UTILIZATION OF SEMI-COKE
OF ESTONIAN SHALE OIL INDUSTRY

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Semi-coke (spent shale) from Kiviter retorts containing organic matter and stored in semi-coke dumps is one of the main problems of Estonian oil shale industry. In 2005 the proposed charge of storing environmentally hazardous semi-coke will be 4.5 times more than that of oil shale ash. This may make shale oil production economically unprofitable. In this paper some methods of semi-coke utilization are presented.

Problems with Semi-Coke

One of the main problems of Estonian oil shale industry is semi-coke waste. There are two methods in use to produce shale oil – processing in Kiviter retorts (Kohtla-Järve and Kiviõli oil plants) and in retorts with solid heat carrier (SHC), (UTT-3000, Narva, Estonian Power Plant (PP)). The semi-coke from SHC retorts is burnt to ashes in circulating aerofountain furnace, and the final waste product is oil shale ash. The semi-coke from Kiviter retorts containing organic matter is, however, mostly not used at present and stored as waste on so-called semi-coke dumps. As semi-coke is an environmentally more hazardous matter than oil shale ash, some of its utilization methods are analyzed below.

Earlier the storing of semi-coke in hills was no big problem. The new pollution charges will change the situation drastically. Storing of wet semi-coke without its utilization may make the production of shale oil economically unprofitable. The taxes for wet semi-coke stored in dumps will in years 2002–2005 increase more than 1.7 times. The growing rate, 20 % per year, will evidently remain stable in the near future. It is clear that utilization of semi-coke is really important for Estonian oil industry.

AS Viru Keemia Grupp (Viru Chemistry Group Ltd., Kohtla-Järve) has reported about manufacturing new products (fertilizer "Viru ramm", compost, rock wool and IVU blocks) from semi-coke. The amounts of semi-coke utilized in this way are much smaller than its total amount produced, and this only mitigates the situation without solving the problem. For complete utilization of semi-coke it would be reasonable to burn it in boilers to produce heat with later utilizing the ash in building material production and in agriculture as fertilizer or alkali-reagent for liming acid soils. As pollution charges for storing wet semi-coke and oil shale ash grow at different rates, 20 and 5 % per year, respectively, the storing of ash is much cheaper. For example, in 2005 the proposed pollution charges for semi-coke will be 4.5 times higher than that for ash.

Burning of Semi-Coke in PF Oil Shale Boilers

Because of economical reasons the transportation of low-calorific semi-coke ($Q^d_b \leq 4.5$ MJ/kg) over long distances is not reasonable. Its burning to ashes must proceed in the oil plant. The present investigation shows technical possibilities to burn semi-coke in the existing pulverized firing (PF) boilers. Economical calculations must be done before using this scheme of utilization in practice. These calculations are not included in the present work.

To elucidate the problems probably arising during co-combustion of semi-coke and oil shale in PF boilers at Thermal Engineering Department of Tallinn Technical University (TED TTU) corresponding investigations were carried out. There could be no specific co-combustion problems, as semi-coke and oil shale ash are of the same origin, and ash composition is similar to that of the ash from PF boilers burning only oil shale. Some problems may rise concerning the equipment for fuel handling and flue gas extraction because higher capacities are needed.
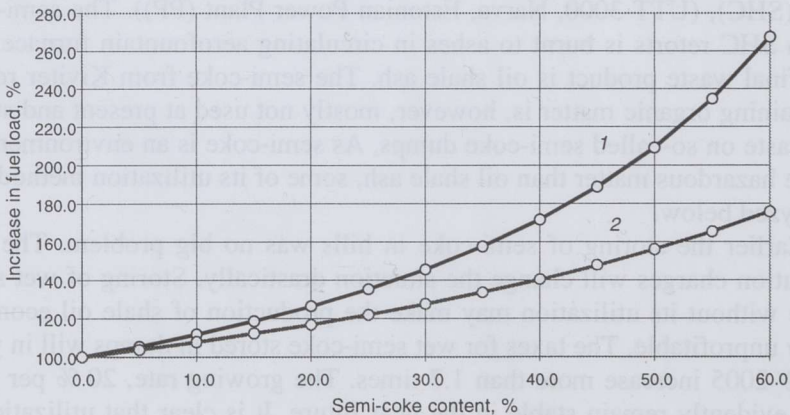

