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SUSTAINABLE UTILIZATION OF OIL SHALE RESOURCES AND COMPARISON OF CONTEMPORARY TECHNOLOGIES USED FOR OIL SHALE PROCESSING

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Processing of oil shale in Estonia was started in the 1920s. Since 1924 to the present time the technology of processing large-particle oil shale in vertical retorts with gaseous heat carrier, and since 1980 that of processing fine-grained oil shale with solid heat carrier are in operation.

To assess the quality of oil shale the standard Fischer assay method (heating in aluminum retort to temperatures 500–520 ºC) is used. For oil shales of all deposits of the world at this temperature the thermal decomposition of organic matter is completed, but practically no decomposition of the mineral portion of oil shale takes place.

At commercial realization of oil shale processing the yield and the quality of products depend on many factors: oil shale particle size, methods of heat input, kind of heat carrier and its temperature, duration of retorting, and also on secondary processes which proceed inside the oil shale particle and in the interparticle space, and others. The comparison of various known technologies for processing oil shales is made, and a possible theoretical foundation of process features is given. An estimation of the impact of the process on the environment is also discussed.

As a result directions for the further development of existing technologies are given.

Current State

Oil shale is one of the most important energy and chemical sources in the world after the exhaustion of oil deposits. For Estonia, oil shale is one of the most important natural resources, exploitation of which is based on the experience gained over eighty years of respective research and processing (Fig. 1).

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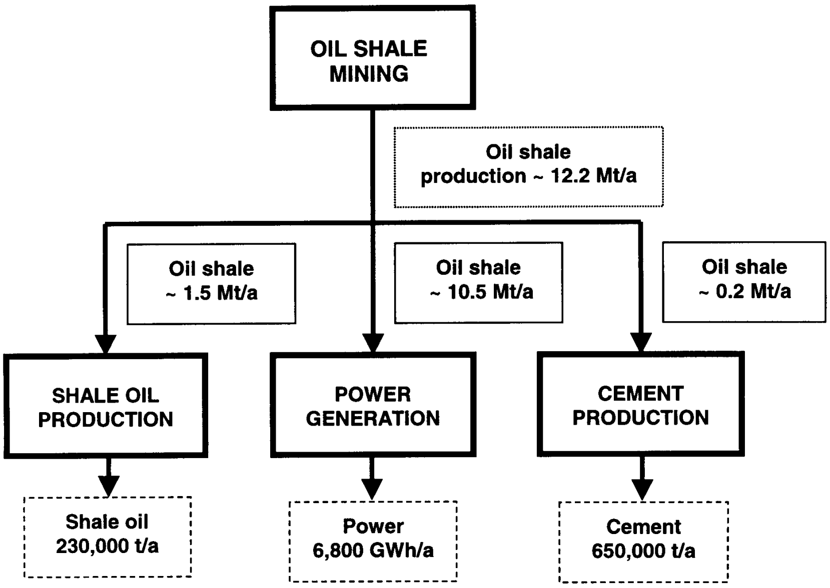

