Developments in Production of Synthetic Fuels out of Estonian Oil Shale

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Abstract *(100 words)*
Estonia is still the world leader in utilization of oil shale. Enefit has cooperated with Outotec to develop a new generation of solid heat carrier technology – Enefit280, which is more efficient, environmentally friendlier and has higher unit capacity. The breakeven price of oil produced in Enefit280 process is competitive with conventional oils. The new technology has advantages that allow easy adaptation to other oil shales around the world. Hydrotreated shale oil liquids have similar properties to crude oil cuts. Design for a shale oil hydrotreater unit can use process concepts, hardware components, and catalysts commercially proven in petroleum refining services.

Keywords: oil shale, retorting, upgrading

1. Introduction

The first written information about oil shale in Estonia was documented already in 1777 [1]. The occurrence of burning rock on the southern coast of the Gulf of Finland is present in the travel notes of the 18th century naturalist and explorer Johann Anton Güldenstädt [1,2]. Studies of Estonian oil shale resources and mining possibilities intensified in the beginning of 20th century due to industrial development of Saint Petersburg and a shortage of fuel resources in the region.

In 1918 the first mine was opened in North-Eastern Estonia. At that time, oil shale was used primarily in the cement industry and as a household fuel. Shale oil production started in Estonia in 1921, when the first experimental oil shale processing retorts were built in Kohtla-Järve [2]. These retorts used vertical retort technology, the forerunner of the current Kiviter processing technology. Between 1924 and 1939 different types of oil shale retorting technologies were implemented in Estonia - horizontal retort (fusion retort), tunnel kilns, internally heated retorts, and Davidson's retorts.

Between 1948 and 1987 Estonian-produced oil shale gas was used in Leningrad (present day Saint Petersburg) and in northern Estonian cities as a substitute for natural gas.

The oil shale-fired power industry started in 1924, when the Tallinn Power Plant switched to oil shale. Afterwards, small oil shale-fired power plants were built in the region. In 1949, the first power plant in the world using pulverized oil shale at an industrial scale was commissioned in Kohtla-Järve. The world's two largest oil shale-fired power stations – Balti Power Plant and Eesti Power Plant – were opened in 1965 and in 1973, respectively. In 2004, two power units with Circulating Fluidized Bed (CFB) combustion boilers were put into operation at Narva Power Plant [2].

Consequently, oil shale is a major natural resource of Estonia and it has been successfully utilized in different applications for almost a century. Despite the fact that Estonia is one of the smallest countries in Europe, Estonia is still the biggest oil shale user in the world. Altogether more than 1 billion tons of oil shale has been mined in Estonia, more than 550 TWh of electricity has been generated and approximately 200 million barrels of oil has been produced from oil shale in Estonia.

2. Oil production by Enefit Oil & Gas

Eesti Energia Oil & Gas (EEOG) uses the solid heat carrier process to produce shale oil. Two unique solid heat carrier (Enefit140, previously branded as TSK140) installations, the only functioning units of their kind in the world, produce over 1 million barrels of shale oil a year.

The history of the development of the solid heat carrier technology reaches back to the 1950s when the Estonian oil shale was first tested in industrial scale plants (1953, UTT-200; 1963, UTT-500). EEOG’s currently operating oil factory at Narva Power Plants was commissioned in 1980 (the initial name of the factory was UTT-3000). The original purpose of the oil factory was to produce fuel oil and gas for the power plants. However, as the quality of the originally delivered equipment was poor in design, the plant initially ran with limited success. It took 20 years of hard work to transform the scaled-up pilot unit into an efficient and profitable factory. Compared with the initial design, 70% of the equipment has been replaced and modernized. The modernized technology was patented in 2005 under the trade name Enefit140. The plant consists of two identical production lines, each with an input of 140 t/h of oil shale. The designed capacity of the plant is 220 000 tons of shale oil and 60 million Nm^3 of retort gas a year.

Oil production numbers of EEOG have continuously increased with annual growth rates of about 20%. In 2008 oil production was for the first time over 1 million barrels of shale oil a year. Development of shale oil production over the years is shown in Figure 1.

