# New developments in oil shale technology

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## Abstract

The prospective method of oil shale processing to obtain liquid fuel is a method of its pyrolysis. Application of this method with a solid heat carrier required carrying out the manyyears of laboratory and pilot investigations of the technology and equipment at ENIN, testing oil shale samples of many different countries for the development of industrial plants. Modules which have passed the industrial approbation include the UTT-200, UTT-500, and UTT-3000, Demo Plant with Spout Fluidized bed.

The process parameters and the processing regime are determined by the physical and chemical properties of the primary shale, the physical and chemical properties of the final and intermediate products, the quality of waste, and ecological characteristics of discharges. Apart from the low calorific value of oil shale, when the process can't be provided by its own heat, *i.e.* it is not autothermal, the cause hindering their processing by means of solid heat carrier may be also

- weak looseness of concrete oil shale,
- tendency to early bituminization,
- possible caking quality in the plant's reactor,
- caking quality of ash in spout fluidized bed,
- the composition of emission in atmosphere, *etc.*

These indices can be revealed only in tests carried out on laboratory and pilot stands and installations modeling or reproducing adequately the real process. For this purpose, the laboratory and pilot plants and stands for the full or reduced scheme of pyrolysis with solid heat carrier were erected in ENIN and at its experimental bases in Estonia (Tallinn, Kiviily) as well as at the Ukrainian Verkhne-Sinevidnoye settlement.

The products and waste obtained from pyrolysis - liquid, gaseous products, mineral residue (ash) and pyrogenetic water - were comprehensively studied, and the ways of their utilization or further processing have been outlined. The technology of oil shale processing for about 30 deposits of different countries has been checked on the above-mentioned plants in accordance with ENIN method.

UTT-500 was in industrial operation for 107,350 hrs; 2,095,000 t of Baltic shale ($Q_i^r$ = 1800-2000 kcal/kg) were processed; 286,000 t of tar and 109 million $nm^3$ of highly calorific gas were obtained. The maximum annual number of unit's operation was more than 6,000 hours. Based on the long-term experience of UTT-500 operation and the design modification, two advanced UTT-3000 units were created and constructed at the Estonian TPP. The units have been in operation since 1990. Each of them can process 3,340 tons of Baltic shale a day and produce about 130,000 t of various fractions of oil shale tar and 42 million $nm^3$ of highly calorific gas. The production cost of one shale oil barrel constitutes from $14-17 US that allows construction of the competitive industrial units practically with unlimited number.

Thus, the industrial technology and unit were created and worked out and allow to solve the problem of obtaining the artificial oil and thereby the problem of 21st century – the reduction of oil production volume.

## Introduction

The explored reserves of oil shales in the world are estimated at the present time as approximately 450 trillion ton and they are spread over all continents. The most part of deposits has a calorific value of oil shale $Qi^r$ = 900-1400 kcal/kg and only some of them -1600-2200 kcal/kg. The USA, Russia, Brazil, China have at its disposal the largest resources of oil shale, whereas other countries such as Israel and Jordan have only oil shale in the capacity of fossil organic fuel.

Oil shale represents a complex raw material suitable for electricity production, the receiving of artificial liquid fuel and combustible gas and also a number of valuable chemical products.  However the commercial consumption of oil shale is now extremely limited, that is determined by the low efficiency of current oil shale technologies,  the ecological problems arising in this case and the considerable difficulties of equipment maintenance.

The present paper describes the current state of development in the technology of oil shale utilization and the last achievements in this direction, in particular, the works fulfilled in G.M.Krzhizhanovsky Power Engineering Institute (ENIN) resulted in the creation of highly efficient industrial technology of oil shale utilisation.

## Review of the world situation

### Works in the world

The oil shale found still a very limited application in 'the electric power engineering of the world. Only the electric power stations created by Russian specialists with the relatively high-calorific ($Qi^r$ = 2000-2200 Kcal/kg) Baltic oil shales (Estonian and Baltic TPPs, TPPs in Akhtme and Kohtla-Yarve) can be here noted. The maximum design unit electric capacity of a power double-unit constitutes 200 MW (the power of boiler is 320 t/h). The power of a Baltic TPP is 1400 MW, an Estonian one- 1600 MW. The design fuel consumption for the electricity output at Estonian TPP with units 200 MW is

about 409 t of equivalent fuel/kWh, TPP efficiency is around 30% (hi reality the pointed indices are a little lower).

