The Impact of Oil Shale Calorific Value on CFB Boiler Thermal Efficiency and Environment

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Declaration:
Hereby I declare that this doctoral thesis, my original investigation and achievement, submitted for the doctoral degree at Tallinn University of Technology has not been submitted for any academic degree.

Kristjan Plamus

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INTRODUCTION

Oil shale is the most important energy resource in Estonia. The share of energy from oil shale has provided approximately 50% of the primary energy consumption of Estonia and up to 90% of electricity production in recent years, and the share of Estonian electricity exports to neighboring countries has been approximately 20-30% from total electricity production. Thus, oil shale usage provides guaranteed energy independence for the Estonian Republic and enhanced energy security in the Baltic region [1, 2].

Estonian oil shale belongs to the carbonate class of fuels, which are known as low quality fuels. Due to the high content of carbonates, their calorific value is low, and their ash content is high [3]. The lower heating value (LHV) of oil shale fired in Estonian power plants is approximately 8.2-8.6 MJ/kg, and the ash content of oil shale is up to 50%. Firing that kind of fuel is associated with high CO₂ emissions and ash landfiling. Due to the decomposition of carbonate minerals, the specific emission of CO₂ is in the range of 0.95–1.12 t/MWhₑ, depending on the combustion technology. CO₂ emissions and ash landfiling are the most important environmental concerns related to oil shale firing [4, 5, 6].

In 2007, the European Union (EU) started an integrated approach to the implementation of climate and energy policy and committed to transforming Europe into a highly energy-efficient and low-carbon economy. Europe has committed to cut its emissions by at least 20% of its 1990 levels by 2020. The EU scheme for trading greenhouse gas emission allowances within the Community (EU ETS) established in 2003 by the European Parliament and the Council promotes achieving this target in a cost-effective and economically efficient manner [7].

The EU has decided that full auctioning of allowances shall be the rule for the power sector, beginning in 2013, and no free allocation shall be made with respect to any electricity production by new entrants to the EU ETS [8]. This decision means that the CO₂ emission level will be a factor of increasing importance for electricity producers. The cost of CO₂ allocation may become a factor in the net-cost of electricity, thereby reducing the competitive ability of oil-shale-based electricity in the electricity market that will be opened in 2013.

To minimize the risk of the uncertain cost of CO₂ allocation in the price of electricity in the near future, some other energy sources should be implemented. The use of biomass or nuclear energy has been discussed, but neither is considered to be a serious alternative to oil shale in the near future. An Estonian-owned nuclear power plant is not an option before 2025-2030 due to the long preparation and construction process. Using biomass is economically reasonable in co-generation mode only; the heat consumption of larger cities enables the production of 200-300 MWₑ of electricity, equivalent to up to 20% of the total electricity consumption in Estonia [9, 10].

EU climate policy has placed the Estonian oil-shale-based energy sector in difficult position. Thus, to reduce the effect on the environment and to minimize the cost of CO₂ emission allowances in the electricity price, oil shale of higher
quality should be used. Estonian oil shale mines can prepare higher quality upgraded fuel with an LHV of 11-11.5 MJ/kg. Such fuel is currently supplied to the shale oil industry.

Applying circulating fluidized bed (CFB) combustion technology in the Eesti Energia Narva power plants AS (Narva PP) provides some advantages in the utilization of oil shale of a higher quality. Because of the lower combustion temperature and large amount of circulating ash in the CFB boiler furnace, it is possible to burn oil shale of higher quality more efficiently than in pulverized firing (PF) boilers.

The use of oil shale of higher quality adds some additional positive aspects to the reduction of CO₂ emission, thereby enabling reduction of the fuel consumption per MWh of power produced, the load of the fuel transportation and preparation system, and the expenses for ash handling and deposition.

There is no previous experience in firing Estonian oil shale with higher quality in CFB boilers. To study the impact of oil shale quality on boiler technical and environmental indicators, full scale firing tests were performed. Based on test data the boiler heat balance is composed by calculating the specific CO₂ emissions (t/MWhₑ), the boiler thermal efficiency, the fuel consumption, and the ash mass flow rates.

The firing tests enable to study the behavior of oil shale mineral matter in combustion process. To calculate the amount of heat liberated in furnace, the extent of endo- and exothermic processes (ash sulfation, carbonates decomposition and new minerals formation) is determined. Based on the algebraic sum of the heat effects, the real heating value of oil shale is calculated. The last one is taken into account when boiler heat balance is compiled.

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I would like to thank my family and friends for constant support and encouragement at my thesis writing.


Publications

The thesis is based on the following publications which are presented at the end of the thesis:


Author's personal contribution

The contribution of the author to the papers included in the thesis is as follows:

Paper I. Planning and conducting the experiments. Participating in interpretation of the results. Major role in writing.

Paper II. The main author of the paper. Participating in planning and conducting the experiments. Interpretation of the results.

Paper III. Participating in planning and conducting the experiments. Interpretation of the results. Participating in writing the paper.

Paper IV. Responsible for data collection and processing. Interpretation of the results. Participating in writing the paper. Presentation of the results on the 20th International Conference on Fluidized Bed Combustion (in China, Xi'an, 2009).
NOMENCLATURE

CFB  circulating fluidized bed (combustion technology)
P F  pulverized firing (combustion technology)
FB  fluidized bed (combustion technology)
EU ETS European Union emission trading scheme
LHV  conditional lower heating value, MJ/kg
PP  power plant
LHV\textsubscript{COR}  corrected lower heating value (heat liberated in furnace), MJ/kg

Ash types:
- BT    bottom ash
- INTREX  external heat exchanger ash
- SH-RH  convective superheater and reheater ash
- ECO  economizer ash
- APH  air preheater ash
- ESP I  electrostatic precipitator field No. 1 ash
- ESP II  electrostatic precipitator field No. 2 ash
- ESP III  electrostatic precipitator field No. 3 ash
- ESP IV  electrostatic precipitator field No. 4 ash

\( k_{\text{CO}_2} \)  extent of carbonate decomposition (ECD)
\( \eta_{\text{(IB)}} \)  thermal efficiency
\( m_F \)  real fuel mass flow rate, kg/s
\( \Delta Q_K' \)  thermal effect due to incomplete decomposition of carbonates, kJ/kg
\( \Delta Q_U' \)  thermal effect due to the formation of new minerals, kJ/kg
\( \Delta Q_{S-T,K}' \)  thermal effect due to the formation of calcium sulfate, kJ/kg
1. LITERATURE OVERVIEW

1.1. Oil shales

Oil shale is a sedimentary rock containing organic matter known as kerogen. The formation of oil shale occurred in marine conditions. Oil shale deposits are surrounded mainly by carbonate, carbonate-terragenic or terrigenic sediments. Oil shale mineral matter can be of the carbonate, carbonate-terragenic or terrigenic type [3, 11].

The properties of oil shale depend strongly on the deposit. The deposit usually determines the mineral content and the heating value of the oil shale it produces. Generally, oil shales are characterized as solid fuels with high mineral content and low calorific value. The mineral content can be in the range of 30-70 %, and the lower heating value can be in the range of 5 to 20 MJ/kg. The LHV of oil shale usually has good linear correlation to its mineral content. Due to the relatively high mineral content of oil shale, its ash content can be up to 85 %. The moisture content of oil shale can be in the range of 4-45 %, and the sulfur content can up to 12 % [11].

Oil shale differs from other humus fuels by the high hydrogen and oxygen content of its organic matter. The atomic ratio of hydrogen to carbon (H/C) is approximately 1.2-1.7, which is approximately that of crude oil: 1.8-2.0. This similarity is the main reason why oil shale is considered to be an alternative resource for liquid fuel production. Comparing oil shale to the primary solid fuels, it is more similar to brown coal, which has an H/C atomic ratio of 0.8. For comparison, the H/C atomic ratio of anthracite coal is approximately 0.3 to 0.4 [12].

Oil shale is widely spread around the world. Oil shale can be found on all continents and in over 600 deposits. Because oil shales exhibit different properties, oil shale resources are often calculated based on the shale oil yield; thus, the supply oil shale in a deposit is presented in tons of shale oil. The total existing world resource of shale oil is estimated to be 690 billion tons, which is twice the reported crude oil resources [13]. This figure is considered to be conservative because the oil shale resources of some countries are not reported, and other deposits have not been fully investigated.

It is estimated that nearly 77 % of the world's potentially recoverable shale oil resources are concentrated in the USA. The largest of the deposits is found in the Eocene Green River Formation, which contains a total estimated existing resource of approximately (USA total) 536,900 million tons. Other important deposits (million tons) include those of China (47,600), the Russian Federation (35,470), Congo (14,310), Canada (2,192), Italy (10,446), Australia (4,531), Brazil (11,734), Morocco (8,167), Jordan (5,242), Estonia (2,494) and Israel (550) [13, 14, 15].

Despite the size of oil shale resources, only a few deposits are currently being exploited. In 2010, approximately 30 million tons of oil shale is mined for electricity and shale oil production, or as raw material for the chemical and
cement industries [16]. The greatest oil shale consumer in the world is Estonia, where each year approximately 15 million tons of oil shale are utilized for electricity and shale oil production (12 million tons is burned in thermal power plants). In China approximately 12-13 million tons of oil shale is utilized for electricity and shale oil production [16]. The shale oil production levels of China, Brazil and Estonia in 2008 were 375, 200, 355 thousand tons, respectively [13].

However, the increase of crude oil price in recent years has driven increased interest in oil shale usage. The oil shale preparation process for shale oil industry is accompanied with great amounts of waste oil shale which can be utilized. The direct burning of waste oil shale in power plants is the most attractive option. However, firing oil shale (which has a very complicated composition) as a fuel requires know-how and technology.

1.2. Combustion of oil shales

Despite the enormous oil shale resources in the world, there is no significant interest in oil shale utilization for power production. Thus, the direct combustion of oil shale is not widely investigated and is only discussed in a few published papers. Direct combustion of oil shale as a domestic resource is most attractive for countries where no other resource is available to produce electricity. There are few countries where oil shale combustion research has been performed due to interest in producing electricity from oil shale, which is their only asset (energy-poor countries are developing their own assets) to guarantee energy security [13]. Today, Estonia is one such country, producing most of its electricity from local oil shale in oil-shale-fired power plants; thus, it has significant utilization experience in operating the largest full scale oil shale fired power units. The investigation of oil shale combustion experiments in Estonia is discussed in the Chapter 1.4.

Research in the field of oil shale combustion is performed in China, Israel and Jordan. In China and Israel, fluidized-bed-based demonstration plants are in operation to investigate the combustion characteristics of local oil shales for the design of full scale boilers. Published research works in the field of oil shale combustion primarily originate from China [17-26], Israel [27-30] and Jordan [31-34].

Oil shale combustion in China

In China, there are three main oil shale deposits: Huadian, Maoming and Fushun. The conventional utilization of oil shale is concentrated mainly on reforming oil shale to produce shale oil and fuel gas and burning oil shale to generate electricity. From the beginning of the last century, a number of oil retorts were installed in Fushun to act as the primary deposit to produce shale oil for domestic use and to decrease the demand for imported crude oil.

Oil shale was first burned as a power fuel in fluidized bed boilers in the mid-1960s. By the end of the 1980s, several oil-shale-fired fluidized bed boilers were
used in industrial enterprises, and small-scale self-provided power stations (6-35 t/h) had been developed one after the other. These boilers may still be in stable operation. A new type of highly efficient oil shale-fired CFB boiler with steam rate of 65 t/h, which was designed for the Huadian thermal power plant, is the largest CFB boiler of Huadian oil shale and was put into commercial operation in 1996. Currently, there are three 65 t/h oil-shale-fired CFB boilers successfully operating in the Huadian thermal power plant. The research on boilers is related to the study of the operating parameters and fouling of the heating surfaces. According to the results of this combustion tests, the design principles of a large-scale super-high-pressure oil-shale-fired CFB boiler with a continuous evaporating capacity of 420 t/h (live steam production) is suggested, and the primary design specifications of the boiler are as follows: the temperature of superheated steam is 540 °C at a pressure of 13.7 MPa, the flow of reheated steam is 350 t/h at a temperature/pressure of 540 °C/2.36 MPa, and the temperature of the feed water is 240 °C. The Huadian oil shale has the following dry-basis characterization: LHV 8.37 MJ/kg, ash 51.61 %, volatile matter 41.89 %, moisture 2.9 %, and sulfur 1 %.