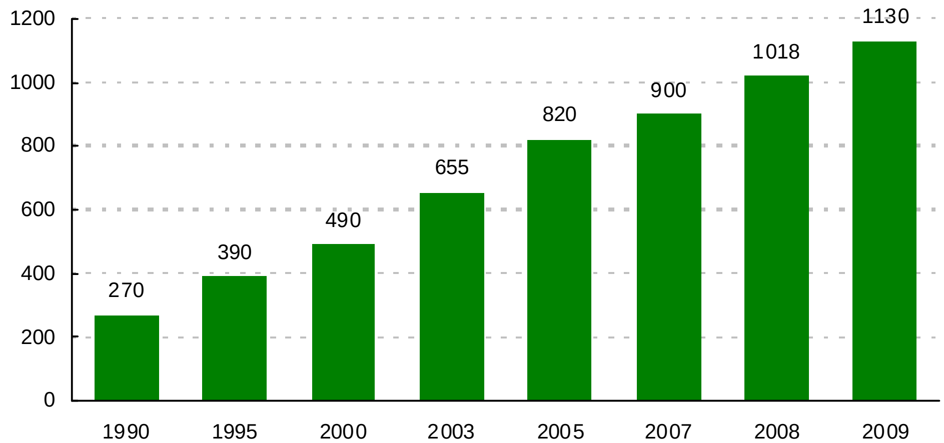

Figure 1 Shale oil production in thousands of barrels by EOG between 1990 and 2009.

3. Enefit140 retorting technology

The main principle of the Enefit140 technology is that hot ash produced within the process is used to pyrolyze the oil shale. The layout of the Enefit140 plant is shown in Figure 2. The Enefit140 process uses oil shale with a particle size below 20mm. Fine grained particles are dried in the lift-pipe dryer using the excess flue gas heat. Dry oil shale is then mixed with hot heat carrier ash and fed into the rotary kiln, where pyrolysis of oil shale takes place at 480-500ºC. Produced vapor-gas mixture and spent shale are separated in the gravitational separation device called the dust chamber. The vapor-gas mixture is sent to condensation section of the plant for cleaning, condensation and fractionation of products. Spent shale is fed by screw feeders into the lift-pipe combustor, where all remaining organic matter is burned out and hot ash at 800ºC is produced. This hot ash is separated from the flue gases, recycled back into the process and used as a solid heat carrier. Remaining flue gases go through the drier, are subsequently cleaned and released into the atmosphere.