The small electric power stations with a direct combustion of oil shale operate in China and in Anin, Romania.

The many-year operation of the boilers for power units 100 and 200 MW of Baltic and Estonian power plants and the former boilers with middle pressure showed, that the combustion of such highly reactive fuel as oil shale having the output of volatile matters for dry ash free mass 85-92% does not present a complicated technical problem. The main problem of oil shale utilization in power engineering is the contamination of heating surfaces, that reduces the thermal efficiency of boiler and restricts its steam production by 15-20% the continuous work more than 1-2 months.

In connection with above presented it is possible to state, that the average annual efficiency of the traditional condensing power plant will not exceed 30-31% both with a chamber combustion of relatively high-calorific oil shale ($Qi^r$ > 1600 Kcal/kg) in a form of dust and with a combustion of the less calorific oil shale in the fluidized bed in the moderate climatic conditions. The efficiency of such TPP will not exceed 28-27.5% in the countries with a hot climate and the same other conditions. These indices will be even oil shale with calorific value less than 1300-1400 Kcal/kg.

The first plant with power around 13 MW on the basis of oil shale combustion in the circulating fluidized bed that was realized in Israel by company "Alstrem" the local company "Pama" showed the practical feasibility of such method.  However, on the one hand,  it is quite not optimal power capacity;  on the other hand,  in our mind its growth will result in the serious problems connected with the aerodynamic and temperature non-uniformity; thirdly, the efficiency of this plant is low.

The technologies of oil shale gasification or pyrolysis developed in the century by many countries (Russia, the USA, China, Brasilia, Germany, Republic of South Africa and oth-

ers) allowed to receive the shale oil first of all by means of gas heat carrier and by using only the classified oil shale with the sizes of separate lumps from 20-25 to 125 mm. However almost 25% of oil shale is lost in this case in a form of the finer dust under the modem methods of its mining. The exception consists of the powerful plants of Brazilian company *Petrobras*, which use the oil shale starting from the lump sizes 6 to 70 mm. However a problem of using the small (up to 6 mm) fractions of oil shale appears here too.

Thus, the following technologies of retorting processing of oil shales are most of interest besides the Russian ones:

- the *Petrosix* process of *Petrobras* in Brasil;
- the *TOSCO-II* process in the USA;
- the LURGI process in FRG.

The works on creating the technology were recently actively were carried out in Canada and Australia: the laboratory installation *Aostra Taciuk* developed in Canada was tested in the experimental scale for bituminous sands and oil shales of Stuart in Queensland (Australia).

The original technology developed in Krzhizhanovsky ENIN and based on the pyrolysis of oil shale by means of solid heat carrier opens the opportunities for creating the large commercial plant with the unit power up to 300 MW (thermal) and having multipurpose energy-technological plant, which allows to use the extracted oil shale (of any size) practically completely with the high economic and ecological indices.

In this case it is possible to receive as the products the shale oil, the chemical products (thiophene, ichthyol, products of perfumery), the highly calorific gas depending on the oil shale quality with $Qi^r$ from 6,000 to 11,000 kcal/nm$^3$, which can be used for the electricity production with the most modern combined cycle (in this case the fuel consumption is reduced by 30%). The oil shale ash is applicable for the production of cement and highly qualitative building sandwich-constructions.

## Russian experience in oil shale utilization

Application of the pyrolysis method with a solid heat carrier in accordance with the ENIN scheme required to carry out the many-year laboratory and pilot investigations of the technology and equipment with checking the samples of different oil shales of the world for the development of industrial plants - modules, which have passed at the present time an industrial approbation (UTT-200, UTT-500, UTT-3000, Demo Plant with Spout Fluidized Bed Combustion - DP SFBC).

The process parameters and the processing schedule are determined by the physical and chemical properties of the primary shale, the physical and chemical properties of the final and intermediate products, the quality of waste, ecological characteristics of discharges.