Fig. 1. Material flow in the Estonian oil shale industry

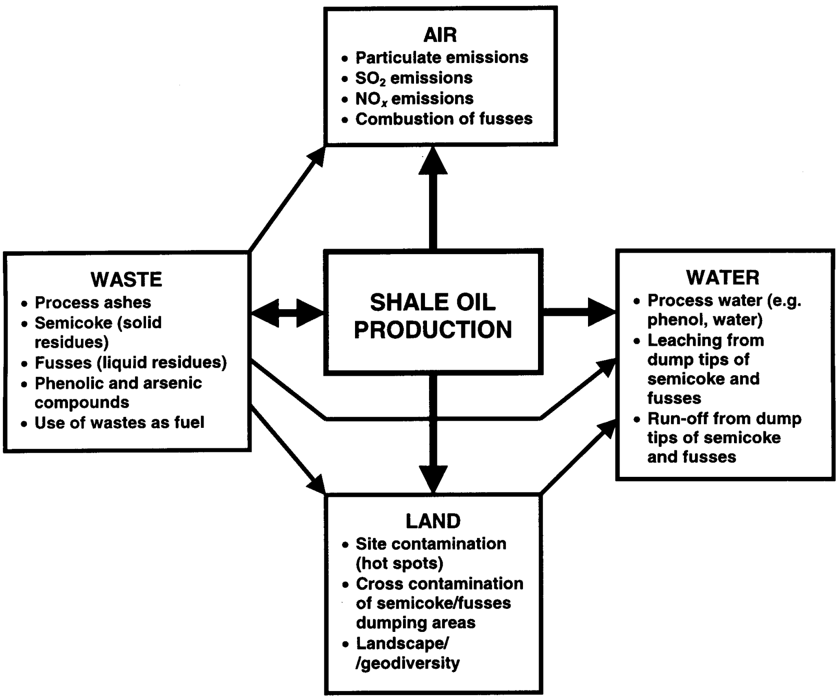

Fig. 2. Environmental impacts of production of shale oil from oil shales (the heaviest high-ash fractions of oil shale are referred to as “fusses”

All enterprises active in the field of oil shale mining and processing, such as *Eesti Põlevkivi AS* (*Estonian Oil Shale* Ltd.), Narva Power Station, *Viru Keemia Grupp AS* (*Viru Chemistry Group* Ltd.) and others are located in Ida-Viru County of North-East Estonia, being at the same time the biggest employers, exporters and environmental polluters of the region (see Fig. 2). The further competitiveness of the region is highly dependent on the ability of oil-shale cluster to introduce new and sustainable technologies and increase the list of value-added oil shale products.

Currently, in Estonia there are more than ten acting research groups and laboratories in Tallinn, Tartu and Ida-Viru County, each of them dealing with certain aspects of the oil shale complex. One of them – founded in 1958 – is for the present time the only specialized oil shale research institute in the world. The Oil Shale Research Institute of at Tallinn Technical University (TTU) at Kohtla-Järve has traditionally been the principal oil shale R&D institution having a long-term experimenting experience and co-operation traditions with the local industry and is the coordinator of R&D activities in the field.

Principal fields of research in the oil shale processing industry are the following.

1. Main Fields of Research:

- Development of technology for thermal processing (retorting) of oil shale and reduction of solid wastes (ash and semicoke) and gaseous emissions
- Development of technology for the manufacture and application of liquid oil shale products, including study of ways for reduction of wastes, particularly for treatment of phenolic waste waters
- Study of conversion processes for the decomposition of oil shale and high-molecular environmentally hazardous materials

2. The Research and Development Activities by the Oil Shale Research Institute at TTU Include the Following Research:

- Research on improvement of oil shale retorting technology, on composition of products obtained and improvement of economic data of their production:
  - fractionation (separation) of shale oil and investigation of possible uses of products
  - studies on production of additives from shale oil fractions used for improvement of combustion properties and storage conditions of fuel oil and diesel fuels
  - studies on production of biocide and antioxidant preparations on the basis of shale-oil-derived alkyl resorcinols

  - extension of the production list of epoxy materials and improvement of their properties
  - collection and analysis of data on production and feasibility of use of oil shale products
  - investigation of light stabilizers produced on the basis of alkyl resorcinols
- Market research for products obtained from shale oil
- Environment protection studies:
  - study on ways and efficiency of utilization of phenols present in waste water of oil shale processing industry
  - studies on technical ways for reduction of environmental hazard caused by ash and semicoke of oil shale retorting
- Compiling of the utilization program and the economic feasibility study for Ida-Virumaa oil shale and the accompanying natural resources
- Research on feasibility of production of non-oil-shale products and improvement of existing technologies

The basic specific property of the Estonian oil shale is its relatively high content of organic matter (32–38 %) characterized by a high content of oxygen compounds and a low concentration of sulphur and nitrogen. In the mineral portion metal carbonates prevail [1].

The first known scientific investigations of oil shale were started already in the 19th century.

Commercial thermal processing of oil shale in the Republic of Estonia has been in operation since the 1920s. Since that time different technologies for low-temperature thermal processing (500–550 ºC) to produce shale oil were used: e.g. externally heated Davidson rotary retorts, tunnel ovens with circulation of oil vapors and gas, chamber ovens for high-temperature (800–850 ºC) carbonization and gasification of oil shale. Due to their low efficiency after the 1950s they were closed.