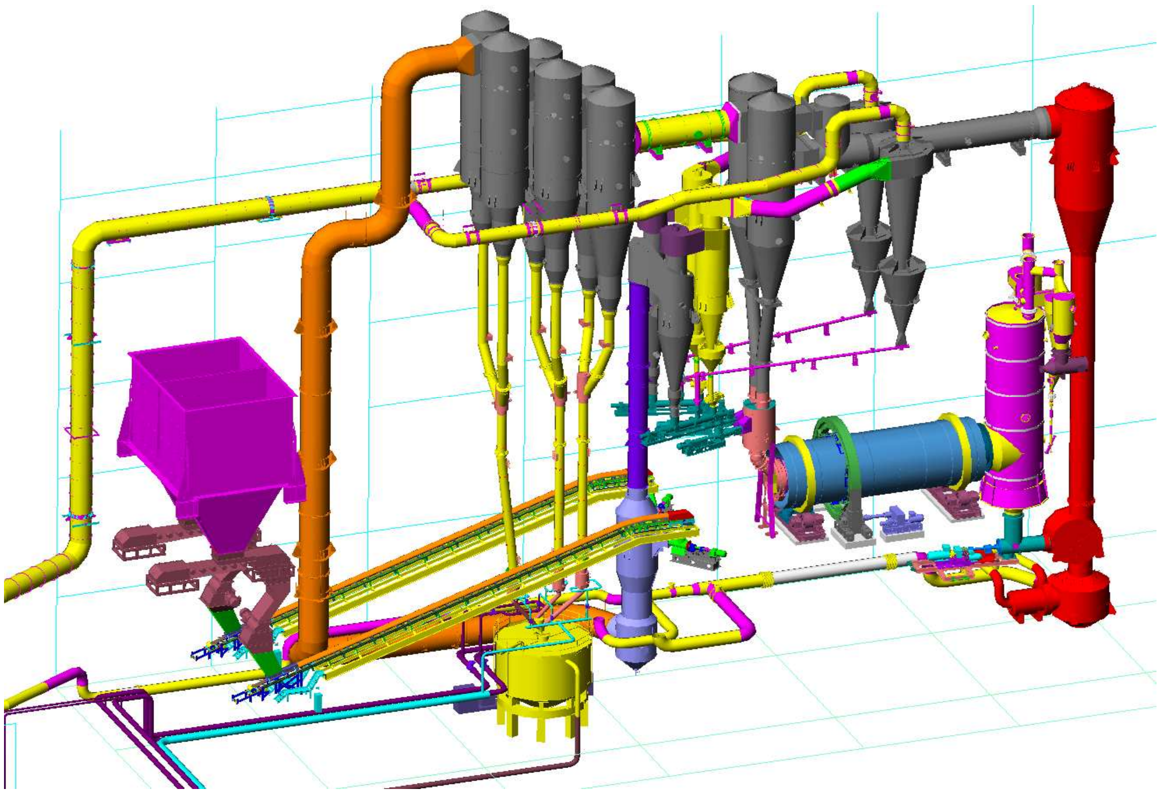

Figure 2 The layout of the Enefit140 plant.

The main advantages of the Enefit140 process are the following:

- Use of fine-grained oil shale, which allows complete utilization of all mined oil shale;
- The only solid residue of the process is a stable ash with a low organic carbon content that is suitable for utilization in the construction industry;
- The process does not produce spent shale or semicoke as a by-product;
- The process is very efficient and uses all energy contained in the oil shale;
- No external energy source is needed to run the process;
- The oil extraction process itself is water free;
- The overall chemical efficiency of the process is 80%;
- The process also produces a high calorific value semi-coke gas, which can be used for hydrogen or power production;
- The technology has proven itself over many years of operation.

Due to the many advantages listed above, the Enefit140 technology is the best available shale oil production technology which is currently being used on an industrial scale.

4. Development of the new Enefit280 retorting technology

Despite the many advantages that the Enefit140 technology possesses, it also has areas that could be improved:

- Relatively high air emissions;
- Thermal efficiency of the process is around 80%;

- Plant availability is around 75%;
- Produced oil has a high dust content;
- Plant has low unit capacity.

Therefore, in order to meet future environmental requirements and apply the process on other oil shales, the technology had to be improved. In 2008, Enefit decided to make the next development step by improving and scaling-up the existing technology. Today the design for the new Enefit280 technology is ready and construction of the new plant based on the improved technology is ongoing in Estonia. The new plant is expected to be comissioned by 2012.

Development of the new solid heat carrier process started already in 2008. For that purpose Eesti Energia cooperated with Outotec Oyi. Outotec (OT) is a Finnish-German technology development company that develops and supplies technologies for mining and metals industries as well as for other process industries. Its expertise covers the whole process chain from mine to metal. Related to our development work, OT has comprehensive expertise and R&D support, proven scale-up capabilities, is a leading provider of fluidizing technologies and has strong global set-up and experience in project implementation. In 2009 Enefit and Outotec established a joint venture (JV) called Enefit Outotec technology OÜ (EOT) whose primary focus is development of shale oil production technologies. Enefit brings into the JV its operating experience from the existing Enefit140 oil plant. Outotec brings its extensive technology development experience and know-how in fluidizing technologies.

EOT development efforts focused on increasing the unit capacity – the new plant should be able to process 280 tons of oil shale per hour. The new plant should also have availability over 90% and should meet strict EU environmental requirements: SO_2 emissions below 50 mg/Nm^3, solid particle emissions below 25 mg/Nm^3 and NO_x emissions below 200 mg/Nm^3. The total organic carbon content of the ash residue should be close to zero. The new plant should have significantly higher thermal efficiency, which will be achieved by installation of a waste heat recovery system, ash coolers and power production units.

A schematic representation of the new Enefit280 process is shown in Figure 3. It still includes almost all main unit processes that were present in the Enefit140 unit. The plant requires a constant, controlled feed of oil shale within the designed particle size and moisture content specifications. Raw oil shale from the mine is crushed and screened to achieve the required particle size distribution of 0-6mm. The wet oil shale is discharged from feed bins by means of screw feeders controlling the volume of the flow to the Venturi dryer. Hot flue gas containing fly ash from the waste heat boiler with a maximum temperature of 500°C is used to evaporate the moisture in direct contact with the particles. The energy consumed by evaporating the moisture cools down the process gas. At the same time the temperature of the oil shale increases. The moisture of the oil shale will be reduced below 0.1 wt.-%. Downstream of the Venturi dryer two cyclones in series separate the dried oil shale from the gas stream. The remaining solids content is discharged by means of an electrostatic precipitator (ESP). The flue gas leaving the ESP is discharged to atmosphere via a stack.