Apart from a low calorific value of oil shale, when the process cannot be provided by its own heat, *i.e.* it is not autothermal, the cause hindering their processing by means of solid heat carrier may be also a weak looseness of concrete oil shale, its tendency to early bituminization, a possible caking quality in the plant's reactor, a caking quality of ash in SFBC, the composition of atmospheric emissions etc.

These indices can be revealed only in the tests carried out on the laboratories and pilot stands and installations modeling or reproducing the process adequately.

For this purpose the laboratory and pilot plants and stands for the full or reduced scheme of pyrolysis with solid heat carrier were erected *at ENIN* and at its experimental bases in Estonia (Tallinn, Kiviily) as well as in the Ukrainian Verklme-Sinevidnoye settlement.

The investigations in Moscow were carried out on the strand of periodic action with the charges up to 1 kg. Apart from it, the express method of pyrolysis was developed for small amounts of oil shale in several grams. In the city Kiviily the enlarged laboratory installation - a stand of continu-

ous action, which reproduced fully the process at all its stages, worked with the oil shale capacity up to *15 kg/hr.* Many-day experiments were carried out on it. A pilot plant at "Illmarine" works (city Tallinn) had an oil shale capacity up to 100 kg/hr and worked successfully, while the enlarged pilot plant with oil shale capacity *500 kg/hr* in the Verkhne-Sinevidnoye settlement is in operation with modelling a purely power variant (without condensation).

The products and waste obtained as a result of pyrolysis: liquid, gaseous products, mineral residue (ash) and pyrogenetic water were comprehensively studied and the ways of their utilization or further processing have been outlined.

The technology of oil shale processing for about 30 deposits of different countries has been checked on the above mentioned plants hi accordance with ENIN method.

The results of the check have been compared with the standard characteristics obtained by means of Fisher assay both for the oil shales tasted in UTT and other shales. It allows to make a conclusion about applicability and economic expediency of utilisation of this method and UTT for the very different oil shales of the world.

The important *autothermal* parameter or the so called factor of oil shale heat excess characterizing the potential heat, which can be used for carrying out the pyrolysis on the plants with using a solid heat carrier, was suggested and verified on the basis of vast experimental material.

The pyrolysis of oil shale by means of solid heat carrier can be recommended in the case, when the quantity of potential heat transferred into a semi - coke becomes equal or higher than the quantity of heat required for carrying out the thermal decomposition, i.e. without the additional input of heat for this purpose from other sources.

Such a parameter ($K_{eh}$) was derived on the basis of statistical processing of numerous data received on the mentioned plants. The nomogram for its determination in practice was suggested and is shown in Fig.1.

It follows from the nomogram that the process of pyrolysis with solid heat carriers intended for the oil shales with $K_{eh} > 1$ and is not expedient for oil shales with $K_{eh} < 1$ , i-e. for too "poor" shales (low-caloric oil shales with the lowest combustion heat < 500-600 Cal/kg).

As to the value of $K_{eh}$ all the deposits fall into one of three groups:

$K_{eh} < 1$:     the heat of semi-coke is insufficient for oil shale processing on UTT;

$K_{eh} > 1$:     the heat of semi-coke is sufficient for economic oil shale processing on UTT;

$K_{eh} >> 1$:     in this case the excess heat of semi-coke can be extracted by means of additional gasification or combustion in the special apparatus.

The dependence (Fig. 2) was received on the basis of analyzing the composition and properties of oil shales from more than 30 deposits by means of an investigation of their samples by Fisher assay and a comparison with the results for 17 samples