In China, investigations have also been performed to utilize local oil shale effectively, where the utilization of oil shale mainly includes burning and oil refining. In the process of oil refining, fine oil shale particles (<10 mm) are usually abandoned, which allows only 75 % of the oil shale to be utilized. To improve the availability of oil shale, many specialists proposed burning oil shale in CFB, which provides satisfactory desulfurization and combustion efficiency, low NOx emission, etc. [17-26].

**Oil shale combustion in Israel**

Oil shale is the main fossil fuel reserve in Israel. The largest oil shale is in the Negev region. Direct combustion is considered to be the most efficient means to use Negev oil shale.

Israel is running a 41 MWth fluidized bed (FB) based demonstration plant, which was built in Negev in 1989 by PAMA, on local oil shale. Research is performed to determine the most suitable CFB boiler solutions and to investigate the fouling and properties of ash deposits and heat transfer. Negev oil shale is characterized as very low grade, with LHV of 3.4-4 MJ/kg and an ash content of up to 60 %, and the total organic carbon concentration ranges from 2 % to 17 %. Still, the unit is operated with high reliability and availability. Based on the test data, commercial power plants were planned to be built [27-30].

**Oil shale combustion in Jordan**

Recently, the utilization of local oil shale has become more popular in Jordan, where 90 % of the primary energy resources are imported. Several firing tests on the direct combustion of oil shale have been performed. Firing tests were performed in test facilities operated by Pyropower (Finland) and Lurgi GmbH (Germany). In both facilities, 75 tons of Sultani oil shale were fired and
investigated. The primary characteristics of the studied oil shale are as follows: organic matter of 25 %, moisture content of 5.5 %, ash content of 55.5 %, sulfur content of 2.4 %, and its calorific value is 6.38 MJ/kg. Based on the results of the combustion tests on Jordan Sultani oil shale, the following can be concluded: Jordan oil shale burns cleanly and efficiently. A combustion efficiency of over 98.5 % was demonstrated. Typical emissions measured during these tests were as follows: SO₂ below 20 ppm, NOₓ in the range between 60-120 ppm, and CO below 50 ppm. These values will generally meet the stringent environmental requirements. Based on the studied combustion test, the world’s largest oil-shale-fired CFB boiler (410 t/h) is under construction in Jordan [31-34].

1.3. Estonian oil shale

The Estonian oil shale deposit is located in the Baltic basin in the North-East of Estonia and covers 5000 km². The oil shale bed is not homogenous but has a complicated structure and consists of oil shale layers of different qualities that lie alternately with limestone interlayers. The total thickness of the payable bed in the Estonian field is 2.5-3.2 m, of which oil shale layers account for 1.8-2.6 m and limestone layers account for 0.6-0.7 m, with these values varying depending on the deposit location. The number of oil shale layers is eight [3, 4].

The main substances in the interbeds are carbonate minerals (mainly calcium carbonate and to a lesser extent dolomite), which also contain a certain amount of terrigenous and organic matter. In an oil shale seam, organic matter is tightly bound with sandy-clay minerals and forms a uniform mixture [3, 4].

Oil shale (as dry matter) can be categorized into three components: organic material, sandy-clay and carbonates. The chemical and mineralogical composition of all of the components by themselves is relatively stable, irrespective of the deposit location and layer. The dry basis chemical composition of oil shale components is presented in Table 1-1 [4].

One peculiarity of Estonian oil shale is that the organic and sandy clay parts of the as-mined oil shale emerge from the carbonate part quite easily during the mining and preparation process (crushing). This characteristic of Estonian oil shale enables the removal of carbonates and improvement of the oil shale quality, which is accomplished by enrichment¹.

In Estonia, oil shale is mined in underground and open-cast mines. The LHV of un-enriched (as-mined) oil shale, known as “mountain massive”, is 6.7-6.9 MJ/kg [4]. For the oil shale industry, oil shales with different qualities are produced. The LHV of oil shale provided to power plants is determined by the

¹ The process of removing carbonates is called enrichment and is based on the density differences of limestone and oil shale. Because the density of limestone (CaCO₃) is higher (2.0-2.5 g/cm³) than that of oil shale (1.3-1.8 g/cm³), the limestone is separated from the crushed as-mined oil shale in a heavy suspension medium in a separator. The suspension medium is a mixture of water and magnetite powder with a density of 2.1 g/cm³.
contracts between the producer and the consumer. The oil shale fired in both in PF and CFB boilers as an energetic fuel has LHV 8-8.5 MJ/kg has the following approximate composition in the as-received basis: moisture 11-12 %, ash 45-48 % and carbonate CO₂ 17-19 %. For the shale oil industry, higher-quality enriched oil shale is supplied, with LHV 11-11.5 MJ/kg and granular composition of 25-125 mm. This fuel is known as technological fuel and is supplied for Kiviter type vertical retorts.

Table 1-1. Chemical composition of the Estonian oil shale (dry basis), % [4]

<table>
<thead>
<tr>
<th>Component</th>
<th>Organic part</th>
<th>Sandy clay part</th>
<th>Carbonate part</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>77.45</td>
<td>SiO₂</td>
<td>CaO</td>
</tr>
<tr>
<td>H</td>
<td>9.70</td>
<td>CaO</td>
<td>MgO</td>
</tr>
<tr>
<td>O</td>
<td>10.01</td>
<td>Al₂O₃</td>
<td>FeO</td>
</tr>
<tr>
<td>N</td>
<td>0.33</td>
<td>Fe₂O₃</td>
<td>CO₂</td>
</tr>
<tr>
<td>S</td>
<td>1.76</td>
<td>TiO₂</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>0.75</td>
<td>MgO</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Total 100</td>
<td>Total 100</td>
<td>Total 100</td>
</tr>
</tbody>
</table>

In general, Estonian oil shale is one of the best oil shales in the world. It has relatively high heating value and oil yield and quite low sulfur and moisture content [3, 11]. However, the oil shale composition and properties are largely determined by the carbonate content of the oil shale [35].

1.4. Combustion of Estonian oil shale

Oil shale has been used in Estonia for nearly 100 years. It has been used for industrial purposes as a raw material in the cement industry and for producing shale gas or shale oil. The main purpose has been its direct combustion for electricity production in power plants [3, 36].

In power plants, several combustion technologies have been used for Estonian oil shale combustion. Estonian oil shale combustion technology has been developing with the development of the combustion systems. Oil shale firing in Estonia started with grate firing in the 1920s, when grate firing was the only known industrial combustion technology. Large scale industrial firing of Estonian oil shale in PF mode started in 1959, when the first high-pressure PF boilers were launched at Balti power plant (Balti PP) and Eesti power plant, which was inaugurated in 1969. An advantage of the PF boiler is the higher heat release rate (MW/m²), which leads to reduced dimensions and to a more complete combustion of gases and higher efficiency than grate firing [3].

The oil shale industrial PF is characterized by a relatively high combustion temperature, which can reach up to 1400 °C. The high combustion temperature
is a disadvantage of the PF technology for oil shale firing. Firing oil shale in PF mode results in intensive fouling of the heating surfaces, especially in the high temperature region (furnace and superheaters). The sulfur content in the combustion gas within the high temperature region generates the appropriate conditions for the formation of hard deposits on the heating surfaces, which results in a reduced heat flux. Due to the high combustion temperature, the extent of carbonate decomposition (ECD or $k_{CO2}$) is high (0.97-0.99), and sulfur capture is only up to 80%, causing a high rate of carbon dioxide and sulfur dioxide emission. The main characteristics of the PF boiler are presented in Table 1-2 [3].

Related to the reconstruction need for Narva PP in 1990s, a question was raised as to whether to continue with PF technology or to find a more suitable combustion technology for Estonian oil shale to satisfy the more environmentally friendly requirements of burning high mineral content Estonian oil shale. The CFB combustion technology was introduced for Estonian oil shale in 2004. As there was no experience with Estonian oil shale combustion in a CFB combustor, firing tests need to be performed. Currently, modern CFB combustion technology stands next to PF technology.

**Estonian oil shale combustion at CFB test facilities**

The combustion tests with Estonian oil shale in FB mode were performed in ~1 MWth test facilities at Hans Ahlstrom Laboratory, Karhula, Finland (in 1994) and at Lurgi AG, Frankfurt/Main, Germany (in 1996). The objective of the tests was to verify whether Estonian oil shale can be burnt in an atmospheric FB boiler at a sufficient carbon conversion rate and with acceptable pollutant emission levels. Four different FB combustion modes were tested: CFB combustion with two fuel feeding modes and fast fluidized bed combustion with/without a cyclone. The results related to combustion tests are presented in [37, 38], and a recommendation for designing a full scale CFB boiler for Estonian oil shale is presented in [39].

The Estonian oil shale tests at both FB combustion facilities, as well as in the following laboratory investigations, yielded quite similar results. For the FB modes, firing of Estonian oil shale using the CFB technology is more effective than the classical fluidized bed. The tests showed that the CFB combustion process operated very smoothly and was easy to control. Control of the burning process in the classical fluid bed was quite problematic due to the high content of volatiles in the oil shale, combustion proceeded to the upper zone of the furnace and temperatures were raised to extremely high levels.

A temperature of 850 °C is considered most suitable for the burning of Estonian oil shale, accounting for fouling and high temperature corrosion of the heat transfer surfaces and for economic and environmental aspects.

The combustion tests exhibited very low emission levels. Burning in CFB mode – free CaO formed by decomposition of the carbonate minerals of oil shale is very active and effectively binds SO$_2$ from the flue gas. The test determined that only a few ppm of SO$_2$ content remained in the flue gas. Due to the low
combustion temperature of 850 °C in the combustor of the CFB boiler, an extremely low NOx emission was observed – lower than 200 mg/nm³ – and the N₂O content in the flue gas was 10-15 ppm [37-39].

**Oil shale combustion experience in CFB boilers**

During 2004-2005, two power units with electrical capacity of 215 MWₑ with two CFB combustion boilers were put into operation at Narva PP. Since the start of operation of the power units, research has continued on the operation conditions of these new CFB boilers. The main operating characteristics of CFB boilers firing Estonian oil shale with an average LHV currently used at Narva PP 8.2-8.6 MJ/kg are presented in Table 1-2. The results are compared with PF boilers that are in operation at Narva PP [6, 35, 40-46].

*Table 1-2. The main indicators of boilers when firing Estonian oil shale [6, 35, 40-46]*

<table>
<thead>
<tr>
<th>Parameter</th>
<th>CFB boiler</th>
<th>PF boiler</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal efficiency at nominal load, %</td>
<td>90-91</td>
<td>81-82</td>
</tr>
<tr>
<td>Combustion temperature, °C</td>
<td>800-900</td>
<td>1300-1400</td>
</tr>
<tr>
<td>Extent of carbonate decomposition kₖ₉₀₂</td>
<td>0.60-0.75</td>
<td>0.97-0.99</td>
</tr>
<tr>
<td>Extent of sulfur binding kₛ</td>
<td>0.99</td>
<td>0.75-0.80</td>
</tr>
<tr>
<td>SO₂ emission*, mg/Nm³</td>
<td>5-20</td>
<td>1500-3000</td>
</tr>
<tr>
<td>NOₓ emission*, mg/Nm³</td>
<td>100-160</td>
<td>ca 300</td>
</tr>
<tr>
<td>CO₂ specific emission, t/MWhₑ (gross)</td>
<td>0.94-1.06</td>
<td>1.20-1.30</td>
</tr>
<tr>
<td>Power unit efficiency at nominal load, %</td>
<td>34-35</td>
<td>28-30</td>
</tr>
</tbody>
</table>

*- dry O₂ 6 %

The CFB boilers meet all of the environmental regulations. The combustion temperature of 850 °C provides suitable conditions for total sulfur capture and partial decomposition of carbonates. In the CFB boiler, sulfur is completely captured by ash, resulting in the concentration of SO₂ in the flue gas being nearly negligible. There is no need to add sorbent (limestone) to the fluidized bed for sulfur capture. The Ca/S molar ratio in oil shale is high, and free lime forms during thermal decomposition of the carbonate minerals.