At the same time (in the 1920s) commercial development of internally heated vertical retorts (historically referred to as ‘gas generators’) was started.

A semi-commercial retort using solid heat carrier for processing fine-grained oil shale with a throughput of 500 tpd represented a prototype for commercial retorts of the *Galoter* type with a throughput of 3000 tpd. Simultaneously, a 25-tpd experimental retort using fluidized-bed technology was also operated at Kiviõli.

The first commercial processing plant equipped with vertical retorts was put into operation at Kohtla-Järve in 1924.

Different commercial vertical retort designs were tested over a period of a number of years. As a result a commercial retort with cross-flow of heat-carrier gas was developed (Fig. 3).

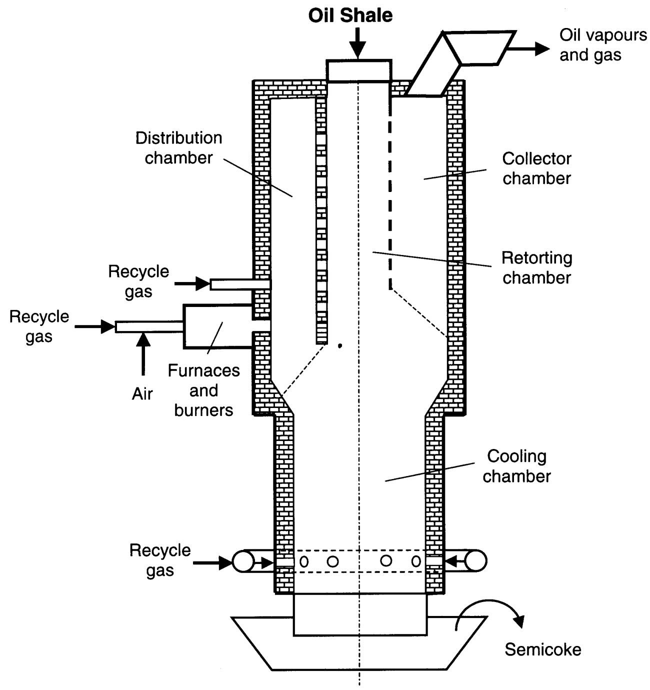

Fig. 3. Principal flow sheet of the retort with cross-flow of heat-carrier gas

The studies conducted by the institute gave a basis for determination of relationships between yields of products and conditions of technological processes and development of their mathematical expressions.

The yield of products and their properties by commercial processing of oil shale are dependent on a number of factors: oil shale particle size, method of heating (indirect, direct), state of the heat carrier (gaseous, solid) and its temperature, duration of retorting and secondary processes taking place in the interparticle space.

The results obtained constituted a basis for reconstruction of existing technologies and for improvement of the technical data of retorting.

To date the operating oil shale processes in Estonia are the *Kiviter* process (particle size 25–125 mm) and the *Galoter* process (particle size < 25 mm) [2].

3. The *Kiviter* Process

The retort is a metal vessel lined from inside with refractory bricks. The oil shale feed charging device and spent shale discharge chute and extractor are arranged on the top and in the lower part of the retort vessel, respectively (Fig. 4).