**Fig. 1. Nomogram for coefficient Keh as a function of physical and chemical properties: Org - concentration of organic material in dry mass of shale, %; Ck - carbon concentration in kerogen, %.**
**T – pyrolysis temperature, K, qsk – semicoke output (after pyrolysis) per conventional organic mass.**
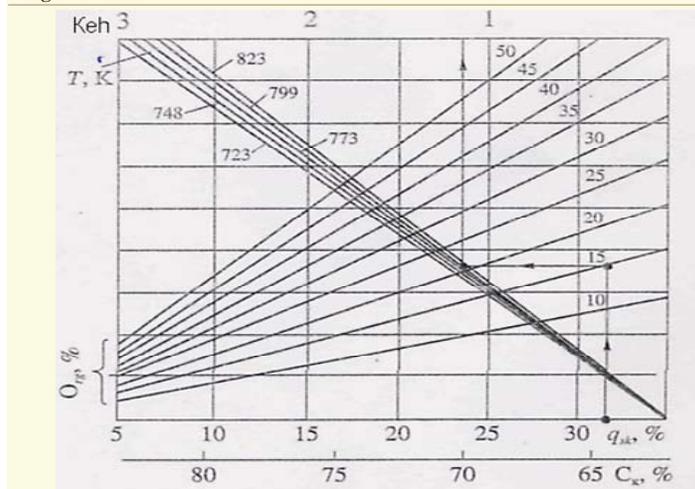
**Fig.2 Dependence of semicoke output per conventional organic mass on carbon concentration in kerogen.**
**Some points in diagram correspond to numbers in table 1.**
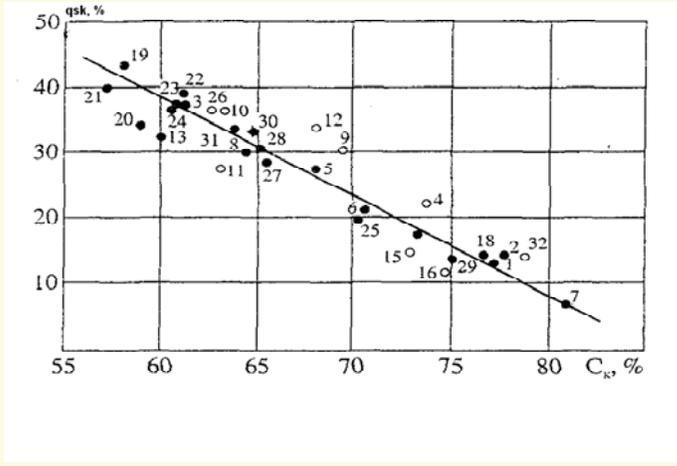


tested on the plants with solid heat carrier (see Table 1). This dependence is approximated by a linear equation.

*Creation of a technological process based on the UTT-3000 modules.*

Within the limits of investigation a mathematical model was developed for a closed circulating system of solid fuel pyrolysis and combustion that comprises three basic

plants:

1.  aerospout furnace (APF) (a combustion path) consisting of three chambers: an ignition chamber, an accelerating-transport section and aerospout chamber;

2.  a cyclone of returning non-burnt up fuel-ash (CA);

3.  a reactor-pyrolyser (RP).

The calculations have been conducted for high ash-content fuels - coals and oil shales (Estonian and Israeli ones).

The mathematical model is based on the equations of hydrodynamics and kinetics of pyrolysis and combustion and heat balance. The kinetic constants for different coals and Estonian and Israeli oil shales determined in experiments have been used in calculations. In the course of these calculations one should take into account that the fuel is characterized by a wide range of particle sizes (from a few microns up to several millimeters). In addition the difference between the fuel particle in a content of combustible mass should be taken into account, because a degree of burning out (a depth of conversion) depends on the time of fuel being in the combustion zone, which is hi its turn determined by the size of particles and the number of cycles occurred in the circulating loop - the furnace, the cyclone and the reactor-pyrolyser. Therefore the key moment of mathematical model is the use of the equation for a probability density in the fuel particle distribution accordingly to their sizes and the content of combustible mass. This equation constitutes the base for description of evo-

| Table 1. Kerogene composition for oil shales of different deposits | | | | |
|---|---|---|---|---|
| **Deposit** | **Composition of kerogene of oil shail** | | | |
| | **C** | **H** | **O** | **S** |
| 1. Pribaltyiskoye (Estonia) | 77.3 | 9.8 | 11.2 | 1.7 |
| 2. Leningradskoye (Russia) | 77.7 | 9.8 | 11.3 | 1.2 |
| 3. Kashpirskoye (Russia) | 61.1 | 7.3 | 23.8 | 7.8 |
| 4. Kenderlikskoye (Uzbekistan) | 73.8 | 8.4 | 17.8 | |
| 5. Boltyshskoye (Ukraine) | 68.0 | 9.3 | 18.3 | 1.9 |
| 6. Timakhdi (Morocco) | 70.5 | 9.3 | 12.4 | 7.8 |
| 7. Green-River (USA) | 80.9 | 11.4 | 6.9 | 0.8 |
| 9. Nerke (Sweden) | 69.5 | 7.7 | 16.8 | 6.0 |
| 10. Lotiani (Scotland) | 63.0 | 10.1 | 26.2 | 0.7 |
| 11. Render (Australia) | 63.1 | 7.9 | 28.3 | 0.7 |
| 12. Irati (Brazil) | 68.1 | 10.3 | 17.9 | 3.7 |
| 30. Rotem (Israel) | 65.0 | 7.0 | 15.4 | 10.7 |

