METHOD FOR IMPROVING THE QUALITY OF MIDDLE-HEAVY SHALE OIL AND FOR INCREASING COMMODITY OUTPUT AT THERMAL PROCESSING OF FUELS IN THE SOLID HEAT CARRIER UNIT

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The offered method for improving the quality of middle-heavy shale oil proposes changes in the condensation system of the solid heat carrier unit. Substitution of parallel flow of heavy shale oil and vapor phase in the air cooler-condenser for their counter-current flow accelerates evacuation of vapor-gas mixture from the high-temperature zone, increases oil yield and decreases the rate of oil bodying.

Introduction

Shale oil products produced at Oil Plant of Narva Power Plant (Oil Plant NPP) are widely used as liquid fuel for furnaces and boilers, and also as constituents for preparing different combustibles, especially for river and sea vessels. The better the quality of middle-heavy shale oil fractions and the less their sulfur content, the better the characteristics of fuels made on their basis. During the last years on the oil export market there has been keen interest in the shale oil fraction characterized by density as low as 1000 kg/m³, viscosity $\gamma_{80} \leq 30$ cSt, and flash point in closed crucible ≥ 55 °C – a

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constituent of bunker fuel for fleet. This fraction is prepared at Oil Plant by compounding the middle-heavy shale oil with gas turbine fuel (GTF) fraction.

Shale oil fractions obtained at oil shale retorting at Oil Plant NPP are used as components for preparing commodity outputs according to Oil Plant Standard EE10579981 [1].

Technological process of thermal processing in the solid heat carrier unit – TSK Oil Plant NPP

The technological process includes three fundamental operations (Fig. 1):

- 1. Drying and preheating of fine-grained oil shale in the drier in the atmosphere of hot stack gas from the heat regeneration furnace.
- 2. Thermal low-temperature carbonization of dry shale in a continuous process of mixing with hot heat carrier in the rotary drum reactor. As heat carrier the ash of spent oil shale is used.
- 3. Combustion of the mixture of semi-coke and heat carrier in the heat regeneration furnace for heating up the ash as heat carrier for the following cycle.

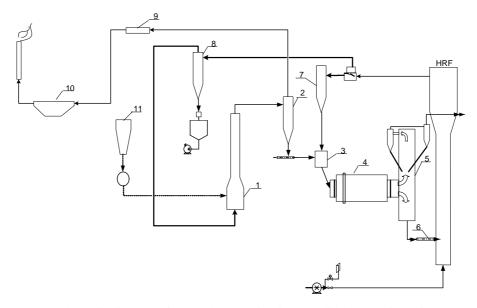


Fig. 1. Schematic diagram of thermal processing in the solid heat carrier unit – TSK Oil Plant NPP.

 $1-drier,\ 2-dry$ oil shale cyclone, $3-mixer,\ 4-rotary$ drum reactor, 5-dust separator, 6-screw-conveyor, 7-heat carrier cyclon, 8-ash cyclone, 9-gas-washer, 10-electrical precipitator, 11-oil shale storage tank, HRF – heat regeneration furnace.

Oil shale crushed to the size <25 mm is fed into the drier (1) where drying and preheating of oil shale are realized in the flow of hot (700–750 °C) stack gas. Dry preheated to 150-160 °C oil shale is separated from stack gas in the dry oil shale cyclone (2) and fed to the mixer (3), where it is mixed with an 1.9–2.1-fold quantity of hot solid heat carrier (ash of spent oil shale). The mixture is fed into the rotary drum reactor (4) where in the course of 15–20 min over 80% of organic substance of oil shale is converted into liquid and gaseous products [2–4].

Very small size and large surface areas of oil shale and heat carrier particles ensure their close contact in the mixing process in the reactor and a high rate of oil shale feed resulting in rapid heating of the reactor.

The mixture of spent oil shale and heat carrier from the reactor is separated from the vapor-gas mixture in the dust separator (5) and fed by the screw-conveyor (6) to the heat regeneration furnace (HFR).