The dried oil shale and the heat carrier, which is essentially ash from the semicoke combustion, are fed via the retort feed chute to the rotary kiln. In the rotary kiln, the oil shale is heated to reaction temperature via direct contact with the heat carrier solids. The organic material in the oil shale decomposes and the hydrocarbon containing vapour-gas mixture is released. The vapour-gas mixture is separated from the remaining solids in the dust chamber and the dust chamber cyclone. The gas leaving the dust chamber cyclone is transferred to the condensation unit for production of oil fractions and high calorific value semicoke gas. To ensure safety in upset conditions, a flap valve allows for the vapour gas mixture to be conducted to a flare and sealing with inert gas is provided.

The solids discharged from the rotary kiln and the separated dust from the dust chamber cyclone accumulate at the bottom of the dust chamber where the screw conveyors transport the material to the CFB for combustion as it contains some remaining carbon. Semicoke from the dust chamber cyclones and the dust chamber is fed to the CFB. The CFB is fluidised with air through a nozzle grid. This primary air together with the secondary air provides the oxygen for the combustion of the carbon residue contained in the semicoke. Hot gases and solids leaving the CFB reactor enter the recycle cyclone and the heat carrier cyclone arranged in parallel. This recirculation of solids maintains a CFB system that ensures a uniform temperature in the CFB reactor. The ash, which is discharged from the CFB, is cooled to 80 – 150 °C in fluidised bed coolers. The heat of the ash is utilised for heating up condensate for use as boiler feed water working therefore as an economizer. At the outlet of the fluidised bed coolers the ash is discharged. The off gas leaving the recycling and heat carrier cyclone is cooled down in a waste heat recovery system, consisting of a waste heat boiler, steam drum and auxiliary systems such as pumps, tanks and boiler feed water preparation.