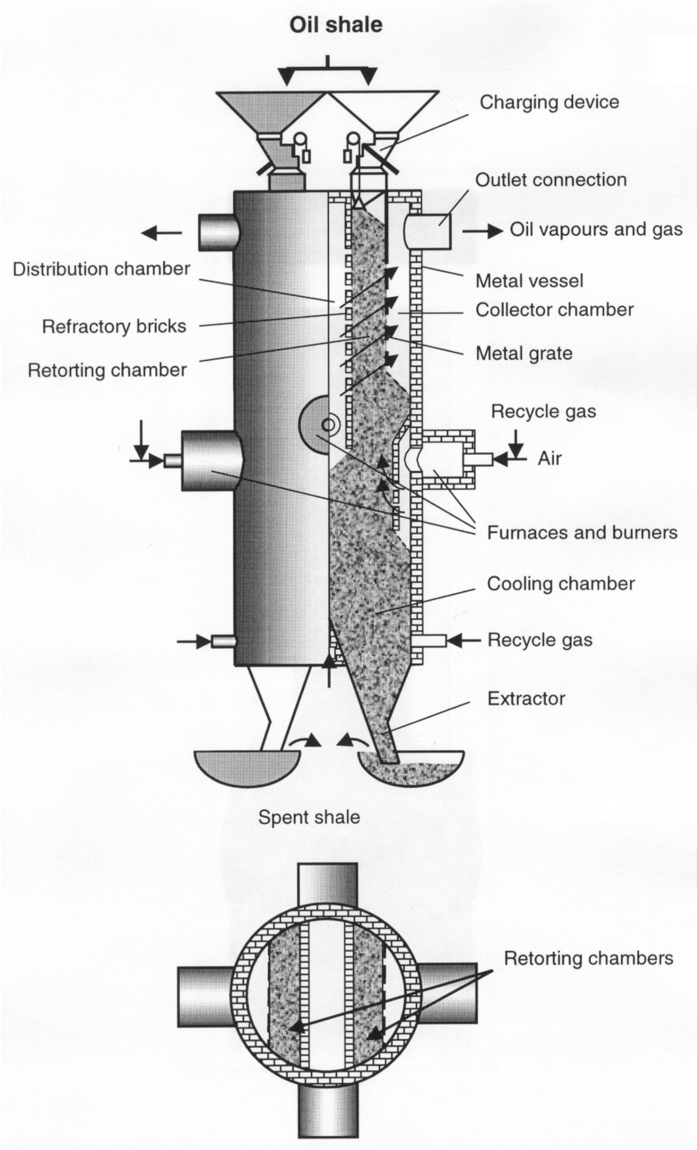

Fig. 4. Principal flow sheet of the *Kiviter* process

For preparing the heat carrier corresponding devices are installed on the retort vessel (furnaces and burners) fed by recycle gas and air. The heat carrier is directed into distribution chamber (hot chamber) designed from two sides by lined metal retort vessel and from two sides by hot walls made of refractory bricks in which nozzles are arranged.

Thermal processing of oil shale takes place in two retorting chambers designed from two sides by lined metal vessel of the retort, from one side by a refractory brick hot wall provided with nozzles and from the other side by a metal grate made of vertical tubes.

The mixture of heat carrier and oil and water vapors moves into two collector chambers encircled by lined metal retort vessel and a metal grate made of vertical tubes. Semicoke (retorted shale) moves downward to cooling chambers.

Oil vapors and gas are let out of the retort *via* two outlet connections to condensation system.

The main process technology conditions are:

Retort throughput	900–1000 tons per day of oil shale
Temperature of heat carrier	750–950 ºC
Temperature in retort outlet connections	150–250 ºC
Specific consumption of air	300–350 m^3 per ton of oil shale

Material and heat balances were compiled using long-term operating data of the *Kiviter* process. Oil yield is as high as 17.0–17.5 % from oil shale (heating value 13.8 MJ/kg), production of gas (heating value of 4.2–5.0 MJ/m^3) is 380–430 m^3 per ton of oil shale, the chemical efficiency of the process is in the range of 72–75 %.

The *Kiviter* process is a universal technology for thermal processing of oil shale which enables to obtain a high oil yield. The process is suitable for retorting high-calorific oil shales (over 15 % of Fischer assay oil) and bituminizing oil shales as well as for lean oil shales.

Besides Estonia, substantial experience in developing and operating vertical retorts for processing oil shales has been also gained in Russia, China, Brazil and other countries, including the development expertise on processes using solid heat carrier in the USA, Germany, and Australia.

As the industrial practice and research have shown, the main drawbacks of the vertical retorts with cross-flow of the heat-carrier are as follows [3]:

- Large particles of oil shale (up to 125 mm) are used and the feed oil shale must be concentrated which leads to substantial increase of production costs and is connected with losses in oil shale mining
- Direct burning of gas for heating up the heat carrier gas. As a result large volumes of low-calorific gas are produced
- The thickness of the retorting bed is maintained within 1.0–1.5 m in the retorting chamber. The result is that the temperature of the oil vapors and gas leaving the retorts remains within 220–240 ºC, and the retorting chamber holds only 30–45 % of the overall volume of the retort
- A high specific air consumption in the process: 350–360 m^3 per ton of shale
- The solid retort residue (semicoke) is hazardous for the environment caused by a high concentration of incompletely retorted organic matter

As for the majority of lean oil shales (incl. the mine-run Baltic kukersite), the costs for their concentration are high, therefore it is inevitable to find technical ways for low-temperature processing of oil shales having low concentrations of organic matter. In connection with this it is important to study the specific features and technical ways of retorting oil shale having low concentrations of organic matter.