**Thermal effects during oil shale combustion**

The compilation of boiler heat balance and the determination of boiler efficiency are based on the heating value of the burned fuel. As a rule, a lower heating value is used for the as-received fuel, which is the value measured experimentally in a calorimetric bomb. In practice, some types of fuel require accounting for several other factors that can affect the heating value. Estonian oil shale is just such a fuel [40].

Thermal effects occur in oil shale mineral matter during the combustion of oil shale in a boiler furnace or in a calorimetric bomb. The extent of thermal effects
was investigated when firing conventional oil shale (8.2-8.4 MJ/kg) in CFB and PF boilers [3, 40].

Because the ECD in PF boilers is high (0.97-0.98 on average) due to high combustion temperature 1400 °C and sulfur binding extent is not very high (0.75-0.80), the increase of the heating value is 1.1-1.3 % [40].

The situation is somewhat different in the case of CFB boilers. Due to the low temperature in the furnace (850 °C), the extent of carbonate decomposition remains 0.70-0.75 (sometimes even less) and there is practically complete binding of sulfur by ash (the extent of sulfur binding at CFB is 0.999), the increase of the heating value of oil shale in a CFB boiler is on average, over 3 % higher than that in PF boilers. Compared to the lower heating value determined in a calorimetric bomb – even ~4 % [3, 40].
2. EXPERIMENTAL

2.1. General

The oil shale firing tests were performed on CFB boiler of the Balti PP. The CFB boiler was specially designed for firing Estonian Oil shale by Foster Wheeler. In consideration of long combustion experience with Estonian oil shale in PF boilers, the main development of CFB boilers construction was in the placement of the convective heating surfaces (from superheaters to air preheaters). Due to the relatively high ash content of Estonian oil shale, the heating surfaces are displaced in series towards the stack (not the standard configuration for coal boilers) to guarantee smooth ash removal from the boiler. The ash removal system is one of the most important subsystems of a CFB boiler. A detailed description of the structure and concept of the boiler are provided in [41].

The firing tests were performed by the Department of Thermal Engineering of TUT with the co-operation of the Narva PP. The tests were performed according to European standard EVS-EN 12952-15:2003 [47] and were run at a boiler nominal load of 85 kg/s of primary steam.

The firing tests with conventional and upgraded oil shale were performed in two series. The firing tests with conventional oil shale with a LHV of 8.2-8.8 MJ/kg, the boiler operated in the steady state regime for 7 days and the tests with upgraded fuel with a LHV of 9.3-11.5 MJ/kg operated for 10 days.

On each test day, the complete process data were collected. At both the beginning and the end of the test, fuel sampling was performed. The time between fuel sampling in a test day was the duration of the test. A total of 17 firing tests were performed, 10 tests with enriched oil shale and 7 with conventional oil shale. The duration of the tests was four hours on average, with a minimum duration of 1.15 hours and a maximum duration of 8 hours.

During each test run, regular fuel and ash sampling from the separation ports was performed. As the CFB boiler was not provided with all of the required solid sampling ports, several ash discharge valves were installed on the boiler ash separation ports during the preparation of the firing tests. A special sampler was designed and constructed to obtain fuel samples for fraction analyses under a secondary fuel crusher. An extra valve was designed and installed on the ash tube to measure the ash mass flow from SH-RH. The locations of the solid sampling ports are shown in Fig. 1 (Paper I). The chemical composition of the ash and fuel samples was determined at the DTE chemical laboratory.

Fuel sampling

The fuel samples for the ultimate and the proximate analyses were taken from the main fuel conveyor (after the primary hammer crusher), followed by averaging and dividing procedures to achieve representative average samples for the test run.
To estimate the effectiveness of the secondary fuel crusher and the granular composition of the fuel fed into the boiler, fuel samples before (A) and after (B) the secondary fuel crusher (Fig. 1 Paper I) were taken. The secondary fuel crushers are located at the end of the fuel-feeding lines (4) and are used to ensure the most suitable fuel granular composition for the CFB boiler. The granular composition of the fuel was measured at the Gas Measurement Laboratory in Balti PP; a 0.5 mm minimal aperture size was used for the sieve.

Ash sampling
To estimate the combustion effectiveness and behavior of the oil shale mineral matter in the furnace, ash samples were obtained to determine the chemical composition. The ash samples were obtained from the collection ports C to K, as indicated in Fig. 1 (Paper I). The INTREX ash samples were collected from the first bottom ash screw. Fly ash samples (F-K) were taken from the left and right outlets.

The granular composition of the ash samples was also determined. Bottom ash samples were analyzed using the “Fritsch” sieving machine at the DTE (sieve apertures: 0.125 – 16.000 mm). The INTREX and fly ash samples were analyzed with a Malvern laser diffractometer (0.02-2000 μm).

Flue gas sampling
Continuous flue gas sampling was performed at a vertical flue gas duct after the air preheater of the boiler. Position L in Fig. 1 (Paper I) indicates the location in the boiler gas pass where the flue gas samples were obtained for analysis. The flue gas composition, including the levels of O₂, CO₂ and H₂O in % and the concentrations of CO, NO, NO₂, N₂O and SO₂ in ppm, were measured according to EN 15259-10:2007. A GASMET DX4000N FTIR flue gas analyzer was used. Readings for flue gas sampling were taken every 60 sec.

Data from data logging system
The data logging system of the plant registers several boiler operation parameters (temperatures, pressures, flows and others, ash senders operating frequencies, and the current fuel consumption rate). These boiler operating parameters were measured in 10 minute intervals.

2.2. Test fuel
The chemical composition of the conventional and upgraded oil shales on an as-received basis is presented in Table 1 (Paper I). The oil shale was supplied by the Aidu open-pit mine. The conventional oil shale supplied to the Balti PP is energetic fuel with a LHV of 8.2-8.6 MJ/kg and with a granular composition of 0-40 mm, in accord with the Estonian trade oil shale standard EVS 670:1998. The Aidu open-pit mine can supply enriched oil shale with a LHV of 11-11.5 MJ/kg and with a granular composition of 25-125 mm as technological fuel.
for retorts of the Kiviter type in the shale oil industry. The firing tests with upgraded oil shale were performed with technological oil shale with a fuel granular composition of 0-40 mm. The upgraded oil shale was specially prepared by sieving with a sieve aperture size of 32 mm. The granular compositions of the conventional and upgraded oil shale taken before (A) and after (B) the secondary fuel crusher (Fig. 1, Paper I) are presented in Figure 2-1.

![Figure 2-1. Granular compositions of oil shales used in tests](image)

From Figure 2-1, the upgraded fuel was somewhat finer than the conventional oil shale. The median sizes of the oil shales fed into boiler R [0.5] were 0.48 mm and 0.56 mm. The reason for the finer upgraded oil shale can be found in the better operating conditions of the primary crusher. Before the tests with the upgraded oil shale, the crusher hammers were replaced with newer ones.

The oil shale composition is determined by its enrichment rate. The carbonate content of the oil shale determines its mineral CO₂ and ash contents. Oil shale mineral CO₂, ash and moisture content influence the boiler technical and environmental indicators. As oil shale composition is strongly correlated to its LHV, it is possible to describe the carbonate CO₂, moisture, and ash content of the oil shale as a function of the oil shale LHV. Figures 2-2 – 2-4 show the oil shale composition used in the firing test as a function of its LHV. In addition, the statistical data obtained over several decades in Estonian power plants are plotted (the line represents the average value of the statistical data) [3, 4, 35].
Figure 2-2 shows that the mineral CO₂ content of the oil shale used in the firing tests agrees with the statistical data in the range of LHV's of the studied oil shale. The ash content of the oil shale is somewhat lower in the LHV region than the statistical data (Figure 2-3). Additionally, the moisture content of the fuel samples is lower in the case of higher oil shale LHV. The oil shale moisture content depends on the enrichment process; it can also be affected by seasonal influences (Figure 2-4).

Figure 2-2. Oil shale carbonate CO₂ content versus LHV (dry basis) (the line represents the average value of the statistical data)
Figure 2-3. Oil shale ash (815 °C) content versus LHV (dry basis)  
(the line represents the average value of the statistical data)

Figure 2-4. Oil shale moisture content versus LHV (as-received)  
(the line represents the average value of the statistical data)
3. BOILER HEAT BALANCE

For calculating boiler thermal efficiency, fuel consumption rate, ash mass flow rate and specific CO$_2$ emission the boiler heat balance was composed. In boiler heat balance the heat input, heat output (useful heat) and boiler losses are determined. Boiler losses include flue gas losses, loss due to unburned CO, losses due to enthalpy and unburned combustibles in slag and flue dust, losses due to radiation and convection.

The heat balance and thermal efficiency estimations of the CFB boiler were performed on the basis of the EN 12952-15:2003 standard [47] by the indirect method taking into account the peculiarity of the oil shale. As regards endo- and exothermic processes in oil shale mineral matter during combustion process the real heating value of oil shale is calculated. In addition to unburned carbon unburned sulfur in slag and flue dust, and ash mass increase in furnace due to processes in oil shale mineral matter has been taken into account when calculating losses due to enthalpy and unburned combustibles.

Herewith, the enthalpies of water and steam were calculated according to “IAPWS Industrial Formulation 1997” [48]. The slag and flue dust enthalpies was calculated according to “Thermal calculation of heating boilers” [49]. Calculation of boiler heat balance was performed at normal conditions $t_r = 0$ °C and $p_r = 101,325$ Pa.

3.1. Thermal efficiency

Boiler thermal efficiency is the ratio of heat given to water-side environment to the heat liberated during the combustion of fuel in furnace. Boiler thermal efficiency is calculated via boiler heat balance considering heat input, output and boiler losses as follows, %:

$$\eta_{(N)B} = 1 - \frac{Q_{(N)\text{Ltot}}}{Q_{(N)\text{Ztot}}} = \frac{1 - \sum I_{(N)F}}{1 + (Q_{\text{RC}} + Q_L - Q_{(N)Z} \sum I_{(N)F})/Q_N},$$  \hspace{1cm} (3-1)

where

$$\sum I_{(N)F} = I_{(N)\text{GF}} + I_{(N)\text{COF}},$$  \hspace{1cm} (3-2)

where

- $Q_{(N)\text{Ltot}}$ total losses, kW;
- $Q_{(N)\text{Ztot}}$ total heat input, kW;
- $I_{(N)\text{GF}}$ the flue gas loss related to the heat input proportional to fuel burned;
- $I_{(N)\text{COF}}$ the loss due to unburned combustibles (CO) related to the heat input proportional to fuel burned;
\[ Q_{RC} \] the heat losses due to radiation and convection, kW;
\[ Q_N \] the useful heat output, kW;
\[ Q_L \] losses independent of fuel flow (losses due to enthalpy and unburned combustibles in slag and flue dust), kW;
\[ Q_{(N)Z} \] the total heat credit \((Q_{(N)Z} = 0)\), kW.

The real fuel mass flow rate can be calculated via boiler indirect heat balance as follows, kg/s:

\[
m_F = \frac{Q_N}{\eta_{(N)B}} - \frac{Q_{(N)Z}}{H_{(N)tot}(1-l_u)}\tag{3-3}
\]

where
- \(H_{(N)tot}\) total amount of heat into boiler, kJ/kg;
- \(l_u\) the ratio of unburned matter to supplied fuel mass flow - can be calculated according to Eq. 7 in Paper III.

### 3.2. Thermal effects

When compiling the boiler heat balance, it is important to determine the heat liberated in the furnace. When firing oil shale, its high content of minerals and its carbonate characteristics strongly influence the heat liberated in combustion. The amount of heat released during oil shale combustion per kg of fuel is significantly affected by the endothermic and exothermic processes occurring in its mineral matter [3]. These processes are calcite and dolomite decomposition, marcasite \(FeS_2\) oxidation, \(CaO\) sulfating and the formation of new minerals. The direction of chemical reactions is shown in Paper III (reactions 1 to 4).

The amount of heat released by thermal effects depends on the oil shale composition and the extent of the reactions. The extent of the reactions (completeness) depends on the combustion conditions, thus the combustion technology (combustion in CFB, PF boiler or in calorimetric bomb).