lution of a solid material in the closed circulating loop.

The circulating scheme includes a consideration of the processes within the interconnected system of all the apparatus. The connection between them is carried out on the basis of both the fuel characteristics and the process temperature - the outlet parameters of one apparatus are used as the inlet parameters for another. The analysis shows, that as a result of interconnected processes the loop "APF-CA-RP" represents as a whole the system with a negative feedback providing a stability of its operation.

The temperature and gas composition in all apparatus of circulating system as well the content of combustible mass (conversion depth) have been determined in the course of calculations depending on the fuel particles' size. The calculated results are well co-ordinated with the experimental data obtained in ENIN and other organizations. The necessary operating parameters for optimization of a process of using the different fuels can be recommended on the basis of fulfilled calculations. In particular, the optimization of aerodynamic parameters, temperatures, ash and gas flows has been carried out, and the optimal shape and parameters for the elements of block equipment have been chosen. It is established that there are the optimal values of the average size of particles and the fuel's circulating factor, for which the maximum degree of burning up is achieved, *i.e.* the incomplete burning (unburned carbon) at the APF outlet becomes minimum. The given model is the most complete one among all the known models in the world practice.

*UTT experimental-industrial plants*

The industrial plants, which are different in the volume of oil shale processing, have been developed and created with taking into account the experience accumulated as a result of theoretical calculations and fulfilled experiment.

UTT-200 was the first of all large experimental-industrial plants for oil shales. It was used for processing 200 t of Baltic shales a day. The process of fine Baltic oil shale's thermal processing was mastered and investigated on this plant in a scale close to the industrial one. The character of basic equipment and the most rational conditions of its operation were here selected, *UTT-200 plant was in operation more than 17000 hours:* 102 thousand tons of oil shale were here processed from which *15.8 thousand tons of tars and more than 3 million nm³* of highly calorific semi-coke gas were obtained.

UTT-500 plant for processing 500 tons of Baltic oil shale a day was constructed for the further perfection of thermal treatment process, its hardware and commercial verification of the method in the conditions of long term operation.

*UTT-500 was in industrial operation for 107350 hrs;* 2095 thousand tons of Baltic shale ($Qi^r$= 1800-2000 Cal/kg) were here processed; 286 thousand tons of tar and 109 million nm³ of highly calorific gas were obtained. The maximum annual number of plant's operation was more than 6000 hours.

UTT-500 was also tested with processing low calorific oil shale in Bulgaria (Nikolayevo-Gurkoskoye deposit) of the following composition:
- humidity - $W^r$ = 9.6 per cent;
- ash content - $A^d$= 84.0 per cent;
- carbonate content - $(CC>2)^d_m$= 4.6 per cent;
- organic substance $O^d$= 11.4 per cent;
- general sulphur - $S^d$= 0.55 per cent;
- $Q^r$= 560 Cal/kg.

The plant proved its normal work also under these conditions.

On the basis of the long-term experience of operation of UTT-500 plant and the design modification of *two advanced UTT-3000 plants* were created and built at the Estonian TPP; each of them can process 3340 tons of Baltic oil shale a day. The plants are in operation since 1987.

Each of them can produce about 130 thousand tons of various fractions of oil shale resin and 42 million nm³ of highly calorific gas when using the Baltic oil shales.

UTT-3000 plant processes about 139 tons of shale per hour. A diagram of the plant (UTT-3000 module) is shown in Fig.3. After hopper the oil shale is crushed in the crusher to maximum size of pieces within 15 mm and is fed into aerospout drier 1 by means of conveyer. The flue gases from a recovery boiler 10 are also fed into the drier with the temperature of about 600°C. The dried oil shale heated in the drier up to 110-150°C is fed to the screw feeder 6 and then - into the mixer 3, into which a heat-carrying ash is also fed with a temperature of 780-800°C.