In experiments of processing lean oil shale by vertical retorts in Kiviõli with cross-flow of heat carrier, their average daily throughput remained low (160–180 tpd) compared to concentrated oil shale at Kohtla-Järve (200 tpd). All efforts to increase the throughput by changing the operating conditions failed. By increasing the injection of air to the process, the temperature of oil vapors in the outlet sharply increased. At the same time the carry-over of dust by oil vapors was increased.

A serious problem in using large deposits of lean oil shale is the development of vertical retorts designed for high throughput. The most important condition for achieving the objective is providing intensive heat transfer from the gas flow to the large-particle material in the fuel bed. It is known that the quantity of heat Q depends on the following parameters:

$$Q = F \cdot \alpha \cdot \Delta T$$

where F is active heat-transfer surface of oil shale particles in the volume of retorting zone, m^2;

α is heat transfer coefficient from gaseous heat carrier to oil shale particles, $W/(m^2 \cdot K)$ [$kcal/m^2 \cdot h \cdot {}^{\circ}C$];

ΔT is temperature difference between gas and surface of oil shale particles, K (°C).

One can see that the intensity of heat transfer depends primarily on active surface of the oil shale bed in the retorting zone, determined mostly by particle size of the material retorted. Fines having a larger surface of contact with gases are heated faster then large oil shale particles. If the size range of oil shale particles is reduced, for example from 25–125 mm to 10–60 mm, the specific surface of the oil shale bed is increased twice.

Another direction for increasing the total heat transfer surface of the fuel bed in the retorting zone lies in the increase of useful volume of the latter, i.e. in the degree of fill up of the retorting zone with oil shale particles. It can be reached with increase of the bed thickness.

The main specific property of organic lean oil shales as technological feed is their relatively high thermomechanical strength, but also absence or formation of bitumen even in negligible quantities on heating of oil shale. In this case oil shale particles of lesser sizes and the greater thickness of bed in the retorting zone compared to richer oil shale may be used as processing feed.

Thanks to this specific property of the retort feed, a large active surface is achieved. A large active surface of the feed shale enables to reach high intensities of the retorting process which lead to favorable shale oil yields.

In the zone of oil shale thermal decomposition, the main factor influencing the intensity of heat transfer is the heat transfer coefficient:

$$\alpha = A \cdot W^{0.9} \cdot T^{0.3} \cdot m/d^{0.75}$$

where A is empirical coefficient (for oil shale the value is 166);

T is absolute temperature of gases, K;

W is gas velocity in the free cross section of the retorting zone, m/s;
d is average particle diameter, m;
m is a factor depending on the bed porosity on the content of fines < 10 mm.

The analysis of this formula indicates that predominantly the heat transfer coefficient is influenced by velocity of heat carrier gas and by the temperature.

For further improvement of conditions of heat exchange in the fuel bed, the temperature of the heat carrier gas should be kept on a higher level. At the same time analysis of process in vertical retorts for retorting Estonian oil shale shows the opposite – the temperature of heat carrier gas should be lower to avoid noticeable decomposition of carbonates.

Thus, the processing of lean oil shale makes possible:

- to increase the active surface of heat transfer in the fuel bed by reducing the particle size of technological feed and by a more complete use of the retorting zone
- to increase the heat transfer coefficient by increasing the velocity of heat carrier gas and by using oil shale particles of lesser size
- to reduce the temperature of the heat carrier gas to such an extent that no noticeable decomposition of carbonates occurs

All these are the preconditions for designing high unit throughput rate vertical retorts using improved technology of processing will enable a deeper utilization of the organic matter of oil shale. The operation of vertical retorts in practice shows that if lean oil shale is used, the gas produced is of lower calorific value. This makes the operation of vertical retorts complicated, because firing of the gas in the burners of the retorts deteriorates. At exceedingly low-calorific value of the gas (0.8–1.2 MJ/m^3) normal operation of vertical retorts may become impossible. Therefore, for thermal processing of lean oil shales it is very important to provide measures for increasing the calorific value of the gas produced.