The thermal effects occurring in a CFB furnace are not equivalent to the effects occurring in a calorimetric bomb. The main difference is assumed to be due to the different carbonate decomposition rates and the sulfation reactions. The thermal effects due to the formation of new minerals are also important.

Because the extents of the reactions 1 to 4 (in Paper III) are different during combustion in a calorimetric bomb and in a boiler, the commonly used heating value of oil shale is known as the conditional LHV. The conditional LHV is the heat released during its combustion under such circumstances when carbonates are decomposed completely (reaction 1 in Paper III) and when neither sulfating nor the formation of new minerals from \(CaO\) occurs (reactions 3 and 4 in Paper III). The amount of heat liberated in a calorimetric bomb and the algebraic sum
of the heats of formation described above are the basis for defining the conditional LHV of oil shale.
The amount of heat released in reactions per kg of oil shale during combustion in furnace is calculated as follows [3):

1. The thermal effect due to the formation of calcium sulfate depends on the sulfur content in the oil shale and the ash sulfation rate, kJ/kg:

\[
\Delta Q^r_{S-T,K} = 0.156 \cdot \zeta_{S-T} \cdot \left( S'_o + S'_p \right) \cdot 1000, \tag{3-4}
\]

where

\[
\zeta_{S-T} = k_{SO_2} = 1 - \frac{S'_l}{(S'_o + S'_p)}, \tag{3-5}
\]

where

\[
S'_l \quad \text{content of sulfur in fuel proceeded into combustion gas, \%};
\]

\[
S'_o \quad \text{content of organic sulfur in fuel as received, \%};
\]

\[
S'_p \quad \text{content of pyritic sulfur in fuel as received, \%}.
\]

2. The thermal effect due to the formation of new minerals depends on the content of free CaO in oil shale, kJ/kg:

\[
\Delta Q^r_u = \left[ 1.248 \cdot \frac{CaO^r_m}{100} \cdot n_1 + 1.4087 \cdot \frac{CaO^r_m}{100} \cdot n_2 \right] \cdot 1000, \tag{3-6}
\]

where

amount of CaO\(_m^r\) which is bound with minerals (fuel as received basis) is calculated as, \%:

\[
CaO^r_m = CaO^r_i - CaO^r_v - CaO^r_{k,t} - CaO^r_{S-T}, \tag{3-7}
\]

where

\[
CaO^r_i \quad \text{total CaO content in fuel, \%};
\]

\[
CaO^r_v \quad \text{content of free CaO in ash (calculated for fuel as received), \%};
\]

\[
CaO^r_{k,t} \quad \text{content of CaO in ash (calculated for fuel as received) bound with carbonate minerals} = ((CO_2)^r_{k,t}) \cdot 56.08/44.01, \%;\]
CaO_{S\rightarrow T}^c content of CaO in ash (calculated for fuel as received) bound with calcium sulfate = \( k_{SO2} \left( 1 - \beta_{p,a} \right) S_p^r + S_o^r \) 56.08/32.06, where \( \beta_{p,a} \) – sulphide sulfur conversion factor = \( S^r_{p,A} / S^r_p \).

Content of CaO\(_m^r\) bound with SiO\(_2\) and Al\(_2\)O\(_3\)-ga \( (n_1) \) and Fe\(_2\)O\(_3\)-ga \( (n_2) \) is calculated as SiO\(_2\), Al\(_2\)O\(_3\) and Fe\(_2\)O\(_3\) proportions in ash, %:

\[
n_1 = \left( \frac{\text{SiO}_2 + \text{Al}_2\text{O}_3}{\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3} \right),
\]

\[
n_2 = \left( \frac{\text{Fe}_2\text{O}_3}{\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3} \right),
\]

3. The thermal effect due to the incomplete decomposition of carbonate minerals depends on the content of carbonates in oil shale and ECD, kJ/kg:

\[
\Delta Q_k^r = 40 \cdot (1 - k_{CO2}) \cdot (CO_2)_k^r,
\]

where

\( k_{CO2} \) extent of carbonate decomposition for total ash;

\( (CO_2)_k^r \) content of mineral CO\(_2\) in boiler total ash (calculated for fuel as received), %.

The corrected lower heating value (LHV\(_{COR}\)), or the actual amount of heat released during combustion per 1 kg of oil shale in boiler, could be determined as the algebraic sum of the thermal effects and is calculated according to Eq. 5 in Paper IV.
4. RESULTS AND DISCUSSION

The tests performed enable the analysis of the impact of the oil shale LHV on the CFB boiler performance. Included in the analysis are the extent of thermal effects in the furnace, the boiler thermal efficiency, heat losses, ash balance and emissions. As there is a strong correlation between oil shale composition and LHV, it is possible to present the test results in terms of the oil shale LHV.

4.1. Technical indicators

*Thermal effects in furnace (Paper IV)*

The thermal effects that occur in a CFB boiler furnace and depend on the oil shale LHV are presented in Fig. 3. The thermal effects are strongly correlated to the oil shale LHV. The extent of the reactions and the amount of heat depend on the composition of oil shale. The combustion conditions, especially at the combustion temperature in the furnace during the firing tests, were at the same level (approximately 850 °C).

As seen in Fig. 3, the primary influence of the oil shale LHV in furnace reactions is in calcium sulfate formation and the incomplete decomposition of carbonate minerals. Calcium sulfate formation tends to increase with higher LHV of the oil shale. As the sulfur in the oil shale is in the form of organics and sulfides and bound in organics and the sandy clay part of the oil shale, its total content in the fuel increases as the LHV is increased. Because the sulfur is almost completely captured during the combustion process in a CFB boiler furnace, as proven by the gas analyses (SO\(_2\) = 5-10 ppm), an increasing thermal effect occurs due to calcium sulfation.

Thermal effects due to the incomplete decomposition of carbonates and the formation of new minerals have a tendency to decrease as the oil shale LHV increases. This tendency is due to the reduction of the total amount of carbonates in the oil shale in the case of higher oil shale quality. The thermal effect due to the formation of new minerals (on the basis of CaO) is low because of the relatively low combustion temperature in the furnace. The thermal effect due to the formation of new minerals increases as the temperature level exceeds 1200 °C and is more prevalent when firing oil shale in PF boilers. Furthermore, in the PF case, the decomposition of carbonates also contributes to the full rate, i.e., more free-CaO is available for the formation of new minerals. Thus, at higher temperatures (PF case) the CaO sulfation process slows down because at lower temperatures free CaO is more active for sulfation, and formation there is no free lime available for the formation of new minerals [3, 50].

Fig. 4 shows the sum of the thermal effects (cumulative thermal effects) of different combustion technologies (for CFB, PF and calorimetric bomb) expressed as percentages relative to the conditional LHV. The cumulative thermal effects in the case of burning conventional oil shale in a CFB furnace reached up to ~6 %, and up to 4 % when upgraded oil shale was fired. Therefore,
ignoring these thermal effects could result in an underestimation of the actual amount of heat liberated in a furnace and thus an overestimation of the fuel mass flow and other related parameters, such as CO₂ emission, thermal efficiency, and the amount of ash.

Comparing the CFB and PF combustion technologies, the thermal effects are more substantial for CFB, primarily due to the greater thermal effect from incomplete decomposition of carbonate minerals (as is apparent from Fig. 4). Here, for the PF case, thermal effects were calculated by taking into account \( k_{CO2} \approx 0.97 \), desulfurization efficiency \(~0.75\), and free CaO content in ash \(~30\%\), in accordance with [3].

Fig. 2 shows the thermal effects corresponding to the reactions in Eq. 1 - Eq. 4 occurring during oil shale combustion in a calorimetric bomb as a function of the conditional LHV. For a calorimetric bomb, the thermal effect due to incomplete oxidation of marcasite is also plotted. In contrast to CFB combustion, marcasite burns out almost completely and therefore it is not shown in Fig. 3.

**Thermal efficiency**

The results for the thermal efficiency of the CFB boiler versus the oil shale corrected LHV are presented in Fig. 2 in Paper III. The oil shale quality had a weak influence on the boiler thermal efficiency. The thermal efficiency was \(~89\%\) for conventional oil shale \((8.71 \text{ MJ/kg})\) and \(~90\%\) for upgraded oil shale \((10.68 \text{ MJ/kg})\), i.e., an increase of 1 % was observed when firing oil shale of a higher quality. The increase in boiler thermal efficiency is mainly caused by a reduction in the physical heat of the slag and flue gas.

The greatest heat loss in the boiler heat balance was the losses due to flue gas, which was during the tests with upgraded oil shale \(~8\%\) and with conventional oil shale \(~8.5\%\). Thereafter losses due to enthalpy and unburned combustibles in slag and flue dust were \(~1.8\%\) when conventional and \(~1.3\%\) when upgraded oil shale was fired. Losses due to radiation and convection formed \(~0.6\%\) and loss due to unburned CO \(~0.01\%\) in case all firing tests. Thus, the increase in boiler thermal efficiency when firing oil shale with higher quality was primarily due to the reduction of ash mass flows (enthalpy of ash) and lower flue gas temperature.

There is a weak dependence of the thermal efficiency on the oil shale LHV for CFB combustion technology, which enables the burning of fuels with different qualities, allowing the same amount of inert material to be burned in the furnace while guaranteeing a suitable combustion temperature.

**The influence of ECD on boiler thermal efficiency**

The flue gas losses are the greatest heat losses of the boiler which depends on the flue gas temperature and the amount of gas leaving boiler. In conjunction with increasing the oil shale LHV, the amount of combustion gas formed per kg of fuel (from increased organic content of fuel) increases, while the specific fuel
consumption rate per unit of heat produced (kg/MWh th) decreases proportionally.

The heat losses due to flue gas can be influenced by the amount of gases, which depends on the amount of mineral CO₂ in the combustion gas. The content of mineral CO₂ in the combustion gas depends on ECD. To demonstrate the influence of $k_{CO₂}$ on the boiler thermal efficiency, a calculation was performed, assuming a flue gas temperature of 170 °C for all tests. The results for the dependence of the boiler thermal efficiency on $k_{CO₂}$ are presented in Figure 4-1. The theoretical line for losses due to flue gas per kg of mass at a flue gas temperature of 170 °C is also plotted. The calculation demonstrates that the specific losses due to flue gas increase to 2.5 % when $k_{CO₂}$ varies from zero to one while proportionally increasing the fuel consumption rate. The absolute losses due to flue gas increase less than 5 % when $k_{CO₂}$ increases from 0 to 1. Considering that 8-9 % of the losses due to flue gas are from the heat liberated in the boiler, the influence of $k_{CO₂}$ on the boiler thermal efficiency is fractional.

![Figure 4-1. Boiler thermal efficiency and flue gas losses versus $k_{CO₂}$](image)

*Figure 4-1. Boiler thermal efficiency and flue gas losses versus $k_{CO₂}$*

*Fuel consumption and ash mass flow rates (Paper I)*

The results for fuel consumption and ash mass flow rates versus oil shale LHV are presented in Fig. 4 (Paper I). As expected, firing oil shale of higher quality resulted in a reduction of fuel consumption and the ash mass flow rates. Due to the higher LHV, the fuel consumption decreased by 22 % and the ash mass flow decreased by up to 25 % when firing upgraded oil shale with LHV of 10.5 MJ/kg instead of conventional oil shale with LHV of 8.4 MJ/kg. The reduction of the ash mass flow rate was achieved due to the lower ash content of the upgraded oil shale.
Ash balance (Paper II)

The ash removal system is one of the most important subsystems of a CFB boiler. The ash is removed from the boiler by several separation ports, as shown in Fig. 1.

The oil shale quality (higher quality corresponds to a reduced amount of carbonate minerals) and granular composition can cause redistribution of the ash mass flows in the boiler separation ports. No previous study has examined the components of ash balance for that CFB boiler.

The following section describes the investigation of the ash balance (mass flow rates from the separation ports) of a CFB boiler when firing oil shales of different qualities. The investigation is based on tests in which conventional oil shale with a LHV of 8.5 MJ/kg and upgraded oil shale with a LHV of 11.1 MJ/kg were fired. The boiler operated continuously for three days and five days for the conventional and upgraded oil shales, respectively. A short characterization of the fuels used in these tests is provided in Table 1.