Fig. 1. Change in fuel load depending on semi-coke content of fuel mixture: $1 - Q^d_b = 1.2$ MJ/kg, $2 - Q^d_b = 4.4$ MJ/kg
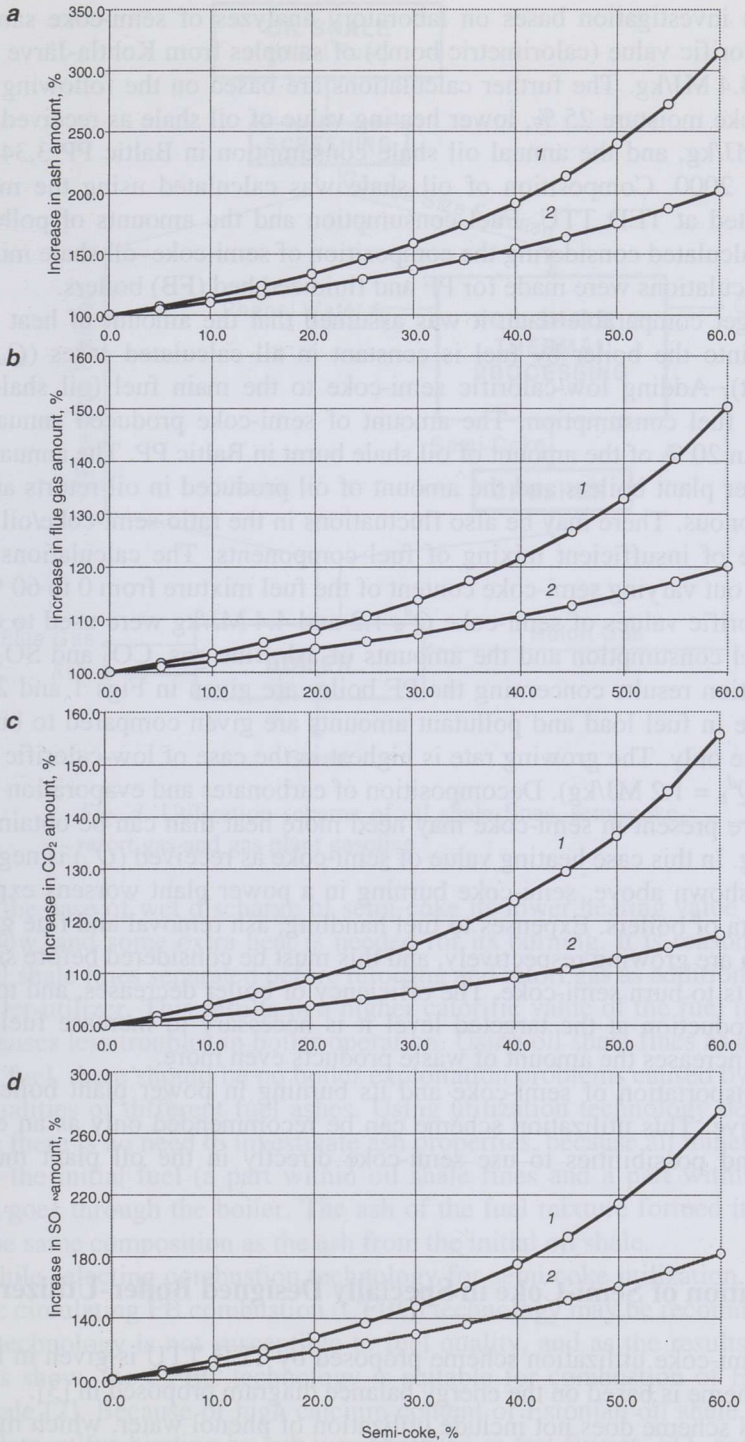
Fig. 2. Increase in ash (*a*), flue gas (*b*), CO_2 (*c*) and SO_2 (*d*) amount depending on semi-coke content of fuel mixture: $1 - Q^d_b = 1.2$ MJ/kg, $2 - Q^d_b = 4.4$ MJ/kg

This investigation bases on laboratory analyzes of semi-coke samples. The calorific value (calorimetric bomb) of samples from Kohtla-Järve $Q^d_b =$ = 1.2–4.4 MJ/kg. The further calculations are based on the following data: semi-coke moisture 25 %, lower heating value of oil shale as received $Q^r_i =$ = 8.3 MJ/kg, and the annual oil shale consumption in Baltic PP 3,343,800 tons in 2000. Composition of oil shale was calculated using the method elaborated at TED TTU. Fuel consumption and the amounts of pollutants were calculated considering the composition of semi-coke–oil shale mixture. The calculations were made for PF and fluidized bed (FB) boilers.