Calorific value 1185–1423 kJ/kg (283–340 kcal/kg) of the spent oil shale and heat carrier mixture whose temperature is in the range 430–450 °C is sufficient to cover heat consumption of thermal processing.

Ash residue from the heat regeneration furnace is transported together with stack gas through the system of cyclons. In the heat carrier cyclon (7) relatively coarse granulometric fraction of ash is separated from the flow of stack gas and directed through the mixer (3) together with oil shale back to the reactor. Exess ash is removed from stack gas in ash cyclones (8).

The heat of stack gas and exess ash can be utilized in the waste heat incinerator. Stack gas is cleaned in the gas-washer (9) and the electrical precipitator (10) before outlet to the open air.

Vapor-gas mixture (VGM) produced in the reactor is sent for condensation through the dust separator (5), where by means of connected cyclones volatile products are separated from the mixture of spent oil shale and heat carrier.

Condensation system of the solid heat carrier unit – TSK Oil Plant NPP

Volatile products of thermal processing leave the dust separator at 465–490 °C and enter the scrubber tower (1) of the condensation system (Fig. 2) where residual dust is removed by washing with circulating condensed heavy shale oil.

Thereafter VGM is directed through the air cooler-condenser (2), where the main condensation of heavy shale oil takes place – separation of liquid and vapour phases in the counter-current process.

Heavy shale oil at the temperature 320 °C is collected in the gas collector. The condensed heavy shale oil is directed to the boiling pulp of the rectifying column (3), where it is mixed with the medium fraction of shale oil, separated in the column. Characteristics of oil fractions are given in Table 1.

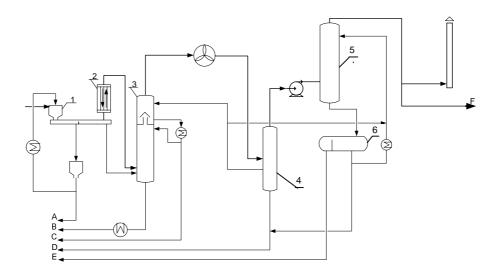


Fig. 2. Condensation system of the solid heat carrier unit – TSK Oil Plant NPP.

- A Heavy shale oil; B Middle-heavy shale oil; C Gas turbine fuel (GTF);
- D Gasoline; E Phenolic water; F Retorting gas.
- 1 crubber tower, 2 air cooler-condenser, 3 rectification column, 4 separator,
- 5 scrubber, 6 intermediate receiver for phenolic water and gasoline.

 $Table\ 1.$ Distribution and characterization of oil fractions produced in the solid heat carrier unit

Characteristics	Middle-heavy oil	GTF	Gasoline
Production quantities, total oil	70	10	20
basis, %	35 middle and 35 heavy		
Viscosity, cSt	≤28 ₈₀	$\leq 3.0_{50}$	_
Density at 15 °C, kg/m ³	≤1045	≤920	≤820
Flash point in open crusible, °C	≥120	≥55	≤ −10
Ash content, %	≤0.15	≤0.015	traces
Water content, %	$max \leq 0.3$	$max \le 0.3$	$max \le 0.3$
Sulfur content,%	0.4-0.7	0.5-1.0	0.9-1.4

In order to get middle-heavy shale oil in accordance with Oil Plant Standard EE10579981, the quantity of heavy shale oil in the mixture is limited (50%). It is necessary to add GTF fraction also for reducing the viscosity of middle-heavy shale oil.

Consequently, for preparation of the commodity output – liquid fuel as required – it is necessary either to increase the yield of GTF, which is complicated enough, or to decrease density and viscosity of middle-heavy shale oil fraction of produced shale oil.

Main factors increasing density and viscosity of heavy shale oil fraction separated in the air cooler-condenser and a feasible method for decreasing their values

In the air cooler-condenser during the counter-current process effective mass exchange between flowing downwards condensed heavy shale oil and moving upwards vapour phase takes place.