For the ash balance, the ash mass flow rates for each separation port were calculated. The calculation was performed based on the frequencies of operation of the ash senders. The detailed calculation methodology is described in Paper II.

The results for the CFB boiler ash balance when firing oil shales of different qualities are shown in Fig. 2. As expected, the firing of oil shales of different qualities resulted in changes in the distribution of the ash mass flows. The main difference is in the bottom ash mass flows.

The fractions of bottom and fly ash were 37% and 63%, respectively, when burning conventional (8.5 MJ/kg) oil shale, but they were 30% and 70%, respectively, when burning upgraded (11.1 MJ/kg) oil shale. This change denotes a reduced bottom ash ratio when firing upgraded fuel.

The main reasons for the reduced bottom ash mass flow when firing upgraded oil shale may be in the reduction of the content of carbonate minerals in the fuel and the finer granular composition of the upgraded fuel used in the tests, with a median particle size (after secondary crusher) of $R_{0.5} = 0.41 \text{ mm}$ instead of the median size of $R_{0.5} = 0.57 \text{ mm}$ when firing conventional oil shale.

When firing oil shale with a LHV of 8.5 MJ/kg (i.e., with the higher content of carbonate minerals), carbonate minerals (i.e., relatively large limestone particles) formed during the combustion process in the furnace subside through the fluidized bed due to their substantial density and can be removed from the boiler along with the bottom ash, thus resulting in a higher fraction of bottom ash mass flow.

Due to the finer fuel particles, limestone decomposes to a greater extent, and the organic part burns more quickly, resulting in a reduction of the bottom ash mass flow rate. The coarser granular composition of the fuel is reflected in the coarser particles of bottom ash when firing conventional oil shale. As shown in Table 3, the bottom ash median size $R_{0.5}$ when firing conventional fuel is 1.13 mm, and when firing the upgraded fuel it is 0.43 mm. The coarser bottom
ash when firing conventional oil shale is caused by the coarser fuel (coarser limestone particles in the fuel) fired.

Note that the difference in the total ash mass flow is not caused by fuel granularity but by chemical composition. Due to the different chemical composition, the absolute values of ash mass flow were different.

*Ash granular composition*

The granular compositions of oil shale ash samples when firing conventional and upgraded oil shale are provided in Figures 4-2 and 4-3. There can be seen that the main differences in ash granular composition can be found in bottom ash samples. In test with conventional oil shale the median size of bottom ash is $R[0.5] = 0.65$ mm and for upgraded oil shale $R[0.5] = 0.35$ mm. The reason of different granular composition of fuels can be found as the firing test with upgraded oil shale was carried out somewhat finer fuel than conventional oil shale (Figure 2-1).

As regards CFB boiler fly ash samples, its granular composition is similar when firing conventional or upgraded oil shale. The CFB boiler is provided with three separators of solids which locate in rear wall of furnace. The amount and velocity of combustion gas is the same firing upgraded or conventional oil shale, the collection efficiency of separator of solids is also the same. The fly ash granular compositions are not depending on fuel quality and granular composition. Coarser and heavier ash particles are captured by the separator of solids and are directed to the circulating medium for burnout.

![Figure 4-2. Granular composition of the CFB boiler ashes firing conventional oil shale](image-url)
The firing of Estonian oil shale in power plants is associated with several environmental concerns, such as high carbon dioxide emission and ash landfilling. Each year, from CFB boilers approximately 3 million tons of CO$_2$ is discharged into the atmosphere, and 1.5 million tons of oil shale ash is stored in ashfields. In this chapter, the impact of the oil shale calorific value on these environmental concerns is analyzed.

**Carbon dioxide emission (Paper I)**

The total CO$_2$ emissions (per one kg of fuel as received) when firing oil shale depend on two factors: the burning of organic carbon and the decomposition of carbonates (Eq. 1). The emission of CO$_2$ from the CFB boiler per produced unit of energy is calculated as described in Paper I.

The specific CO$_2$ emissions depend on the mineral CO$_2$ content in the oil shale, in addition to the combustion efficiency and the extent of carbonate decomposition. The ECD depends on the behavior of the oil shale mineral matter in the furnace. The firing tests enable the study of the behavior of the oil shale mineral matter, particularly the extent of carbonate decomposition in the furnace. The ECD may depend on the furnace temperature, the fuel particle size.
and the partial pressure of CO\textsubscript{2} in the surrounding medium, as well as the operation load of the boiler [3, 42, 45, 50].

The ECD for CFB boiler total ash was calculated based on the ash chemical composition (Tables 4-2 and 4-3) as a weighted average taking into account the ash mass flow rates (kg/s) from the separation ports. The ECD calculation methodology is presented in [6].

The results for specific CO\textsubscript{2} emissions from the CFB boiler calculated per electric power (bruto) are presented in Fig. 2. According to the results, the total CO\textsubscript{2} specific emissions were 1.01 t/MWh\textsubscript{e} and 0.94 t/MWh\textsubscript{e} for the firing of conventional oil shale and upgraded oil shale, respectively; i.e., a reduction of CO\textsubscript{2} emissions by 7 % was observed when firing upgraded oil shale. The decrease in CO\textsubscript{2} emissions was mainly achieved due to the reduction of CO\textsubscript{2} emissions from the decomposition of carbonates because oil shale of higher quality contains a smaller quantity of carbonates.

Fig. 2 shows that the CO\textsubscript{2} emissions from the decomposition of carbonates have a strong dependence on the oil shale LHV and, as described above, it depends on the mineral CO\textsubscript{2} content in the oil shale and on the extent of carbonate decomposition – $k_{CO2}$. The $k_{CO2}$ value for the CFB boiler total ash in the firing tests remained between 0.58–0.82. Here, the $k_{CO2}$ values were higher (0.75–0.82) when oil shale of higher LHV was fired. Because the boiler operated at the same heat load and furnace temperatures during the tests, the reason for the higher $k_{CO2}$ value when firing oil shale of higher quality can be found in the granular composition of the fuel. The upgraded oil shale was finer than the conventional oil shale. The median sizes of the fuels R [0.5] were 0.39-0.6 mm and 0.48-0.65 mm for the upgraded oil shale and conventional oil shale, respectively.

For estimating CO\textsubscript{2} emissions from the CFB boiler assuming a similar granular composition of oil shale for all tests, calculations were performed assuming $k_{CO2} = 0.7$ (the average value for tests when firing conventional oil shale) for all tests. The dashed line in Fig. 2 indicates the results of that calculation. An additional reduction of CO\textsubscript{2} emissions from the decomposition of carbonates can be achieved, resulting in a total CO\textsubscript{2} emissions reduction of 7.8 % instead of 7.0 %. The granular composition of the oil shale has a direct influence on the carbon dioxide emission.

A small reduction of the CO\textsubscript{2} emissions was also achieved from the burning of carbon as the boiler efficiency increased by up to 1 % when firing oil shale of higher quality (8.4 → 10.5 MJ/kg).

The ratio of carbonate CO\textsubscript{2} to total CO\textsubscript{2} emissions versus oil shale LHV is presented in Fig. 3. The CO\textsubscript{2} emissions from the decomposition of carbonate minerals accounted for 14.4 % (conventional fuel) and 11.2 % (upgraded fuel) of the total CO\textsubscript{2} emissions.
Other emissions

The flue gas composition measured with an FTIR gas analyzer (SO₂, CO, NOₓ, N₂O) are presented in Table 4-1. During all of the tests, the CFB boiler met emissions requirements set by the Large Combustion Plants (the LCP Directive) directive 2001/80/EC.

Here, depending on the fuel quality, the concentration of nitrogen oxides in the flue gas had a slight tendency to increase with a higher oil shale LHV. The concentration of NOₓ in the flue gas is proportional to the nitrogen content of the fuel [3]. Still, the NOₓ emission for upgraded oil shale stayed below the level of 200 mg/Nm³.

As the gas analyses demonstrated, carbon monoxide emissions varied over the range of 18–87 mg/Nm³ during the tests and had no significant correlation with the fuel quality. The CO emissions depended on the combustion efficiency rather than the fuel LHV.

The SO₂ and N₂O concentrations in the flue gas during all of the tests stayed below 15 mg/Nm³, i.e., below the measurement level of the gas analyzer. Due to the large amount of free lime available in oil shale (usually a molar ratio of Ca/S = 8-10 [5]) and the low combustion temperature, the SO₂ formed during combustion is completely bound in the ash; therefore, practically no SO₂ is emitted. The SO₂ in the combustion gas from the combustion of Estonian oil shale originates from organic and pyritic sulfur.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Unit</th>
<th>Upgraded oil shale</th>
<th>Conventional oil shale</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>min</td>
<td>max</td>
</tr>
<tr>
<td>LHV</td>
<td>MJ/kg</td>
<td>9.25</td>
<td>11.54</td>
</tr>
<tr>
<td>H₂O</td>
<td>% vol wet O₂ 6%</td>
<td>8.48</td>
<td>10.07</td>
</tr>
<tr>
<td>CO₂</td>
<td>% vol *</td>
<td>11.61</td>
<td>12.79</td>
</tr>
<tr>
<td>CO</td>
<td>mg/Nm³ *</td>
<td>18.35</td>
<td>42.72</td>
</tr>
<tr>
<td>NO₂</td>
<td>mg/Nm³ *</td>
<td>168.25</td>
<td>196.21</td>
</tr>
<tr>
<td>O₂</td>
<td>% vol dry</td>
<td>3.31</td>
<td>4.84</td>
</tr>
</tbody>
</table>

*- dry O₂ 6%

Ash chemical composition

Chemical composition of the ash samples when firing upgraded (9.3-11.5 MJ/kg) and conventional (8.2-8.8 MJ/kg) oil shale is provided in Tables 4-2 and 4-3. Firing oil shale with different quality resulted in formation of different composition of boiler ashes. Due to a lower content of carbonates in upgraded oil shale the content of the components related to the carbonates in total ash (CO₂-6.84 %, CaO + MgO = 38.44 %) is lower when firing conventional oil shale (CO₂-11.18 %, CaO + MgO = 44.21 %).

The sulphur content in CFB boiler total ash is 8.46 % when upgraded oil shale and 6.86 % when conventional oil shale was fired. The higher sulfur (organic
and pyritic) content in total ash when firing upgraded oil shale is related to its higher content in upgraded oil shale. The sulfur in combustion process is captured totally by ash.

The components related to the oil shale sandy-clay part of oil shale (SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$), theirs content in total ash was higher when upgraded oil shale was fired, as follows: SiO$_2$-29.41 %, Al$_2$O$_3$-8.16 % and Fe$_2$O$_3$-4.79 %. When firing conventional oil shale the numbers were: 24.29 %, 6.21 % and 4.33 %, correspondingly. The reason can be found in the higher content of sandy-clay part of upgraded oil shale which consists of less carbonates.

