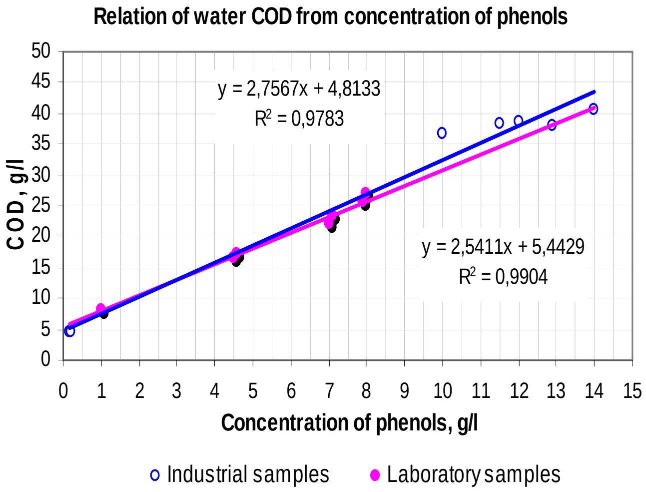

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Fig. 6

At the final stage of dephenolation process, dephenolized water is steam distilled to remove remnants of extraction agent as an azeotrope. Carbonyl compounds, which have significant influence on COD of water canalized for biological treatment, are also in part removed in the operation. For determining, how phenols and other impurities will influence water COD, a model sample of dephenolized water was prepared.

Summary results of phenol waters studies

Analyses of phenol waters prepared by washing of model oil samples with water show that addition of grade A and/or B fuel oils to retorting oils results in increased concentration of phenols. Regardless of the oil combination in the samples a linear dependence between washing water COD and concentration of phenols in the range of 1 – 8 g/l was observed.

Concentration of impurities in laboratory samples of phenol water is for volatile bases 10 – 27 mg/l, and volatile acids 36 – 78 mg/l. Concentration of volatile bases in phenol water from washing of retorting oil is about twice as much as that from washing of grade A and/or B fuel oils. Changes in concentration of volatile acids (from 40 to 60 mg/l in average) in phenol water samples are connected with variations in gasoline fraction content in oil samples, and

in all cases exceed concentration of volatile bases in 2 – 3 times.

Concentration of impurities in industrial samples of phenol water is as follows: volatile bases 480 – 590 mg/l, volatile acids 744 – 912 mg/l. Concentration of volatile bases and volatile acids changes very little in the course of dephenolation process, but concentration of phenols decreases from 12 g/l to 0,2 g/l. There is a linear dependence between COD of industrial water samples and phenol concentration.

The influence of certain groups of compounds on COD of their water solutions has been established. Contribution of impurities to COD of dephenolized water is about 90 %.

Reduction of dephenolized water COD needs as maximum decrease of phenol concentration as diminishing the amount of remnants of extraction agent and of carbonyl compounds.

ATMOSPHERIC EMISSIONS

In Kiviter process 1,6 kg of dangerous atmospheric emissions per 1 tonne of oil shale is formed, including 0,57 kg of volatile hydrocarbons.

In Galoter process 14,2 kg of dangerous atmospheric emissions per 1 tonne of oil shale is formed, including 12,8 kg of carbon monoxide and 0,96 kg of volatile hydrocarbons.

COMPILATION OF CARBON, CHEMICAL AND ENERGY BALANCES BY OIL SHALE RETORTING PROCESSES.

The balances of carbon in products in relation to organic matter were compiled to compare the processes. As laboratory investigations have shown, samples of oil shale with different heating values (10170 and 13814 MJ/kg) contain, correspondently, 26,9 and 35,7 % of organic matter, but carbon content in the matter is much the same, about 77,5 %. Distribution of carbon between products of Fischer assay is as follows: 54,2 % in oil, 6,4 % in gas and 16,9 % in retorting residue (77,5 % in total).

In case of gaseous heat carrier: 41,8 % in oil, 20,2 % in gas, 2,5 % in gas gasoline, and 13,0 % in retorting residue.

In case of solid heat carrier: 40,4 % in oil, 10,5 % in gas, 2,1 % in gas gasoline, and 25,5 % in retorting residue.

Energy supply for processes and control is essential in environmental and economic feasibility studies of the processes.