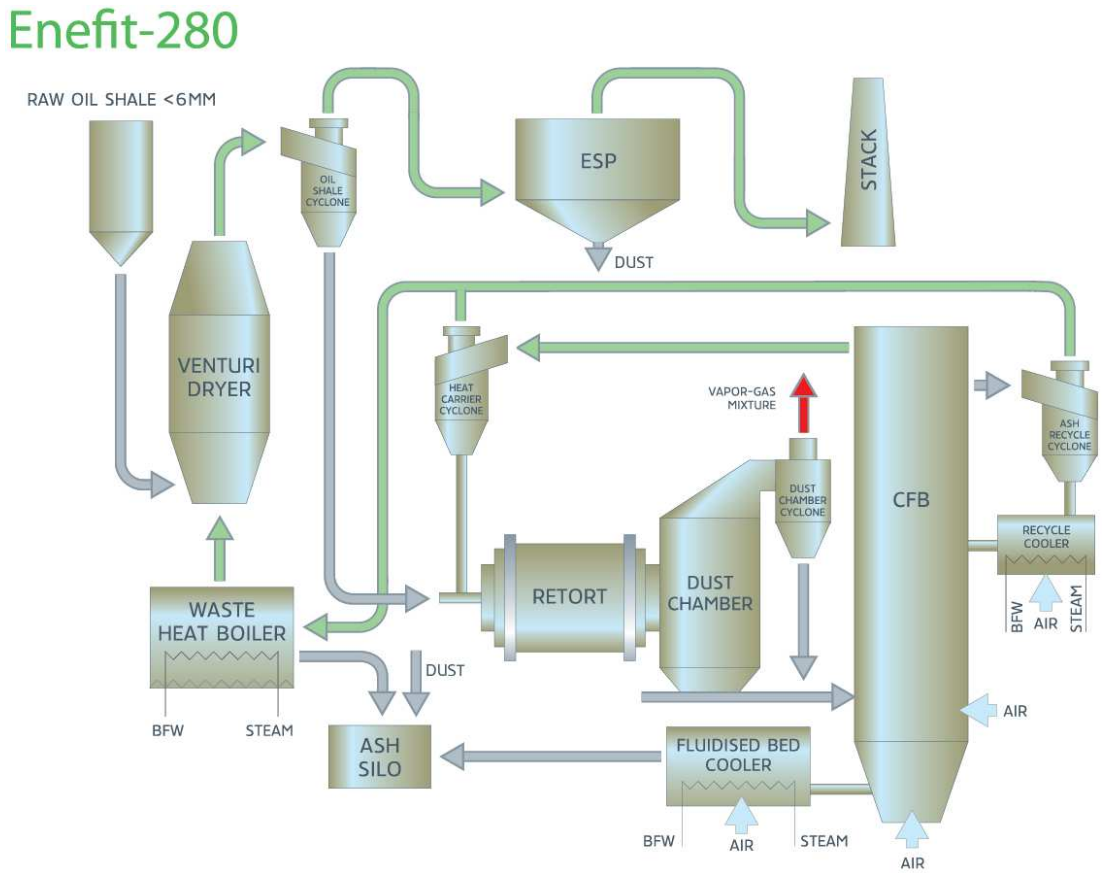

Figure 3 Process diagram of the new Enefit280 oil shale processing technology.

In addition to retorting technology, the new Enefit 280 plant will also include, a feed preparation system, condensation section and power generation unit, which converts steam produced in the waste heat recovery system into electricity.

The new plant will have an annual oil shale consumption of 2.26 million tons. It will produce 290,000 tons of shale oil annually. Power production capacity is roughly 35 MW_e. Start-up of the plant is expected in 2012. The investment cost of the whole plant is approximately 200 million EUR. The breakeven oil price for production of shale oil using the Enefit280 technology is 65 USD per barrel.

The new Enefit280 technology takes shale oil production a step further by extracting additional valuable products out of oil shale. Oil shale processing plants can offer much more than just oil production. In addition to considering oil production, energy efficiency has to be maximized. The Enefit280 process does not need external energy sources to run the process, it is a net energy producer that converts all excess heat into power. Wider utilization of by-products like retort gas and solid residues (ash) in the case of the Enefit technology or wastes (spent shale or semicoke) in the case of other technologies is important as well. The Enefit280 process produces high calorific value retort gas and this gas can be either used for hydrogen or power production (in the Estonian case some 50MW of electricity can be produced from retort gas). The ash residue produced from the Enefit280 process has good quality indicators, which will allow it to be sold to the cement industry as clinker substitute or alternatively it can be used in road construction. Using the ash as a clinker substitute would provide the cement industry with substantial CO_2 savings by offsetting the CO2 produced from combustion of limestone to produce clinker. Shale oil production technologies also have to maximize process efficiency, which include resource utilization efficiency, thermal and chemical efficiency of the process. Excellent environmental performance of shale oil production process is a key in getting acceptance from the local authorities and the public. The Enefit280 process is able to meet strict EU environmental standards. Enefit280 technology is currently the only technology that is simultaneously maximizing oil production, energy efficiency, utilization of byproducts and environmental performance.

5. Application of Enefit technology on other oil shales

Even after peak oil has been reached oil discoveries are still expected, but thereafter conventional oil will no longer be able to cover increasing demand. Therefore, new alternatives are needed to replace declining crude oil production. In addition, new crude oil reserves will be in remote regions and harder to find than ever, raising the costs of extracting newly found oil. This gives huge opportunities for shale oil. Even at prices below the current highs, oil production out of oil shale can be economic. Although information about many oil shale deposits is rudimentary, the potential world resources of shale oil are huge. The global volume of potential shale oil resource (based on known oil shale reserves) is conservatively estimated to be 2.8 trillion barrels [3]. This is 3 times as much as the current proved conventional oil reserves on the earth.

Development works in cooperation with Outotec has also focused on applying the Enefit technology on other oil shales. Enefit is the best available technology today due to its high efficiency and low environmental impact. Enefit technology has advantages that allow it to be applied on different oil shales around the world:

- Easy process control due to separation of units;
- Easy to modify process units according to properties of the oil shale;
- Built in flexibility with respect to variation in fuel properties;
- No technical limitations regarding oil content of oil shale.

EOT was established with the primary goal to develop shale oil production technology for different shales. EOT owns or has access to the following testing facilities required to develop the Enefit280 technology for different oil shales:

- Laboratory equipment to determine the key oil shale characteristics;
- Bench-scale unit for Enefit retorting process with a capacity of 20 kg/h;
- Bench-scale units to test fluidizing behavior of material;
- Pilot plant for combustion of spent shale in the CFB;
- Pilot plant for drying of oil shale.