As regards chemical composition of the ash samples for separation ports similar conclusions can be drawn for both fuels utilization. The components in ash which are originated from carbonates (CaO, MgO and CO$_2$) their content in ashes is higher coarser ash samples (especially in bottom ash) than in finer fly ash samples. The chlorine content increases in ash samples towards to the stack, resulting in the lowest content in bottom ashes and the highest content in ESP IV ashes. The chlorine has tendency to subside into ash with finer granular composition [3].
Table 4-2. Chemical composition of the CFB boiler ashes when firing upgraded oil shale

<table>
<thead>
<tr>
<th>Separation ports</th>
<th>CO₂</th>
<th>SO₃</th>
<th>SiO₂</th>
<th>Fe₂O₃</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>BT</td>
<td>12.80</td>
<td>16.19</td>
<td>7.80</td>
<td>3.56</td>
<td>2.65</td>
<td>48.05</td>
<td>8.01</td>
<td>0.66</td>
<td>0.09</td>
<td>0.19</td>
</tr>
<tr>
<td>INTREX</td>
<td>1.27</td>
<td>23.01</td>
<td>12.38</td>
<td>4.07</td>
<td>4.17</td>
<td>44.56</td>
<td>9.21</td>
<td>1.00</td>
<td>0.10</td>
<td>0.24</td>
</tr>
<tr>
<td>SH-RH</td>
<td>5.24</td>
<td>7.67</td>
<td>33.49</td>
<td>5.06</td>
<td>8.61</td>
<td>29.71</td>
<td>5.94</td>
<td>3.76</td>
<td>0.16</td>
<td>0.36</td>
</tr>
<tr>
<td>ECO</td>
<td>4.52</td>
<td>7.05</td>
<td>34.11</td>
<td>5.14</td>
<td>9.72</td>
<td>29.25</td>
<td>5.82</td>
<td>3.86</td>
<td>0.15</td>
<td>0.39</td>
</tr>
<tr>
<td>APH</td>
<td>3.99</td>
<td>8.91</td>
<td>31.00</td>
<td>5.11</td>
<td>8.41</td>
<td>32.73</td>
<td>6.15</td>
<td>3.21</td>
<td>0.15</td>
<td>0.35</td>
</tr>
<tr>
<td>ESP I</td>
<td>4.25</td>
<td>4.61</td>
<td>39.69</td>
<td>5.35</td>
<td>10.86</td>
<td>25.06</td>
<td>4.83</td>
<td>4.75</td>
<td>0.17</td>
<td>0.44</td>
</tr>
<tr>
<td>ESP II</td>
<td>3.83</td>
<td>4.65</td>
<td>39.60</td>
<td>5.42</td>
<td>11.08</td>
<td>24.62</td>
<td>5.32</td>
<td>4.83</td>
<td>0.18</td>
<td>0.46</td>
</tr>
<tr>
<td>ESP III</td>
<td>3.35</td>
<td>4.37</td>
<td>40.14</td>
<td>5.69</td>
<td>12.43</td>
<td>23.38</td>
<td>4.94</td>
<td>4.94</td>
<td>0.18</td>
<td>0.57</td>
</tr>
<tr>
<td>ESP IV</td>
<td>7.08</td>
<td>5.26</td>
<td>34.40</td>
<td>5.60</td>
<td>11.52</td>
<td>26.03</td>
<td>4.71</td>
<td>4.30</td>
<td>0.19</td>
<td>0.89</td>
</tr>
<tr>
<td>CFB boiler total ash*</td>
<td>6.84</td>
<td>8.46</td>
<td>29.41</td>
<td>4.79</td>
<td>8.16</td>
<td>32.48</td>
<td>5.96</td>
<td>3.40</td>
<td>0.15</td>
<td>0.36</td>
</tr>
</tbody>
</table>

Table 4-3. Chemical composition of the CFB boiler ashes when firing conventional oil shale

<table>
<thead>
<tr>
<th>Separation ports</th>
<th>CO₂</th>
<th>SO₃</th>
<th>SiO₂</th>
<th>Fe₂O₃</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>BT</td>
<td>20.88</td>
<td>9.89</td>
<td>6.77</td>
<td>2.86</td>
<td>1.98</td>
<td>53.88</td>
<td>2.98</td>
<td>0.51</td>
<td>0.08</td>
<td>0.17</td>
</tr>
<tr>
<td>INTREX</td>
<td>1.42</td>
<td>20.56</td>
<td>11.29</td>
<td>3.96</td>
<td>4.26</td>
<td>52.71</td>
<td>4.76</td>
<td>0.70</td>
<td>0.09</td>
<td>0.26</td>
</tr>
<tr>
<td>SH-RH</td>
<td>6.72</td>
<td>6.66</td>
<td>30.87</td>
<td>5.04</td>
<td>7.12</td>
<td>36.00</td>
<td>4.05</td>
<td>3.05</td>
<td>0.16</td>
<td>0.33</td>
</tr>
<tr>
<td>ECO</td>
<td>5.86</td>
<td>5.55</td>
<td>33.16</td>
<td>5.18</td>
<td>8.17</td>
<td>34.37</td>
<td>3.69</td>
<td>3.47</td>
<td>0.16</td>
<td>0.41</td>
</tr>
<tr>
<td>APH</td>
<td>5.33</td>
<td>8.22</td>
<td>28.53</td>
<td>5.17</td>
<td>6.71</td>
<td>37.92</td>
<td>4.82</td>
<td>2.79</td>
<td>0.15</td>
<td>0.35</td>
</tr>
<tr>
<td>ESP I</td>
<td>5.27</td>
<td>4.77</td>
<td>35.39</td>
<td>5.22</td>
<td>8.94</td>
<td>32.52</td>
<td>3.66</td>
<td>3.63</td>
<td>0.17</td>
<td>0.43</td>
</tr>
<tr>
<td>ESP II</td>
<td>4.87</td>
<td>5.02</td>
<td>35.11</td>
<td>5.32</td>
<td>9.24</td>
<td>32.33</td>
<td>3.55</td>
<td>3.88</td>
<td>0.20</td>
<td>0.46</td>
</tr>
<tr>
<td>ESP III</td>
<td>4.22</td>
<td>5.15</td>
<td>35.47</td>
<td>5.50</td>
<td>10.36</td>
<td>30.62</td>
<td>4.00</td>
<td>3.93</td>
<td>0.18</td>
<td>0.59</td>
</tr>
<tr>
<td>ESP IV</td>
<td>5.72</td>
<td>6.08</td>
<td>31.67</td>
<td>5.14</td>
<td>11.41</td>
<td>31.42</td>
<td>3.95</td>
<td>3.48</td>
<td>0.22</td>
<td>0.91</td>
</tr>
<tr>
<td>CFB boiler total ash*</td>
<td>11.18</td>
<td>6.86</td>
<td>24.29</td>
<td>4.33</td>
<td>6.21</td>
<td>40.78</td>
<td>3.43</td>
<td>2.44</td>
<td>0.14</td>
<td>0.32</td>
</tr>
</tbody>
</table>

*- calculated based on ash balance as weighted average
4.3. Economic aspects

The firing tests with upgraded oil shale indicated a significant reduction of fuel consumption, ash mass flow rate and air emissions from the CFB boiler. The results of the firing tests enable the analysis of the potential extent of cost reduction in Narva PP. The costs analyzed for introducing upgraded oil shale are as follows: fuel costs, transportation costs, operational costs and costs related to the environmental impact.

Paper I presents the calculations for the potential savings regarding the pollution charges and the exploitation costs for the year 2010, when 430 MW (CFB technology) is installed in Narva PP, and for 2015, when 300 MW or 300+300 MW new CFB units will be commissioned, resulting in a total capacity of 730 in 2015 or 1030 MW as an option.

Here, the analyzed cost calculations were performed for the potential savings regarding the current pollution charges for the year 2012, when a 430 MW CFB units are operating in Narva PP, and for 2015, when a new 300 MW CFB unit will be commissioned (construction work in Narva PP for new 300 MW has started and is planned for 2015), resulting in a total capacity of 730 MW in 2015. The annual electricity production assumed is 2.92 TWh in 2012 and 4.96 TWh in 2015.

Consequently, the actual electrical output of Balti PP is approximately 185 MW due to a decrease of 30 MW for the Narva city district heating. In the current analysis, Balti PP is assumed to be operating in condensing mode only (215 MW).

Fuel costs

The fuel cost is an important component of electricity production expenditures. In Estonia, according to the Electricity Market Act, the price of oil shale sold to large power plants must be regulated. Currently, the Competition Authority has set a price cap for oil shale 10.55 EUR/t (8.4 MJ/kg) supplied to the Narva PP.

The current analysis assumes that the price of oil shale is proportional to the heating value. The enrichment expenses of upgraded oil shale are assumed to be covered by the higher cost of upgraded oil shale. Therefore, assuming the price of energy in fuel (EUR/MJ) to be the same for conventional and upgraded oil shale, the prices of the conventional and upgraded fuels are 10.55 EUR/t and 13.24 EUR/t, respectively.

Nevertheless, due to the higher combustion efficiency, EUR 0.55 million in 2012 and EUR 0.94 million in 2015 can be saved by firing upgraded oil shale.

Transportation costs

The use of upgraded fuel enables the reduction of oil shale transportation costs from mines to power plants. Considering the location of power stations and mines, the fuel can be transported to the Balti PP (for the only CFB unit in operation) from the Aidu open-pit and the Estonian underground mine. Both
mines are located 67 km from the Balti PP. The fuel for the Eesti power plant (for CFB and PF units) is supplied from the Estonian and Viru underground mines and the Narva open-pit mine. The distance from the mines is different, so the average value of 32 km is used for the calculation.

According to the current (in 2012) railway tariffs, the total reduction of transportation costs in Narva PP is approximately EUR 0.76 million a year. In 2015 (total installed capacity of 730 MW_{e}), the annual savings could approach EUR 1.1 million (assuming 2012 tariff levels). Accounting for the plans to open new mines during the next few years, which are located farther than the current mines, and the increase of railway tariffs due to inflation, the annual savings in 2015 would be even greater.

**Operational costs**

As the introduction of upgraded oil shale results in smaller volumes of fuel, it enables the reduction of the variable component of operational costs by 22 % for the fuel and by 25 % for the ash handling in power plants. Considering the operational costs of fuel and ash handling, as presented in Paper I, and assuming an annual increase of 6 % for the operational costs the annual savings can be EUR 0.14 million in 2012 and EUR 0.25 million in 2015. In the economic calculation for the new power units, the production costs were assumed to be similar to those of the Narva PP. Nevertheless, the savings value of the Narva PP is rather modest in absolute terms.

**Environmental impact cost**

The reduction of air emissions (carbon dioxide and particulates) and ash disposal is achieved when introducing upgraded oil shale. The following describes the analysis and assessment of the economic effect of these reductions.

According to the Environmental Charges Act, the rates of pollution charges (bottom ash landfilling and particulates to the atmosphere) will be increased gradually in the years up to 2015. The rates relevant to the present study are presented in Table 4-4.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>In 2012</th>
<th>In 2015</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash landfilling*, EUR/t</td>
<td>2.07</td>
<td>2.98</td>
</tr>
<tr>
<td>Particulates*, EUR/t</td>
<td>86.47</td>
<td>146.17</td>
</tr>
</tbody>
</table>

*- must be multiplied by 1.2

The calculations indicate that, at the level of the CFB-based capacities installed in 2012, replacing conventional oil shale (8.4 MJ/kg) with the upgraded one (10.5 MJ/kg) would reduce the pollution charges (for the emission of particulates and for ash landfilling) paid by the Narva PP by EUR 1.03 million. In 2015, assuming an installed capacity of 730 MW_{e}, the annual savings from reduced pollution charges would be EUR 2.51 million.
CO₂ emissions

The emission of CO₂ has an increasing impact on the environment and on the economic results of power plants. In the EU, full auctioning of allowances has been determined to be the rule for the power sector beginning in 2013, and no free allocation shall be made for any electricity production by EU ETS new entrants [8]. These rules make the CO₂ emissions level a factor of increasing importance for electricity producers.

In the current analysis, basic cost calculations were performed with the assumption of an emission allowance price of 10 EUR per ton of CO₂. According to the calculation, the use of upgraded oil shale would save EUR 2.04 million (installed capacity of 430 MWₑ) or EUR 3.47 million (730 MWₑ).

Hence, the cost of the CO₂ allowance is the main contributor to the economic savings in the current analysis. Therefore, a sensitivity analysis was performed to determine the impact of a higher price level for the CO₂ emissions allowance. The results for 20 EUR/t indicate that the annual savings could reach up to EUR 4.09 million (430 MWₑ) or even to EUR 6.94 million (730 MWₑ installed capacity).

The potential savings of the production costs in the Narva PP are presented by their cost elements in Table 4-5 (for upgraded oil shale in CFB power units).

Table 4-5. Potential annual savings in Narva PP (in million EUR)

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Electricity production, TWh</td>
<td>2.92</td>
<td>4.96</td>
</tr>
<tr>
<td>Fuel cost</td>
<td>0.55</td>
<td>0.94</td>
</tr>
<tr>
<td>Fuel transportation cost</td>
<td>0.76</td>
<td>1.10</td>
</tr>
<tr>
<td>Operational cost</td>
<td>0.14</td>
<td>0.25</td>
</tr>
<tr>
<td>Ash landfilling and particulates</td>
<td>1.03</td>
<td>2.51</td>
</tr>
<tr>
<td>CO₂ emission allowances</td>
<td>2.04</td>
<td>3.47 (6.94*)</td>
</tr>
<tr>
<td>TOTAL</td>
<td>4.52</td>
<td>8.27 (11.74*)</td>
</tr>
</tbody>
</table>

*- when cost of CO₂ allowance is 20 EUR/t

In conclusion, accounting for the current pollution charges, transportation costs, operational costs of fuel and ash handling in Narva PP and the cost of the CO₂ allowance, the potential savings in 2012 would be EUR 4.5 million. For an additional power unit of 300 MWₑ, the savings could be up to EUR 8.3 million in 2015. Here, the major effect of cost reduction is due to the lower emissions levels of CO₂. The sensitivity analysis indicated that raising the price on CO₂ emissions allowances to EUR 20 in 2015 would increase the relevant specific savings to EUR 11.7 million.
CONCLUSIONS

Oil shale firing tests with LHV levels from 8.2-11.5 MJ/kg on a CFB boiler were performed for the first time. The number of firing tests enables an estimate of the boiler technical and environmental indicators and a study of the processes occurring in oil shale mineral matter.