To get comparable data, it was assumed that the amount of heat introduced into the boiler by fuel is constant in all calculated cases (Q_{introd} = = const). Adding low-calorific semi-coke to the main fuel (oil shale) increases fuel consumption. The amount of semi-coke produced annually is less than 20 % of the amount of oil shale burnt in Baltic PP. The annual load of power plant boilers and the amount of oil produced in oil retorts are not synchronous. There may be also fluctuations in the ratio semi-coke/oil shale because of insufficient mixing of fuel components. The calculations were carried out varying semi-coke content of the fuel mixture from 0 to 60 %.

Calorific values of semi-coke Q^d_b 1.2 and 4.4 MJ/kg were used to calculate fuel consumption and the amounts of ash, flue gas, CO_2 and SO_2. The calculation results concerning the PF boiler are given in Figs 1 and 2. The increase in fuel load and pollutant amounts are given compared to burning oil shale only. The growing rate is highest in the case of low-calorific semi-coke (Q^d_b = 1.2 MJ/kg). Decomposition of carbonates and evaporation of the moisture present in semi-coke may need more heat than can be obtained by burning. In this case heating value of semi-coke as received (Q^r_i) is negative.

As shown above, semi-coke burning in a power plant worsens exploitation data of boilers. Expenses to fuel handling, ash removal and flue gas extraction are growing respectively, and this must be considered before signing contracts to burn semi-coke. The efficiency of boiler decreases, and to keep heat production at the targeted level it is necessary to increase fuel load, which increases the amount of waste products even more.

Transportation of semi-coke and its burning in power plant boilers are expensive. This utilization scheme can be recommended only as an exception, and possibilities to use semi-coke directly in the oil plant must be found.

Utilization of Semi-Coke in Specially Designed Boiler-Utilizer

The semi-coke utilization scheme proposed by TED TTU is given in Fig. 3. The scheme is based on the energy balance diagram proposed in [3].

This scheme does not include utilization of phenol water, which must be treated separately.
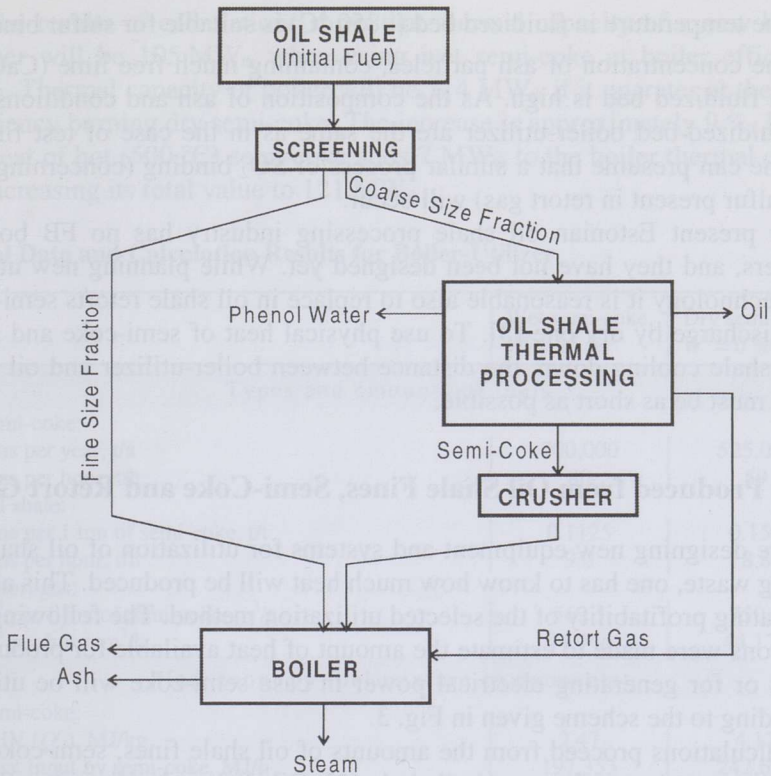
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                          ┌─────────────────┐
                          │   OIL SHALE     │
                          │ (Initial Fuel)  │
                          └─────────────────┘
                                   │
                          ┌─────────────────┐
                          │   SCREENING     │
                          └─────────────────┘
                              Coarse Size Fraction
                                   │
                          ┌─────────────────┐
      Phenol Water ◄──────│   OIL SHALE     │──────► Oil
                          │   THERMAL       │
                          │   PROCESSING    │
                          └─────────────────┘
                                   │
                              Semi-Coke
                          ┌─────────────────┐
                          │    CRUSHER      │
                          └─────────────────┘