To eliminate the mentioned deficiencies in the operation of vertical retorts with cross-flow heat carrier, in Estonia the scientists of the Oil Shale Research Institute and engineers of the former *SlantseKhim* Production Association developed the design of vertical retorts with a circular retorting chamber and arranged its testing under the industrial conditions at the shale-processing plants at Kiviõli and Kohtla-Järve (Estonia), and Slantsy (Leningrad Region, Russia) [4] (Fig. 5).

The studies of the performance of vertical retorts with a circular retorting chamber and its analysis were carried out in 1985 on one of the vertical retorts of GGS 5 in Kohtla-Järve, in 1986–1990 on five vertical retorts at the Slantsy plant, and in 1987 on one vertical retort at Kiviõli.

- Due to increased useful volume of the low-temperature carbonization chamber the throughput of the retort was raised from 160–180 to 250–300 t per day
- As a result of the improved heat exchange in the low-temperature semi-coking chamber, the temperature of the oil vapors and gas at the exit from the retort decreased from 220–240 to 170–180 ºC, and the retorting chamber holds as much as 70–80 % of the overall volume
- The specific air consumption in the process was reduced from 340–380 to 220–250 m^3 per tone of shale on the average
- The yield of shale oil increased from 74–78 to 82–85 % of the Fischer assay oil

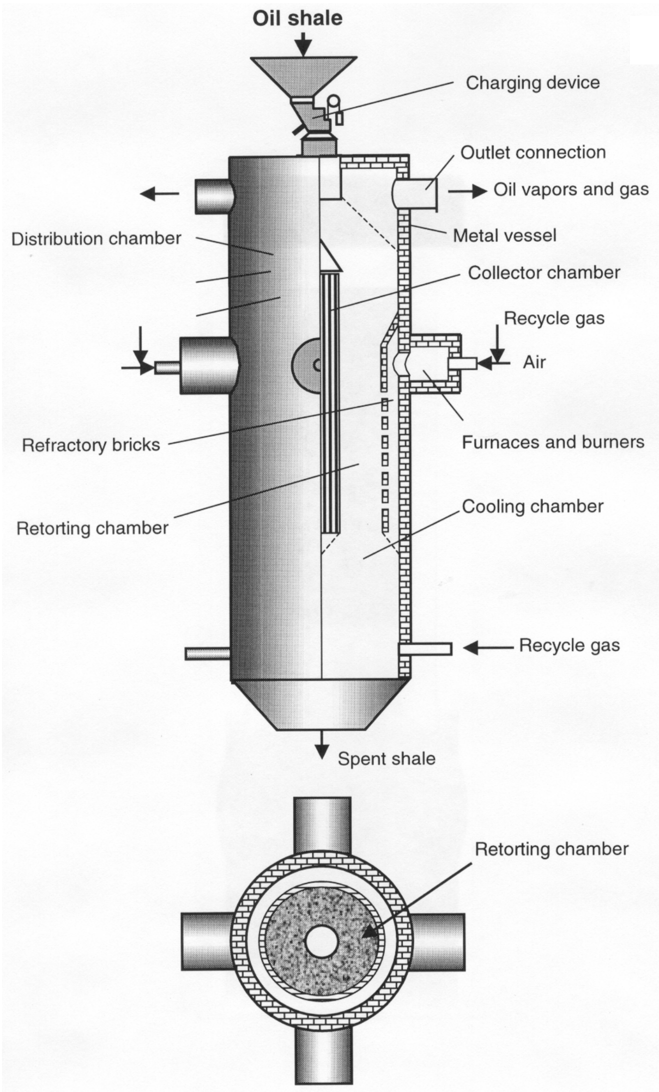

Fig. 5. Principal flow sheet of the vertical retorts with circular retorting chamber

On the basis of the research results and the industrial operation of the retorts with circular low-temperature carbonization chambers with a daily capacity of up to 250 t, the design of retorts with a throughput of 1500 t per day was proposed.