The introduction of upgraded oil shale (LHV 10.5 MJ/kg) would enable a significant reduction of the environmental impact of power production. Impact calculations were performed for 430 MW<sub>e</sub> installed capacity (the current situation) and assuming that additional new capacity of 300 MW<sub>e</sub> will be commissioned by 2015, resulting in a total capacity of 730 MW<sub>e</sub>. Firing upgraded oil shale instead of conventional oil shale (LHV 8.4 MJ/kg) affects the technical, environmental and economic aspects as follows:

1. In the context of the environmental impact of power production, the reduction of CO<sub>2</sub> emissions by ~7 % and the ash mass flow by 25 % were achieved when firing upgraded oil shale. A reduction of the annual discharge of ash by 0.41 million tons and by 0.69 million tons and a reduction of the annual CO<sub>2</sub> discharge into the atmosphere by 0.2 million tons and 0.35 million tons can be achieved for 430 MW<sub>e</sub> capacity and for 730 MW<sub>e</sub> capacity, respectively.

2. Regarding the impact of upgraded oil shale on boiler technical indicators, the boiler thermal efficiency increased by 1 % due to the reduction of ash and flue gas enthalpies, while the fuel consumption decreased by 22 %. The annual savings of fuel will be 0.73 million tons and 1.24 million tons for installed capacities of 430 MW<sub>e</sub> and 730 MW<sub>e</sub>, respectively.

3. When firing conventional oil shale, the fraction of the bottom ash mass flow in the total ash is 37 % instead of 30 % when firing upgraded oil shale. The reduced bottom ash mass flow when firing upgraded oil shale is due to the reduced content of carbonate minerals in the fuel and the finer granular composition.

4. The extent of carbonate decomposition for the total ash from the CFB boiler in the firing tests remained between 0.58–0.82. Here, the ECD values were higher (0.75–0.82) when oil shale of higher LHV was fired. The reason for the higher ECD value is due to the finer granular composition of the fuel. The median size of the upgraded oil shale was R [0.5] 0.39-0.6 mm instead of R [0.5] 0.48-0.65 mm for the conventional oil shale.

5. Due to the exo- and endothermic processes in the oil shale mineral matter, the cumulative thermal effects when burning conventional and upgraded oil shale reached up to 6 % and 4 % of the LHV, respectively. The main effects were due to the incomplete decomposition of carbonates and ash sulfation.

6. The economic calculations clearly indicate that the introduction of upgraded oil shale in power plants has a positive effect on electricity production costs, especially on environmental-related expenditures. The potential savings for the CFB units will be 4.52 million EUR and 8.27 million EUR for installed capacities of 430 MW<sub>e</sub> and 730 MW<sub>e</sub>, respectively. The cost of the CO<sub>2</sub>
allowance is the main contributor to the economic savings, with savings of 2.04 million EUR and 3.47 million EUR occurring for installed capacities of 430 MW_e and 730 MW_e, respectively, when the cost of CO_2 allowance is 10 EUR/t. The potential annual savings in Narva PP 2015 when the cost of CO_2 allowance is 20 EUR/t could reach up to EUR 11.74 million in the case of 730 MW_e of installed capacity.

The firing tests demonstrated that CFB combustion is the most suitable technology available today for firing high-ash-content and sulfur-rich Estonian oil shale. The CFB technology enables the burning of upgraded oil shale, thereby minimizing the impact of electricity production on the environment while increasing the competitiveness of oil-shale-based electricity production due to the lower production cost in the market, where the CO_2 trade system dominates.

Most of the world’s oil shale resources are not utilized. Oil shale utilization will become more attractive as the price of crude oil continues to increase. Low grade oil shale may be produced in conjunction with the preparation of mined oil shale for the shale oil industry, and this low grade oil shale may be utilized for the direct burning production of electricity, thereby enabling the sustainable use of local resources.

The investigation demonstrated that the methodology used for compiling boiler heat balance can be used in the investigation of oil shale firing, and the results enable the prediction of the combustion parameters of CFB units when interest increases in the use of oil shale for direct burning.
REFERENCES

10. Ots, A. There is no serious alternative for oil shale power engineering in Estonia. Newspaper Äripäev, 27.05.2004.


27. Fainberg, G. H. Research and development in oil shale combustion and processing in Israel. Oil Shale, 1996, 13/2, 87-99.


# LIST OF AUTHOR’S PUBLICATIONS


ABSTRACT

The goal of this thesis is to investigate the quality of Estonian oil shale in terms of the relevant circulating fluidized bed (CFB) boiler technical and environmental indicators. The investigation is based on full-scale firing tests when oil shales with lower heating values (LHV) of 8.2-11.5 MJ/kg were fired.

The utilization of oil shale with higher quality enables the reduction of CO\textsubscript{2} emission and thus the reduction of the cost of CO\textsubscript{2} allowance to the electricity price. In addition, a reduction of the fuel and ash mass flow rates can be achieved leading to the reduction of power production costs in power plants.

For the calculation of boiler thermal efficiency, fuel consumption and ash mass flow rates, CO\textsubscript{2} emissions, the boiler heat balance is composed. The heat balance is composed according to the EU standard EN 12952-15:2003. In the compilation of the boiler heat balance endo- and exothermic processes in oil shale mineral matter, which influences the heat liberated in the furnace, and the ash mass increase during combustion is taken into account.

The firing tests demonstrated that oil shale quality significantly influences the CFB boiler technical and environmental indicators. When firing upgraded oil shale with LHV 10.5 MJ/kg instead of conventional fuel with LHV 8.4 MJ/kg, the specific CO\textsubscript{2} emission per MWh\textsubscript{e} is reduced by 7\% and the ash mass flow rate is reduced by 25\%. Here, oil shale quality had a weak influence on the boiler thermal efficiency, which increased by 1\% due to the reduction of ash and flue gas enthalpies.

Introducing upgraded oil shale enables savings in the electricity production costs (fuel costs, transportation costs, operational costs and costs related to the environmental impact) in power plants. For a CO\textsubscript{2} allowance cost of 10 EUR/t, the potential savings in current CFB power units with 430 MW\textsubscript{e} of capacity will be 4.52 million EUR, and the potential savings will be 8.27 million EUR in 2015 when an additional new 300 MW\textsubscript{e} CFB power unit will be installed.
Käesoleva doktoritöö eesmärk on uurida Eesti põlevkivi kvaliteedi mõju keevkihttehnoloogia töödavat katla tehnilistele parameetritele ja keskkonnaheitmetele. Uuring põhineb Balti elektrijaamas teostatud keevkihtkatla soojustehnilistel katsetustel, mille raames põletati põlevkivi alumise kütteväärtusega vahemikus 8,2 - 11,5 MJ/kg.

Eesti põlevkivi kuulub karbonaatsete kütuste klassi, millele on iseloomulik kõrge tuhasisaldus ning madal kütteväärtus. Eesti põlevkivielektrijaamades kasutatakse põlevkivi kütteväärtuse 8,2 - 8,6 MJ/kg ning tuha sisaldus kuni 50 %. Selle madala kvaliteedilise kütuse põletamisega on seotud mitmed keskkonnaprobleemid, milleks on kõrge CO₂ eriheide karbonaatse CO₂ tõttu ja suur tuha teke.

Põlevkivi kaevandustest aga on võimalik saada madalama karbonaatosa sisaldusega ehk kõrgema kütteväärtusega kaalutatud kütust, mida on võimalik põletada keevkihtblokkides efektiivsemalt tänud suurele hulgale tsirkuleerivale tuhamassile. Kõrgema kütteväärtusega kütuse kasutamisel väheneb lisaks CO₂ eriemitseerimine veel ka kütuse erikulu ja tuha teke. Seega vähenevad elektrijaama tarmitavad kütusevood ja tuhavaljade ladustatavad tuhakogused ning CO₂ eriemitseerimine, mis omakorda kajastub energiaploki tootmiskulude vähenemises.

Kõrgema kütteväärtusega põlevkivi põletamise mõju uurimiseks keevkihtkatla tehnilistele ja keskkonnaheitmetele teostati 17 katset, mille põletati harilikku põlevkivi kütteväärtusega 8,2 - 9,1 MJ/kg ning rikastatud põlevkivi kütteväärtusega 9,3 - 11,6 MJ/kg. Katsete käigus võeti mitmeid tuhast ja kütuseproove keemilise- ja fraktsioonhoite järele analüüsitsemiseks, teostati põlemisgaaside analüüs ning koguti andmeid katla andmehõiveseadmest katla mitmete tööparametrede kohta.


Soojustehnilised katsed näitasid, et põlevkivi kvaliteedel mõjutab oluliselt keevkihtkatla tehnilisi ja keskkonnaheitmeid. Põlevkivi alumise kütteväärtusega 10,5 MJ/kg põletamisel 8,4 MJ/kg asemel väheneb katla CO₂ eriheitse soojusvoimuse kohta ~7 % vórra, kütuse erikulu ~22 % ja tuha teke ~25 % vórra. Seejärel katla soojusefektiivsus tõusis ~1 % vórra vähenedes tuha ja lahkuvagaaside entalpiaid tõttu. Katla tuhabilansi mõõtmised näitasid, et harilik kütuse põletamisel moodustas põhjatuha osa 37 % katla kogutuhast. Rikastatud kütuse põletamisel
vähenes põhjatuha osa 30 %-le kogutuhast. Põhjatuha osakaalu vähenemine rikastatud kütuse põletamisel oli tingitud kütuse madalamast karbonaatide sisaldusest ja mõnevõrra peenemast kütuse fraktsioonkoostisest.

Põlevkivi mineraalosa käitumise uurimise näitas, et soojusefektide ulatused sõltusid oluliselt kütuse koostisest (karbonaatide sisaldusest). Katsed näitasid, et soojusefektide tõttu tõusis küttevääratus harilikku põlevkivi põletamisel kuni 6 % ja rikastatud kütuse põletamisel kuni 4 %. Siinjuures enim mõjutasid kütteväärust karbonaatide mittelagunemise ja tuha sulfatiseerumise protsessidest tulenevad soojusefektid.

Karbonaatide lagunemine jäi katsetel vahemikku 0,6 - 0,8 kusjuures karbonaadid lagunesid suuremas ulatuses rikastatud kütuse põletamisel (lagunemisaste oli 0,7 - 0,8), mis oli tingitud mõnevõrra peenemast kütuse fraktsioonkoostisest.

ORIGINAL PUBLICATIONS
FIRING ESTONIAN OIL SHALE OF HIGHER QUALITY IN CFB BOILERS – ENVIRONMENTAL AND ECONOMIC IMPACT

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In this article environmental and economic impact of firing oil shale of higher quality is analyzed.

Fuel consumption, emission indicators (CO₂, SO₂, CO, NOₓ, N₂O, particulates) and ash mass flow of a circulating fluidized bed (CFB) boiler firing oil shale of lower heating value (LHV) of 8.2–11.5 MJ/kg are presented. The investigation is based on full-scale firing tests.

Based on test results the impact of transportation and operational costs of oil shale and ash handling on electricity price is analyzed. The pollution charges and CO₂ emission allowances are considered when analyzing the environmental impact on costs.

Firing upgraded oil shale (10.5 MJ/kg) leads to substantial reduction of environmental impact and enables to save costs of electricity production. Reduction of CO₂ emission by 7%, ash mass flow by 25% and fuel consumption by 22% when firing upgraded oil shale instead of conventional one (8.4 MJ/kg) enables to save up to 3 EUR/MWh, achieving the major savings from environmental costs, especially from reduced need for purchasing CO₂ emission allowances.