Because all oil shales are different, every new plant has to be tailor made to take into account specific properties of that shale. Therefore, a systematic approach is needed to develop a new technology. The approach used in designing the Enefit280 plant for Estonian oil shale included the following phases: conceptual study (3 month), testing and basic engineering (8 month), and detailed engineering (9-12 month). Similar approaches can be applied on other shales to develop a modified Enefit280 process for that specific shale. EOT has started conceptual studies on US and Chinese oil shales. During a conceptual study EOT will work out the process block diagram, plant description, plot plan, list of main equipment, and investment cost estimate with accuracy of ±30%. EOT will soon start the basic engineering phase for Enefit's project in Jordan.

6. Hydrotreatment of Estonian shale oil liquids

EEOG currently produces three oil fractions and their mixtures. These products have traditionally been compared with heating fuels such as heavy fuel oil. The main consumers of these products are:

- Marine fuel producers (bunkering);
- Local boiler houses and small power plants.

In recent years, EEOG has been encountering significant resistance to placement of raw shale oil fractions on the markets. This resistance translates into deep discounting of Estonian shale oil liquids. This resistance derives from the unusual composition of Estonian shale oil liquids, especially the very high content of aromatic phenolic species and a very high Bromine number test response. The organic sulfur content is moderate at 0.7 wt% for the composite oil. See Table 1 for comparison of properties of the Estonian shale oil composite and Brent crude oil analog.

Table 1 Comparison of properties of Estonian shale oil composite and Brent crude oil analog.

Quality	Units	Raw Estonian shale oil composite [C5 to 525°C]	Brent crude oil analog [C5 to 565°C]
API Gravity	°API	12° to 15°	42°
Sulphur	Wt%	0.8	0.3
Nitrogen	Wt%	0.25	0.045
Oxygen	Wt%	6.1	< 0.15
Hydrogen	Wt%	9.8	13.3
Cetane in diesel	CI(D976)	~ 28	~ 49
Bromine Number	g Br_2/100g	~ 45	< 2
UOP/Watson K	-	10.5±	11.9±

The aromatic phenolic species result in organic oxygen content in the range of 6.1 wt% for the shale oil composite, versus organic oxygen of less than 0.1-0.2 wt% in similar naphtha-distillates distilled from conventional crude. The high content of aromatic phenolic species and polynuclear aromatics lead to specific gravity in the range of 1.06 at 15.5ºC for vacuum gas oil fraction. Typical vacuum gas oils from conventional crudes run about 0.90 at 15.5ºC. High density can be a barrier to placement of shale medium-heavy distillate as low-sulfur cutter stock for making low-sulfur heavy fuel oils.

The high content of heteroatoms, aromatic phenolic species and unsaturated bonds in Estonian shale oils prevent their direct utilization as transport fuels. Hydrotreating of shale oil is seen as the most efficient approach to remove heteroatoms and saturation of double bonds. Hydrotreatment of shale oil has not been studied extensively, but published papers reveal that removal of nitrogen species is more difficult compared to other heteroatoms [4, 5]. Estonian shale oil has relatively low nitrogen content compared to other shale oils, but it has high oxygen content, which distinguishes it from other shale oils around the world. H. Luik *et al.* [6-8] have studied hydrogenation of Estonian shale oil liquids and they have foreseen it as a promising method for upgrading of shale oil. However, they performed their experiments in batch-type reactors only.

To improve sales revenues coming from shale oil liquids, upgrading the shale oil composite via hydrotreating into premium synthetic crude oil fractions was proposed. Such hydrotreating into synthetic crude oils is the key analogous step in upgrading of Canadian bitumens. Estonian shale oil liquids are considered to be non-conventional oils since the shale oil liquids are distinctly different in molecular species and character from naphtha-distillates distilled from conventional crudes. Consequently, it was not clear whether refinery-type hydrotreating operations and crude-oriented hydrotreating catalysts could hydrotreat Estonian shale oil liquids for heteroatom and hydrogenation to lower the high content of polynuclear aromatics. In order to clarify this issue, a hydrotreating pilot plant program was performed.