In the case of counter-current moving, overheating of condensed heavy shale oil at the temperature 340 °C takes place, which leads to its intensive polymerization in the piping of the air cooler-condenser. Primary decomposition products of VGM are thermally unstable and inclined to subsequent thermal bodying.

It is essential to note that the light fractions, which in the condensation process are captured by heavy shale oil, also take part in bodying reactions (polycondensation and polymerization) being at the same time interversibly bound.

From this follows the principal rule of shale oil treatment: acceleration of evacuation of VGM from the high-temperature zone has a positive effect on shale oil yield and decreases the rate of bodying [5, 6].

To decrease density and viscosity of heavy and middle-heavy shale oil and also the yield of the GTF fraction, the residence time of heavy shale oil and VGM in the high-temperature zone is to be reduced converting the counter-current flow of VGM and heavy oil condensate to a parallel process.

The residence time of the liquid phase of heavy shale oil in the air cooler-condenser was calculated according to the procedure treating the flowing of film-liquid and VGM for both processes. Initial data are given in Table 2.

It was determined that the residence time of the heavy shale oil fraction in the air cooler-condenser in the parallel process conditions becomes about 100 times shorter compared with the counter-current conditions.

Table 2. Characterization of VGM flowing through the air cooler-condenser

	At entering	At outlet
Quantity, kg/h	28,000	21,296
Molecular mass	53	50
Pressure, Pa	91,332	91,082
Speed of VGM, m/s	4.96	3.02

Calculation of residence time of heavy shale oil fraction in the air cooler-condenser at the existing counter-current process and the proposed parallel one [7]

1. Tension of frictional force of VGM in the pipe element of the air cooler-condenser at the counter-current flow:

$$\tau_{\rm M} = \frac{(P_{\rm s} - P_{\rm v}) \cdot d}{4 \cdot L} = \frac{(91332 - 91082) \cdot 57 \cdot 10^{-3}}{4 \cdot 6} = 0.59375 \,\text{Pa},$$

where

P_s – pressure of VGM at entering the air cooler-condenser, Pa

 $P_{\rm v}$ – pressure of VGM at outlet from the air cooler-condenser, Pa

d – pipe diameter, m

L – pipe lenght, m

2. Mean thickness of the heavy shale oil film in the pipe:

$$\delta = \sqrt[3]{3 \cdot \mu_{\text{ho}} \cdot V_1 / \rho_{\text{ho}} \cdot g} = \sqrt[3]{3 \cdot 0.001 \cdot 1.522 \cdot 10^{-5} / 1055 \cdot 9.8} = 1.64 \cdot 10^{-4} \text{ m},$$

where

 μ_{ho} – viscosity of heavy shale oil at 320–340 °C, Pa·s

 V_1 – line density of wetting, m³/ m·s

 ρ_{ho} – density of heavy shale oil at 320–340 °C, kg/m³

3. Mean speed of the heavy shale oil film in the pipe of the air cooler-condenser at the counter-current flow of VGM:

$$\begin{split} w_{\text{ho}} &= \frac{\rho_{\text{ho}} \cdot g \cdot \delta^2 \cdot (1/3 - \tau_{\text{M}}/2\rho_{\text{ho}} \cdot g \cdot \delta)}{\mu_{\text{ho}}} \\ &= \frac{1055 \cdot 9.8 \cdot (1.64 \cdot 10^{-4})^2 \cdot (1/3 - 0.59375/2 \cdot 1055 \cdot 9.8 \cdot 1.64 \cdot 10^{-4})}{0.001} \\ &= 0.044 \text{ m/s}. \end{split}$$

4. Line density of wetting:

$$V_1 = \delta \cdot w_{\text{ho}} = (\rho_{\text{ho}} \cdot g \cdot \delta^3)/3\mu_{\text{ho}} = V_{\text{ho}}/\pi \cdot d =$$

$$= (2.724 \cdot 10^{-6})/3.14 \cdot 57 \cdot 10^{-3} = 1.522 \cdot 10^{-5} \text{ m}^3/\text{m} \cdot \text{s}.$$

where

 V_{ho} – volume of condensed heavy oil in tube in time, m³/s.