Energy supply for the process of shale oil production consists of two parts: internal energy of organic matter of oil shale that is distributed between products, and flows of heat and electricity that are needed for the operation.
Use of internal energy in the process of oil shale thermal treatment is best described by chemical efficiency of the process that is traditionally defined as the share of internal energy of oil shale turned into internal energy of useful products.
Energy efficiency of the process takes into account also energy from the outside consumed in the process.

$$K\eta = (Qoil + Qrg + Qgg) * 100 \ / \ Qos$$

$$E\eta = ((Qoil + Qrg + Qgg) + Qrr) * 100 \ / \ (Qos + Qel + Qsteam)$$

$K\eta$ – chemical efficiency (%);
$E\eta$ – energy efficiency (%);
Qoil – chemical heat of total shale oil (combustion heat);
Qrg – chemical heat of retorting gas (combustion heat);
Qgg - chemical heat of gas gasoline (combustion heat);
Q_{os} - chemical heat of oil shale (combustion heat);
Q_{rr} - chemical heat of retorting residue used in the process;
Q_{el} – electric power used in the process;
Q_{steam} – steam used in the process.
Efficiencies of lump oil shale retorting with gaseous heat carrier were calculated.:
Chemical efficiency. 68,9%
Energy efficiency. 72 %
For solid heat carrier process respectively: Chemical efficiency. 71,5 %
Energy efficiency. 64,5 %
Analysis and comparison of the processes show that both of them need optimization to enhance their chemical and energy efficiencies.
Evaluations with the use of chemical efficiency and chemical potential of oil shale resource require refined method for their determination. Besides distribution of energy resource of the raw material between products, it is advisable to consider in greater extent chemical value of products, energy consumption in the process and utilization of energy of waste products

CONCLUSIONS

Results of so far carried out investigations are not sufficient to make final conclusions on choice between Galoter and Kiviter processes on the basis of only BAT criteria. These processes use oil shale pieces of different dimensions and do not exclude each other. Both of them have proved their economic viability. However, from environmental viewpoint both processes need additional investigations and development of new technologies, and should comply with European regulations.
For Kiviter process it means:

- Yield of oil could be increased by lower temperature of gaseous heat carrier Kiviter process to curtail the secondary processes. Decomposition of carbonates is also diminished that way. But at the same time content of organic compounds in retorting residue is rising.

- To use heat of retorting residue and diminish TOC content below 1 %, retorting residue in the lower part of the retort could be gasified. At the same time additional amount of gas rich in combustible substances is produced.
- Another possibility of using heat of retorting residue is to discharge it from the retort without cooling and then burn in a separate furnace for steam production or for heating air used in the process.

It is necessary to reduce atmospheric emissions and solve the problem of utilization phenol water in case of *Galoter* process.

REFERENCES

1. Directive 96/61/EC concerning integrated pollution prevention and control, Official Journal L 257, 10/10/1996 P. 0026 – 0040. Website:ec.europa.eu/environment/air/stationary
2. COUNCIL DIRECTIVE 1999/30/EC of 22 April 1999 relating to limit values for sulphur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter and lead in ambient air (OJ L 163, 29.6.1999, p. 41). Piirväärtused on umber arvutatud 01.01.04-le.
3. DIRECTIVE 2000/76/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 4 December 2000 on the incineration of waste (OJ L 332, 28.12.2000, p. 91).
4. DIRECTIVE 2000/69/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 16 November 2000 relating to limit values for benzene and carbon monoxide in ambient air (OJ L 313, 13.12.2000)..
5. European Parliament and Council Directive 94/63/EC of 20 December 1994 on the control of volatile organic compound (VOC) emissions resulting from the storage of petrol and its distribution from terminals to service stations (Official Journal L 365, 31/12/1994 P. 0024 – 0033).
6. COUNCIL DECISION of 19 December 2002 establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of and Annex II to Directive 1999/31/EC (2003/33/EC) (OJ L 11, 16.1.2003, p.27-49).
7. DIRECTIVE 2000/76/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 4 December 2000 on the incineration of waste (OJ L 332, 28.12.2000, p. 91).
8. J. Soone, S. Doilov Resources and comparison of contemporary technologies used for oil shale processing. // Oil Shale. 2003. Vol. 20, No. 3S. P. 311-323.
9. .J. Kann, A. Elenurm, I. Rohla, N. Golubev, A. Kaidalov, B. Kindorkin. About thermal low-temperature protsessing of oil shale by solid heat carrier metod. // Oil Shale. 2004. Vol. 21, No. 3. P. 195-203.
10. Tiikma L., Molder L., Tamvelius H. Resources of water-soluble alkylresorcinols in oil fractions and retort water formed by processing oil shale in generators of high unit capacity // Oil Shale. 1991. vol.8, No.4. P. 350-354.