Now the Oil Shale Research Institute has developed the technology for retorts with circular retorting chamber and gasification zone to use all the potential energy of semicoke, and that for indirect heating enabling highly-efficient cogeneration of power.

Estonian oil shale scientists and specialists of the processing industry have close co-operation to date on the development of new resource-saving and sustainable technologies on the basis of the network of the Oil Shale Development Center to be originated.

Close co-operation is developed in the framework of different international projects, such as:

- US-Estonia science and technology co-operation on oil shale research and utilization
- Co-operation with the Harbin Gas Chemical Corporation (China)
- Co-operation with Canada and Australia for introducing the ATP technology at *Viru Keemia Grupp* AS
- A project will be initiated for introducing the technology using solid heat carrier at Slantsy
- Co-operation with Kazakhstan for utilization of their local and other oil shales would be of high interest and productive

4. Prospected Research in Estonia. Oil Shale Processing

1. Estimation of oil shale resources including prospective oil shale mining
2. Research of the chemical structure of kukersite kerogen and the value-added processing of kerogen
3. Technical and economic comparative evaluation of different domestic and foreign methods of oil shale processing
4. Development of a system model of oil shale processing oriented to different oil shale types, future products and EU environmental requirements
5. Balance tests and development of mathematical models for different retorting processes and performing test experiments
6. Development of theoretical foundations for the utilization of polymeric wastes produced by the *Kiviter* and *Galoter* processes
7. Development of a model for processing low-calorific (lean) oil shale in retorts with a circular retorting chamber
8. Studies on gasification processes of semicoke and other low-calorific solid fuels with high-efficient power generation from produced gas
9. Studies on co-processing heavy petroleum, industrial and residential wastes with oil shale

10. Preparation of industrial data for description of oil shale processes by using BAT (Best Available Technology) criteria

5. Extension of Production of Oil Shale Chemicals

1. Extraction and study of oil-soluble shale-oil-derived alkyl resorcinols for the production of antioxidant, biocidal and other preparations on their basis.
2. Development of additives for fuels, oil and greases on the basis of shale oil fractions.
3. Attestation of oil shale chemicals in compliance with EU requirements.
4. Study of motor and gas turbine fuels produced from gases of oil shale processing.
5. Optimization of product list structure of oil shale chemicals on the basis of light fractions of shale oil.
6. Development of instructions for the production of quality bitumens from heavy fractions of shale oil.
7. Study on conversion processes of polar and non-polar fractions of shale oil.
8. Research on agrochemical properties of solid fuels.
9. Studies on the production of roof mastics and other materials from oil shale kerogen.
10. Studies on fractionation of heavy fractions of benzoic acid.
11. Development of epoxy compositions.

6. Environment Protection

1. Investigation and systematization of solid, liquid and gaseous wastes of oil shale processing in compliance with EU requirements.
2. Studies on the utilization of chemical heat of spent shale (retorted shale) produced by vertical retorts.
3. Study on the production of building materials from oil shale ash and semicoke (retorted shale).
4. Systematization, development and introduction of analytical methods for oil shale processing ecology.
5. Assessment of environmental impact in chemical productions.

Summary

The current status of oil shale processing in Estonia:

1. Estonia has a long-term expertise on processing oil shales and on the production of liquid fuels and chemicals on the basis of shale oil in three

successfully operated enterprises, *Viru Keemia Grupp* AS, *Kiviõli* joint-stock company (now *Tamme Auto*) and the Narva Power Station.
2. Long-term R&D has created a basis for the development and commercial introduction of retorting units with unit throughput rates of 1500–3000 tpd for processing both large particle and fine-grained oil shale.
3. According to growing environmental requirements the recent research has been directed to the development of resource-saving and sustainable processes, incl. the reduction of hazard of solid, liquid and gaseous processing wastes.
4. Development of R&D for studying the structure of the organic matter and for producing liquid and gaseous products with improved properties.
5. Development of R&D for co-processing oil shale retorting wastes and different liquid and solid industrial and residential wastes.
6. Development of international co-operation with oil shale experts and specialists of the U.S.A., China, Russia, Canada and Australia for introducing the best possible technological processes for different oil shales of the world.

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