5. Mean speed of the heavy shale oil film in the pipe of the air cooler-condenser under gravitational force:

$$w_{\text{ho}} = V_1 / \delta = 1.522 \cdot 10^{-5} / 1.64 \cdot 10^{-4} = 0.093 \text{ m/s}.$$

6. Throughput time of the heavy shale oil film in the pipe of the air cooler-condenser under gravitational force:

$$t_t = L/w_{ho} = 6/0.093 = 64.5 \text{ s.}$$

7. Throughput time of the heavy shale oil film in the pipe of the air cooler-condenser at counter-current flow of VGM:

$$t_p = L/w_{ho} = 6/0.044 = 136.4 \text{ s}.$$

8. Throughput time of the heavy shale oil film in the pipe of the air cooler-condenser at parallel flow process:

$$t_s = L/w_s = 6/4.96 = 1.2 \text{ s},$$

where

 w_s – mean speed of VGM at entering, m/s.

Calculation shows that in the case of parallel flow of condensing heavy shale oil and VGM, the residence time of heavy shale oil in the air cooler-condenser decreases about 100 times, from 136 sec to 1.2 sec.

According to the calculations given above we can propose that:

Converting the counter-current flow of VGM in the air cooler-condenser into the parallel flow process is a method for decreasing density and viscosity of the heavy shale oil fraction separated in the air cooler-condenser of the condensation system of thermal processing.

The parallel flow process in the air cooler-condenser enables to reduce the residence time of condensing heavy shale oil essentially, to decrease the temperature of condensing heavy shale oil from 320 °C to 210 °C, to eliminate the active mass exchange between liquid and vapour phases, as a result of which the commodity output of shale oil increases by about 20%.

The next step was a laboratory research of converting the counter-current flow of VGM in the air cooler-condenser into the parallel flow process.

The research was made by A. Elenurm, I. Rohtla and K. Kaidalov in the laboratory of Department of Chemical Engineering of Tallinn University of Technology.

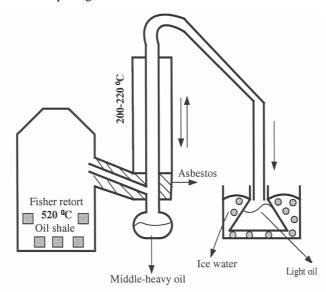
The results of the experiment were very positive.

A potential alteration in the share of valuable GTF used for obtaining a blend with middle-heavy shale oil of above-mentioned parameters (density as low as 1000 kg/m³, viscosity $\gamma_{80} \le 30$ cSt and flash point in closed crucible ≥ 55 °C) at introducing parallel flow in the solid heat carrier unit TSK of Oil Plant NPP must be 0.32 - 0.278 = 0.042 or 4.2% GTF.

 $\it Table~3.$ Results of laboratory-scale retorting of oil shale in an externally heated retort

Characteristics	Flow of VGM in the air cooler-condenser		
	Counter-current flow	Parallel flow	
Oil yield, dry oil shale basis, %			
Middle-heavy oil	13.16	15.26	
Light oil	2.53	1.51	
Density of shale oil, ρ_4^{15} , kg/m^3			
Middle-heavy oil	1083	984	
Light oil	807.4	786.1	
Viscosity at 50 °C, cSt			
Middle-heavy oil	30.6	22.7	

Variant 1 Counter-current contact of condensate (middle-heavy oil) and vapour-gas mixture in the cooler-condenser



Variant 2
Parallel flow contact of condensate (middle-heavy oil) and vapour-gas mixture in the cooler-condenser

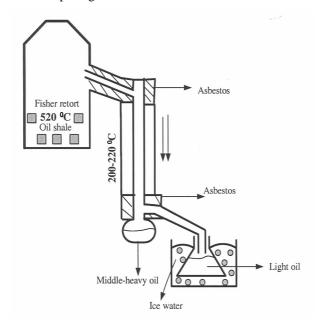


Fig. 3. Laboratory equipment for thermal processing of oil shale (counter-current and parallel flows in the cooler-condenser).