The flue gases pass through a drier after dust removal in a cyclone 2, and are discharged into a chimney.

The oil shale and heat-carrying ash mixture are fed from a mixer into a reactor-pyrolyser 4. As a result of interaction with the heat carrier the oil shale is heated up to 470-500°C and releases a steam-and-gas mixture in the reactor. The mixture flows into the settling chamber 5, where it is purified from suspended particles owing to both low speed of motion and special cyclones. After purification the steam-and-gas mixture is withdrawn to the condensation compartment.

Organic substance which was not transferred into the gas phase in the reactor together with the mineral part of fuel is fed by screw feeder into the aerospout furnace 6, where it is burnt up in the air flow. The formed combustion products (with temperature 780-800°C) after separator 7 are partially fed to the heat-carrier cyclone 8 and the ash cyclone 9 where they are purified from ash.

The ash collected by cyclone 8 serves as a heat-carrier for heating the oil shale and is fed to the mixer, while the ash collected by cyclone 9 is removed from the cycle after cooling in heat exchanger 11.

The high-temperature combustion products purified from ash are discharged from the cyclones into the recovery boiler for utilization of heat they contain. The semi-coke gas from the condensation compartment is also fed in the recovery cooler for further burning up. The energy received in recovery boiler is consumed for auxiliaries (in the form of steam) and for generating electricity.

The steam-and-gas mixture that was fed into the condensation compartment is directed into scrubber, where its temperature drops down below a dew point as a result of irrigation by cooled heavy oil and diesel fraction. In this case the heavy oil fraction from steam-and-gas mixture is condensed, while the mixture is enriched with diesel fraction owing to



Schematic diagram of thermal processing of Baltic oil shale.
**Unit UTT-3000**

Fig. 3

1 – aero-fountain air spray drier, 2 – dry shale cyclone, 3 – mixer,
4 – drum reactor, 5 – dust separator, 6 – aero-fountain furnace, 7 – flow separator,
8 – heat carrier cyclone, 9 – ash cyclone,
10 – recovery boiler, 11 – ash heat exchanger, 12 - filter
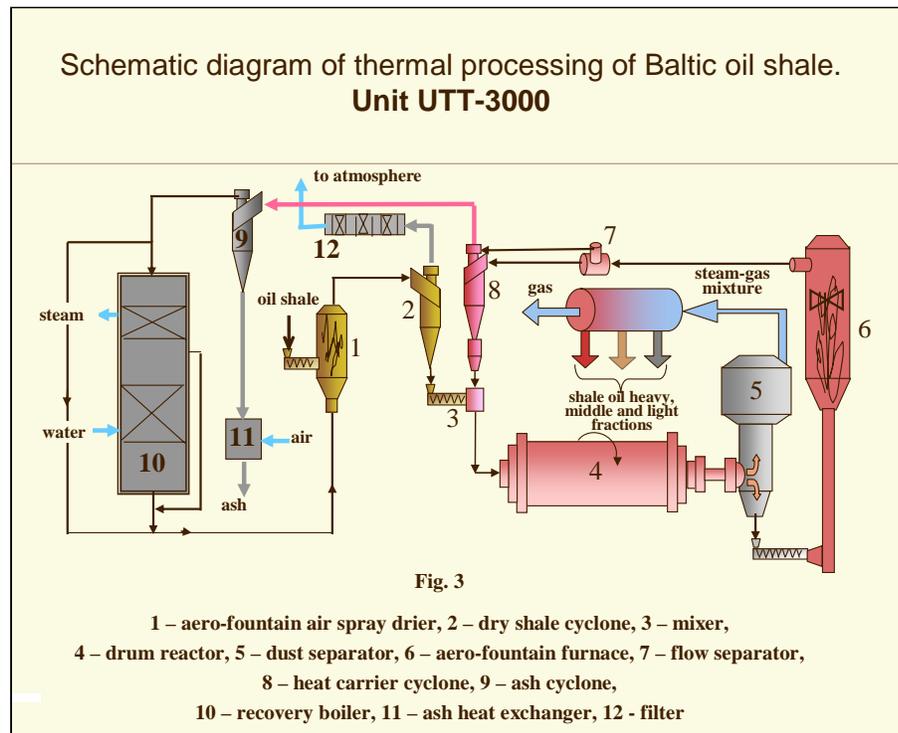
evaporation of the latter from the irrigating mixture. After that the steam-and-gas mixture passes through a cooler and is fed into the rectification column at a temperature 250°C. The steam-and-gas mixture temperature is reduced in this column due to irrigation with diesel fraction (in the lower part of column) and petrol fraction (in the upper part of column).  As a result the middle oil is collected in the lower part of column, whereas the diesel fraction of shale oil is collected in its upper part and then is pumped over to the store-room.