Pilot plant tests showed that Estonian shale oil liquids can be successfully hydrotreated into low-sulfur synthetic crude oil, low-sulfur light gas oil and vacuum gas oil with qualities similar to and compatible with conventional crude oil fractions. Comparison of properties of the raw shale oil composite, hydrotreated shale oil product and Brent crude oil analog is presented in Table 2.

Table 2 Comparison of properties of the raw shale oil composite, hydrotreated shale oil product and Brent crude oil analog.

Quality		Raw shale oil composite [C5 to 525°C]	Hydrotreated shale oil product [C5 to 525°C]	Brent crude oil analog [C5 To 565°C]
Volumetrics	Vol %	100 % In	107 % Out	-
API Gravity	°API	15°	35°	42°
Sulphur	Wt%	0.8	0.015	0.3
Nitrogen	Wt%	0.25	0.025	0.045
Oxygen	Wt%	6.1	< 0.3	0.15
Hydrogen	Wt%	9.8	12.9	13.3
Cetane in diesel	CI(D976)	~ 28	~ 47	~ 49

Bromine number	g Br_2	45	1	< 2
UOP/Watson K	-	10.5±	11.7±	11.9±

Data in Table 1 show that the shale oil composite hydrotreated well with respect to sulfur, nitrogen, API gravity, volume swell, and Bromine number test response:

- Sulfur dropped from about 8,000 wppm to less than 150 wppm;
- Nitrogen dropped from about 2,500 wppm to less than 250 wppm;
- API gravity increased from 8-9º to 35º;
- Volume swell more than offset 6-7 wt% C5+ mass shrinkage, with C5+ volume yield around 107± vol% on feed oil;
- Low residual Bromine number test responses.

The chemical hydrogen consumption for Estonian shale oil composite within a commercial-scale shale oil hydrotreater unit is estimated to be around 35 to 38 kilograms of H_2 per ton of shale oil composite. The hydrotreating pilot plant program confirmed that the design for a shale oil hydrotreater unit can use process concepts, hardware components, and catalysts commercially proven in petroleum refining services.

7. Shale oil upgrader plant

EEOG is currently carrying out construction of a new generation of surface retorting unit, the Enefit280. By 2016, the vision is for EEOG to be comprised of the two previous generation Enefit140 units and four new Enefit280 units. Rated oil shale rock handling capability will be 1400 metric tons per hour or 11 million metric tons per year with daily output of raw shale oil liquids approaching 30,000 bbl per day (4650 metric tons per day). EEOG intends also to build a shale oil upgrader plant to upgrade upwards of 30,000 bbl per day of raw shale oil liquids and to utilize the co-produced shale retort gas. The shale oil upgrader plant is anticipated to incorporate the following:

- Shale oil hydrotreater unit;
- Product fractionation into three hydrotreated co-products;
- Pretreatment for sour semicoke gas;
- Air separation unit;
- Hydrogen synthesis plant;
- Sulfur block;
- Auxiliary power generation unit;
- Tank farm and utilities.

The preliminary process diagram is shown schematically in Figure 4. The raw shale oil fractions recovered via the condensate recovery unit are forwarded to the high pressure shale oil hydrotreater unit. The high pressure reactor loop within the shale oil hydrotreater unit reacts raw shale oil composite and hydrogen in two fixed bed catalytic reactors in series in order to remove most heteroatom oxygen and sulfur, hydrosaturate reactive bonds, mitigate organic nitrogen and hydrogenate many poly-nuclear aromatic cores. Necessary hydrogen is produced from retort gas. Hydrogen production is based on non-catalytic partial oxidation of compressed retort gas in gasifiers followed by a gas treatment unit including pressure swing absorption hydrogen purification and a tail gas treater. The process also includes a sulfur block, which converts removed sulfur compounds into solid sulfur pastilles.