                          ┌─────────────────┐     Retort Gas
      Flue Gas ◄──────────│     BOILER      │◄──────
      Ash ◄───────────────└─────────────────┘
                                   │
                                 Steam
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Fig. 3. Utilization scheme of oil shale fines, semi-coke, retort gas and gas plant gasoline

In the case of wet discharge of semi-coke its lower heating value may be very low, and some extra heat is needed for its burning. It is reasonable to use oil shale fines separated before retorting and retort gas as additional fuels in boiler-utilizer. This results in a higher calorific value of the fuel mixture, and causes less troubles in boiler operation. Using oil shale fines as an additional fuel, there should be no boiler exploitation problems caused by different qualities of different fuel ashes. Using utilization technology described above there is no need to investigate ash properties, because all mineral matter of the initial fuel (a part within oil shale fines and a part within semi-coke) goes through the boiler. The ash of the fuel mixture formed in boiler has the same composition as the ash from the initial oil shale.

While selecting combustion technology for semi-coke utilization, atmospheric circulating FB combustion (CFBC) technology may be recommended. This technology is not susceptible to fuel quality, and as the results of test firings show, the CFBC technology is suitable for combustion of Estonian oil shale [2]. Because of high calcium content of Estonian oil shale, almost complete sulfur binding by ash was observed in test firings. SO_2 content of flue gas from test facilities of various companies did not exceed 5 ppm. This was caused by two main reasons:

– The temperature in fluidized bed (~850 °C) is suitable for sulfur binding.

– The concentration of ash particles, containing much free lime (CaO_{free}), in fluidized bed is high. As the composition of ash and conditions in a fluidized-bed boiler-utilizer are the same as in the case of test firings, one can presume that a similar process of SO_2 binding (concerning also sulfur present in retort gas) will occur.

At present Estonian oil shale processing industry has no FB boilers-utilizers, and they have not been designed yet. While planning new utilization technology it is reasonable also to replace in oil shale retorts semi-coke wet discharge by dry one [3]. To use physical heat of semi-coke and minimize shale cooling down, the distance between boiler-utilizer and oil shale retort must be as short as possible.

Heat Produced from Oil Shale Fines, Semi-Coke and Retort Gas

Before designing new equipment and systems for utilization of oil shale retorting waste, one has to know how much heat will be produced. This allows estimating profitability of the selected utilization method. The following calculations were made to estimate the amount of heat available for production needs or for generating electrical power in case semi-coke will be utilized according to the scheme given in Fig. 3.

Calculations proceed from the amounts of oil shale fines, semi-coke and retort gas per 1 ton of retorted oil shale [3]. Oil shale calorific value (LHV) $Q^r_i = 11.05$ MJ/kg, that of oil shale fines is also 11.05 MJ/kg, and oil shale fines constitute ~9 % of oil shale total amount (data of *Viru Chemistry Group Ltd.*). From one ton of oil shale 600 kg semi-coke is formed, and its calorific value $Q^d_i = 4.12$ MJ/kg, on dry basis. Wet discharge of semi-coke is used in the existing retorts. In this case the moisture content of semi-coke is 25–30 %. In calculations $W^r = 25$ % was taken. The amount of wet semi-coke per 1 ton of oil shale is 800 kg, and its calorific value recalculated to the mentioned moisture content $Q^r_i = 2.47$ MJ/kg. The amount of retort gas per 1 ton of oil shale is 450 m^3 and its calorific value is 2.85 MJ/m^3 [3]. According to the handbook [4], the retort gas contains up to 25 g/m^3 of gas plant gasoline, which increases gas calorific value by about 1 MJ/m^3. Calorific value of retort gas containing gas plant gasoline is approximately 3.9 MJ/m^3.

As semi-coke will be the main solid fuel for a boiler-utilizer, it seemed reasonable to proceed from one ton of semi-coke in calculations. The amounts of materials added into the boiler are 0.1125 t oil shale fines and 562.5 m^3 retort gas per ton of wet semi-coke ($Q^r_i = 2.47$ MJ/kg, $W^r = 25$ %).