At the present time density of the middle-heavy shale oil produced in Oil Plant $\rho_{\rm mho}$ is 1045 kg/m³, that of GTF $\rho_{\rm GTF}$ – 904 kg/m³. For obtaining the product shale oil with $\rho_{\rm p}$ 1000 kg/m³, the required share of GTF for adding to middle-heavy shale oil makes:

$$X_{\text{GTF}} = (\rho_{\text{mho}} - \rho_{\text{p}}) / (\rho_{\text{mho}} - \rho_{\text{GTF}}) = (1045 - 1000) / (1045 - 904) = 0.32.$$

In this case we receive an oil constituting of 32% GTF and 68% middle-heavy shale oil.

In the case of introducing parallel flow, the yield of GTF increases by 0.5 t/h on account of reduced temperature and avoiding the gripping of GTF by middle-heavy shale oil:

$$G^{\text{ho}} = 6704 - 500 \approx 6200 \text{ kg/h}.$$

$$\rho_{\text{p}} = \rho_{\text{mho}} \cdot x_{\text{mho}} + \rho_{\text{ho}} \cdot x_{\text{ho}} = 1045 \cdot 0.504 + 1033 \cdot 0.496 = 1037,$$
 ere
$$x_{\text{mho}} = 6200/12300 = 0.504,$$

 $x_{\text{ho}} = 0.496$ The share of GTF constitutes:

$$X_{\text{GTF}} = (\rho_{\text{mho}} - \rho_{\text{p}}) / (\rho_{\text{mho}} - \rho_{\text{GTF}}) = (1037 - 1000) / (1037 - 904) = 0.278.$$

Basing on truthworthy calculations and laboratory-scale experiments, a project was worked out and put into practice at TSK Oil Plant NPP in 2006.

In the course of exploitation of parallel flow during may-june 2006 under established optimal pyrolysis conditions in the retorting section of Oil Plant, changes in density and viscosity of middle-heavy shale oil were proved. Industrial experiments gave the following average results (Table 4):

Additional calculations give

$$X_{\text{GTF}} = (\rho_{\text{mho}} - \rho_{\text{p}}) / (\rho_{\text{mho}} - \rho_{\text{GTF}}) = (1040 - 1000) / (1040 - 896) = 0.278.$$

 $0.32 - 0.278 = 0.042 \text{ or } 4.2\% \text{ GTF}.$

We drew the conclusion that the set purpose – decrease in density and viscosity of middle-heavy shale oil through converting the movement of VGM in the air-cooler-condenser resulting in essential reduction of the residence time of shale oil vapors in the high-temperature zone – was achieved.

Table 4.	Comparative	characeteristics	of two	shale oi	l fractions

Characteristics	Flow of VGM in the air cooler-condenser		
	Counter-current flow	Parallel flow	
Density of shale oil, ρ_4^{15} , kg/m^3			
Middle-heavy oil	1045	1040	
Light oil (GTO)	904	896	

It confirms once more the postulates concerning thermal processing of vapor-gaseous products of oil shale and shale oil:

The components of primary vapor-gaseous products are thermally labile and incline to further thermal transformation – mainly in the direction of bodying.

From this follows the fundamental rule without exceptions: acceleration of evacuation of vapor-gas products from high-temperature zone increases oil yield and decreases oil bodying.

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Presented by J. Soone Received January 20, 2007