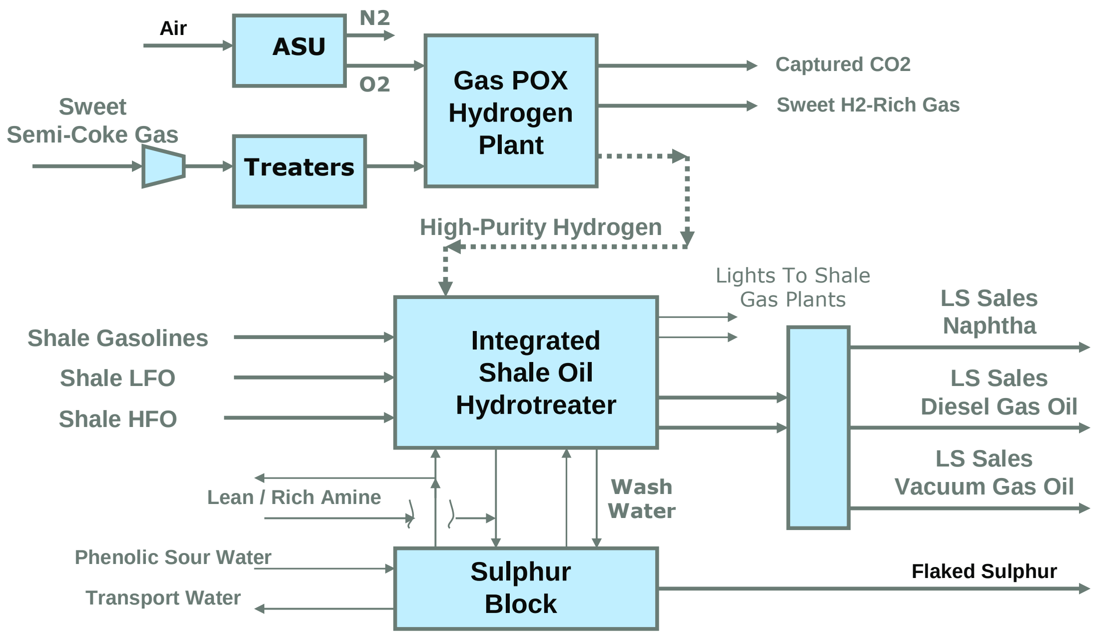

Figure 4 Process diagram of the shale oil upgrader plant

Resultant hydrotreated hydrocarbon liquids are split into naphtha, diesel gas oil and vacuum gas oil. The processing objective is for these three derivative cuts to be similar in terms of qualities and organic hydrogen content to corresponding cuts distillable from conventional light-medium crudes.

Enefit's strategy foresees building-up of an oil industry in Estonia based on the Enefit280 technology and to have a 30,000 barrels per day shale oil upgrader in place by 2016. Expansion of raw shale oil production is progressing with construction of the first Enefit280 unit. Development of the shale oil upgrader plant has entered into the basic engineering phase, which includes the next round of hydrotreatment pilot plant tests, preparation of front end engineering design and more precise estimation of capital investment.

8. Conclusions

Estonia is still the world leader in utilization of oil shale for oil and power production. Eesti Energia is the world largest oil shale processing company with activities ranging from oil shale mining, shale oil production and power production out of oil shale. EEOG is the only company in the world that commercially produces oil out of oil shale using the solid heat carrier technology (called Enefit140).

Enefit, in cooperation with Outotec, has developed a new, more environmentally friendly and more efficient technology for shale oil production out of fine-grained oil shale. The new Enefit280 technology combines EE's improved solid heat carrier technology and Outotec's fluidized bed technologies. The main principle of Enefit280 technology is that hot flue gases and hot ash produced within the process are used to dry and pyrolyze oil shale. In addition to retorting technology and other important sections like the feed preparation system and oil condensation section, the new Enefit280 plant will include, a power generation unit. EEOG has made an investment decision to build a new shale oil production plant based on Enefit280 technology in Estonia and it should be commissioned in 2012. The breakeven price of oil produced in the Enefit280 process is competitive with conventional oils.

The Enefit280 technology has advantages that allow easy adaptation to other oil shales. It is easier to control the process due to clear separation of unit processes and therefore, it is easier to design all unit processes according to specific oil shale properties. EOT has started to perform conceptual studies based on the Enefit280 technology on Jordanian, US and Chinese oil shales.

Eesti Energia is also developing the necessary upgrading process and facility for the shale oil fractions produced. Conceptual design for a 30,000 bbl per day shale oil hydortreater unit has been envisioned based on a successful preliminary hydrotreating pilot plant program testing Estonian shale oil liquids. Estonian shale oil is unique among non-conventional oils due to very high organic oxygen content along with high aromaticity. Design for a shale oil hydrotreater unit can use process concepts, hardware components, and catalysts commercially proven in petroleum refining services. Eesti Energia has been developing strategic plans and conceptual designs for a shale oil upgrader plant to enhance the value added production from the ten fold expansion of EEOG.

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