The calculations were made for capacity of 700,000 t/a, which is 80 t/h of wet semi-coke. Calculations were made also for dry discharge; in this case the capacity is 525,000 t/a (59 t/h). Initial data and calculation results are given in the Table.

The results of calculations show that thermal capacity of a new boiler-utilizer will be 105 MW_{th} when using wet semi-coke at boiler efficiency 80 %. Thermal capacity of boiler will be 114 MW_{th} if it operates at the same efficiency burning dry semi-coke. The increase is approximately 9 %. Physical heat of hot (500 °C) semi-coke adds 7 MW_{th} to the boiler thermal capacity increasing its total value to 121 MW_{th}.

Initial Data and Calculation Results for Boiler-Utilizer

	Wet semi-coke, $W^r = 25\ \%$	Dry semi-coke, $W^r = 0\ \%$
Types and amounts of fuels		
1. Semi-coke:		
tons per year, t/a	700,000	525,000
tons per hour, t/h	80	59
2. Oil shale:		
tons per 1 ton of semi-coke, t/t	0.1125	0.150
tons per hour, t/h	9.0	8.8
3. Retort gas:		
m³ per 1 ton of semi-coke, m³/t	562.5	750.0
m³ per hour, m³/h	44,944	44,175
Heat input by fuel mixture components		
1. Semi-coke:		
LHV (Q^r_i), MJ/kg	2.47	4.12
Heat input by semi-coke, MJ/h	197,353	242,668
2. Oil shale:		
LHV (Q^r_i), MJ/kg	11.05	11.05
Heat input by oil shale, MJ/h	99,450	97,240
3. Retort gas and gas plant gasoline:		
LHV (Q^r_i), MJ/m³	3.9	3.9
Heat input by gas, MJ/h	175,282	172,283
Total heat, MJ/h	472,085	512,191
Thermal capacity of boiler by fuel introduced, MW_{th}	131	142
Thermal capacity of boiler-utilizer, MW_{th}		
At 80 % efficiency	105	114
With physical heat of hot semi-coke added	–	121*

* Hot semi-coke temperature is 500 °C.

Conclusions

It may be concluded that the burning of semi-coke discharged from Kohtla-Järve oil plant retorts in PF boilers of Baltic PP is possible in principle. The problems arising while burning fuel mixtures are as follows:

1. Adding semi-coke to oil shale causes a rise in fuel consumption to keep the heat production of a boiler at the same level. The amounts of combustion products will rise as well.

2. The increase in fuel consumption and in the amounts of combustion products will lower the gross and the net efficiency of the boiler burning fuel mixture. One the one hand, it is caused by an increase in the amounts of heat leaving with flue gas (q_2) and with ash and slag (q_6). On the other hand, it is caused by increased expenses of fuel transportation and handling, and of ash and flue gas removal from the boiler. Keeping heat production of the boiler at a constant level while the efficiency goes down demands more fuel to be fed into the boiler even more increasing the amounts of combustion products.

3. As annual changes in the load of power plant boilers and in the amount of oil produced in oil retorts are not synchronous, there might occur periods when semi-coke amounts exceed those fixed in agreements between power plant and oil producer to keep the proper ratio semi-coke / oil shale. This requires extra depots for storing fuel components.

4. Insufficient mixing of fuel will increase semi-coke content of the fuel mixture. Feeding insufficiently mixed fuel into the boiler (even during a short period) may have a serious impact on boiler's operation. Consequently, an appropriate mixing technology must be worked out and corresponding devices installed in power plants using fuel mixture.

5. The heating value of semi-coke may be even negative because of the low calorific value, high content of moisture and nondecomposed carbonates. Burning of such semi-coke does not release heat but consumes it.

6. Burning of semi-coke yields more SO_2 and CO_2 in flue gas worsening environmental impact of the power plant, and increasing pollution charges.

Taking into account these conclusions it seems reasonable to utilize semi-coke in a boiler-utilizer considering the following recommendations:

1. Semi-coke, retort gas and oil shale fines must be burnt together. Using fuel mixture instead of low-calorific semi-coke enables better boiler operation under unfavourable conditions.

2. The type of boiler to be used is CFBC boiler. This type of boiler is not susceptible to fuel quality, and intensive sulfur binding by ash in the fluid bed occurs resulting in low SO_2 content of flue gas.

3. At the present oil production (~700,000 t/a semi-coke) thermal capacity of the boiler-utilizer ought to be 105–120 MW_{th}.

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