The remaining part of steam-and-gas mixture from the rectification column is fed with temperature 110°C into the cooler in which this temperature is decreased to 30°C and petrol fractions and water steams are condensed from the flow.  The cooled flow is directed to separator where gas is separated from liquid and the latter is separated into layers of petrol and tar water. The petrol is pumped over to the store-room, whereas the tar water may be used depending on its quality as the raw material for extraction, for example, of phenols or rendered harmless.

The gas is withdrawn from the condensation compartment for burning up in the recovery boiler or can be used in steam-gas (combined) cycle after being compressed.

In accordance with the data of many-year operation of UTT-500 and the experience of UTT-3000 operation in Estonia, the specified life of the lining in the basic equipment constituted:

- aerospout furnace - 35000 hours;
- rotator drum-type reactor - 50000 hours;
- cyclones,  communications and other apparatus in the hot pass - 70000-75000 hours.

It should be also noted, that the plants UTT-3000 can be used for the utilisation of soils containing the residual fuel oil or greased on and formed as a result of failures in the oil and petroleum industry with the transport of petroleum products.  Besides it, as a result of many technological

enterprises' activity there is an accumulation of organic waste (the sediments in storage tanks and reservoirs, the worked out tires and also the oil spillages etc.) demanding   the measures for their liquidation with the obligatory condition, that the technologies used for it are ecologically acceptable and do not result in the secondary pollution of environment.

All mentioned wastes have been successfully processed in the recent years at the plants UTT-3000. The addition to oil shale of materials rendering it harmless can constitute up to 20% by weight. Moreover, after processing the initially grinded automobile tires with the lump sizes about 25 mm the total output of oil is increased (due to the fact, that the resin output from tires is about 50% per a unit of weight in comparison with 7-12% per a unit of weight with the oil shale processing), and its characteristics are unproved. This circumstance results in the considerable improvement of economic indices of plants' operation together with the high ecological advantages of tires' processing process.

*Technical and economic data on UTT-3000 operation*

The following characteristics were determined as a result of technical-economic calculations for the construction of energy-technological complex consisting of three units UTT-3000, which will use Leningradsky oil shale with the lowest heat of combustion $Qi^w$ = 2000 Kcal/kg in a amount of 2.5 mln tons a year: capital expenditure for the complex including its construction part, mounting of equipment and infrastructure -120 mln US$;

*output of shale oil* - 345000 tons a year;

*output of semi-coke gas* - 89.2 million $m^3$/year, that with the gas heat of combustion 48.41 $MJ/m^3$ constitutes 147.34 thousand tef (tons of equivalent fuel);

With the oil shale price 5 US$ per ton and carrying out the construction under condition of 35% of share capital and 65%  of borrowed capital or liabilities (rate of in-

terest 9%, a credit time - 15 years, grace period - 3 years), the inner rate of profitability is equal to 18% and the payback period since the beginning of operation is 6 years. The cost of produced shale oil constitutes 65 US$ per a ton.

These characteristics and circumstances allowed to the consortium of scientific-research and production organizations under leadership of JSC "ENIN" to begin the realization of two large projects on using the oil shales in Russia and Jordan on the basis of new technology corresponding to the requirements of the coming 21st century.

Thus, the creation of high-efficient technology of oil shale pyrolysis by means of solid heat carrier allows to solve the many problems of using such low-grade fuel with receiving the' highly qualitative final products, that permits us to speak about the large world-wide process of oil shale utilization.