Introduction

The European Union (EU) is working actively for a global agreement to control climate change, and since the early 1990s several steps have been taken to limit greenhouse gas emissions. In 2007 the EU started an integrated approach to climate and energy policy and committed to transforming Europe into a highly energy-efficient and low carbon economy. The commitment that Europe would cut its emissions by at least 20% of 1990 levels by 2020 was made. This commitment has a great impact on Estonia’s electricity sector as up to 90% of electricity is produced in oil shale firing power plants.

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Narva power plants (AS Narva Elektrijaamad) with total capacity of 2380 MWₘ consist of two oil shale firing plants – Baltic (Baeti) and Estonian (Eesti), including 430 MWₑ of CFB combustion technology based power units. Nevertheless, it is planned to introduce up to two new CFB units (2×300 MWₑ). Thus, reduction in the CO₂ emission is a great challenge for the energy sector in Estonia.

At present, the LHV of oil shale fired at Narva power plants is approximately 8.3–8.4 MJ/kg (conventional oil shale). That fuel contains carbonate minerals (mineral CO₂ content up to 20%) resulting in high specific emission of CO₂ (in a range of 0.95–1.12 t/MWhₑ depending on combustion technology) due to dissociation of carbonate minerals.

For minimizing CO₂ emission, oil shale of higher quality should be used. Enrichment reduces the content of carbonate minerals resulting in increased heating value and improved quality of oil shale.

Applying CFB combustion technology gives some advantages in utilization of oil shale of a higher quality. Because of lower combustion temperature and a large amount of circulating ash in the CFB boiler furnace it is possible to burn oil shale of higher quality more efficiently than in pulverized firing boilers.

Using the oil shale of higher quality adds some additional positive aspects to reduction of CO₂ emission enabling to reduce:
- fuel consumption per produced kWh of power;
- load of the fuel transportation and preparation system;
- expenses for ash handling and deposition.

Content of ash, mineral CO₂ and moisture are in a strong correlation with oil shale LHV [1, 2]. These fuel characteristics influence boiler emissions and economic indicators of the power plant.

To study the influence of oil shale quality on thermal efficiency and on environmental indicators of the CFB boiler the firing tests were carried out.

Experimental setup

The oil shale firing tests were carried out on the CFB boiler of the double power unit (215 MWₑ) of the Baltic Power Plant. The main steam parameters of the boiler (Fig. 1) were as follows: capacity (primary/secondary) – 95/76 kg/s, pressure – 12.7/2.4 MPa and temperature – 535/535 °C. Detailed description of the structure and the concept of boiler are given in [3].

To compare the boiler performance, oil shale (LHV 8.2–11.5 MJ/kg) of various composition was used. In total 17 firing tests in two series were carried out according to EVS-EN 12952 – 15:2003 [4]. The same standard was applied for estimating the boiler efficiency and compiling boiler heat balance taking into account the peculiarity of the oil shale. The number of tests enables to analyze the impact of oil shale LHV in a large range on

the CFB boiler performance. The tests were run at boiler load of 85 kg/s of primary steam.

During the tests the following process data were collected. The location of ports for collecting solid samples is shown in Fig. 1. To determine the granular composition of the fuel, the samples were taken before (A) and after (B) the secondary fuel crusher. The fuel samples for ultimate and proximate analysis were taken from the main fuel conveyor (not shown in Fig. 1). The characterization of oil shale used is provided in Table 1.

For determining the chemical composition of ash the samples were taken from the following collection ports (Fig. 1): C – bottom ash, D – INTREX, E – convective superheater and reheater, F – economizer, G – air preheater and from four fields in electrostatic precipitator (ESP: H, I, J, K). Also, the ash mass flow rates from ash separation ports (C to K) were measured.

The main flue gas composition (O₂, CO₂, CO, NOₓ, N₂O, SO₂, moisture) and temperature were measured in order to estimate the boiler combustion efficiency. Position L in Fig. 1 indicates the location in a boiler gas pass where the flue gas samples were taken for analysis.

In addition, the plant’s own data logging system was used to register several boiler operation parameters.
Table 1. Composition of oil shale as received, mass %

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Parameter</th>
<th>Series 1</th>
<th>Series 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q_i</td>
<td>Lower heating value, MJ/kg</td>
<td>8.2–8.8</td>
<td>9.3–11.5</td>
</tr>
<tr>
<td>C</td>
<td>Carbon</td>
<td>20.06–21.94</td>
<td>22.64–27.40</td>
</tr>
<tr>
<td>H</td>
<td>Hydrogen</td>
<td>2.30–2.69</td>
<td>2.51–3.33</td>
</tr>
<tr>
<td>O</td>
<td>Oxygen</td>
<td>2.76–4.67</td>
<td>3.36–4.56</td>
</tr>
<tr>
<td>N</td>
<td>Nitrogen</td>
<td>0.04–0.06</td>
<td>0.04–0.07</td>
</tr>
<tr>
<td>S_o</td>
<td>Organic sulfur</td>
<td>0.39–0.54</td>
<td>0.41–0.60</td>
</tr>
<tr>
<td>S_p</td>
<td>Pyritic (marcasite) sulfur</td>
<td>0.76–1.07</td>
<td>0.89–1.16</td>
</tr>
<tr>
<td>S_k</td>
<td>Sulfate sulfur</td>
<td>0.06–0.09</td>
<td>0.04–0.12</td>
</tr>
<tr>
<td>Cl</td>
<td>Chlorine*</td>
<td>0.19–0.21</td>
<td>0.22–0.27</td>
</tr>
<tr>
<td>(CO_2)</td>
<td>Mineral CO_2</td>
<td>19.46–17.10</td>
<td>16.88–13.37</td>
</tr>
<tr>
<td>A_{ Ash}</td>
<td>Ash content (corrected)**</td>
<td>41.83–39.54</td>
<td>41.19–37.89</td>
</tr>
<tr>
<td>W_{cr}</td>
<td>Crystal water</td>
<td>0.50–0.54</td>
<td>0.56–0.62</td>
</tr>
<tr>
<td>W</td>
<td>Moisture</td>
<td>10.40–12.75</td>
<td>9.30–11.95</td>
</tr>
</tbody>
</table>

* – chlorine is calculated on the basis of its average content (0.75% [1]) in organic matter of oil shale;
** – is calculated as A_{ Ash} = A_{ Lab} – A_{ ash}, where A_{ Lab} – content of laboratory ash; A_{ ash} – ash mass increase due to reactions (oxidation of marcasite FeS_2, formation of calcium sulfate CaSO_4 and incomplete decomposition of carbonate minerals) occurring during laboratory ashing of oil shale sample.

Test results and discussion

Based on the collected process data several CFB boiler parameters are analyzed. Concerning environmental indicators the fuel consumption and ash mass flow rates as well as emissions of the boiler are presented. In the current study the results of tests with conventional oil shale (8.4 MJ/kg) are compared with the results for the oil shale with LHV 10.5 MJ/kg, conditionally termed – upgraded oil shale.

In Balti Power Plant the produced heat is used for electricity generation and for district heating. In this article tests results for useful heat (MWh_{th}) are recalculated per electric energy (MWh_{el}) assuming that electricity is produced in condensing mode only. For that purpose the ratio 0.35/0.90 = 0.389 was used, where 0.35 is the average electricity production efficiency of the power unit working in condensing mode, and 0.90 is the boiler average thermal efficiency observed in tests. That ratio reflects the efficiency of energy conversion from the boiler thermal output to electric energy.

CO_2 emission from a CFB boiler

It is well known that total CO_2 emission (per one kg of fuel as received) when firing oil shale depends on two factors: burning of carbon and decomposition of carbonates:

\[ V_{CO_2} = V_{CO_2 \text{ carbon}} + V_{CO_2 \text{ ash}}, \text{ nm}^3/\text{kg}. \]  (1)
The amount of CO₂ arising from burning of carbon in mm³/kg is presented as \( V_{\text{CO}_2\text{carbon}} = 0.01853 \, C \), where \( C \) – carbon content in oil shale in %. The amount of CO₂ arising from decomposition of carbonates in mm³/kg is calculated as follows: \( V_{\text{CO}_2\text{carbon}} = 0.00509 \, k_{\text{CO}_2} \, (\text{CO}_2)_e \), where \( k_{\text{CO}_2} \) – extent of carbonate minerals decomposition (ECD) and \( (\text{CO}_2)_e \) – content of mineral CO₂ in oil shale in % [1, 2].

The amount of CO₂ formed from burning of organic carbon per one kg of fuel depends on the carbon content of the fuel and also upon the completeness of combustion. When firing oil shale of higher LHV the emission of CO₂ formed from organic carbon increases due to higher organic carbon content in fuel. But when the fuel consumption rate decreases due to higher LHV, the amount of CO₂ from burning of carbon per produced heat (MWhₑ) does not depend on LHV but only on the combustion efficiency.

The amount of CO₂ released from carbonate minerals depends on their total content \((\text{CO}_2)_t\) in fuel and their ECD during combustion which is influenced by the fuel combustion technology used. The ECD depends on the furnace temperature, fuel particle size and partial pressure of CO₂ in the surrounding medium [1] as well as upon operation load of boiler [5]. During oil shale combustion in industrial pulverized firing boilers, where combustion temperature is high (1400 °C and even higher) and fuel particles are extremely fine (median size of fuel, by mass \( R[0.5] = 35–60 \mu \text{m} \)), carbonate minerals decompose to a large extent, \( k_{\text{CO}_2} = 0.96–0.98 \) [1]. In this case CO₂ from decomposition of carbonates is up to 18–22% from the total CO₂ emission. During oil shale firing in a CFB furnace at atmospheric pressure, carbonate minerals decompose to a smaller extent because of the lower combustion temperature (800–820 °C) and coarser particles. The extent of decomposition of carbonates \( k_{\text{CO}_2} \) usually remains between 0.7–0.8 [1].

The test results for specific CO₂ emissions from the CFB boiler calculated per electric power are presented in Fig. 2. According to the results, total CO₂ emission was 1.01 t/MWhₑ when firing conventional oil shale and 0.94 t/MWhₑ in the case of upgraded oil shale, meaning reduction of CO₂ emission by 7%. The decrease in CO₂ emission was mainly achieved due to the reduction of CO₂ emission from decomposition of carbonates as oil shale with higher quality contains less carbonates.

As it can be seen in Fig. 2 CO₂ emission from decomposition of carbonates has strong dependence on oil shale LHV and, as it was described above, it depends on mineral CO₂ content in oil shale and on the extent of carbonate decomposition – \( k_{\text{CO}_2} \). The \( k_{\text{CO}_2} \) for the CFB boiler was calculated on the basis of ash composition as described in [6]. It was calculated as weighted average taking into account the ash mass flow rates (kg/s) from separation ports. As regards the calculation, the \( k_{\text{CO}_2} \) value for CFB boiler in firing tests remained between 0.58–0.82. Herewith, \( k_{\text{CO}_2} \) values were higher (0.75–0.82) when oil shale of higher LHV was fired. As boiler operated during the tests at the same heat load and furnace temperatures, the reason for higher \( k_{\text{CO}_2} \) value when firing oil shale of higher quality can be found in
granular composition of fuel. Oil shale of higher quality (Series 2) was finer than oil shale used in test Series 1. Median size of fuel R[0.5] was 0.39–0.6 mm and 0.48–0.65 mm, respectively.

For estimating CO₂ emission from CFB boiler assuming the similar granular composition of oil shale for all tests, calculations were made taking $k_{CO2} = 0.7$ (the average value for tests when firing conventional oil shale) for all tests. The dashed line in Fig. 2 presents the results of that calculation. As it can be seen, additional reduction of CO₂ emission from decomposition of carbonates can be achieved resulting in total CO₂ emission reduction by 7.8% instead of 7.0%.

As regards CO₂ emission from burning of carbon, the firing tests indicated a weak dependence on oil shale LHV. Still, small reduction of CO₂ emission from burning of carbon was achieved as boiler efficiency increased by up to 1% when firing oil shale with higher quality (8.4 → 10.5 MJ/kg).

The ratio of carbonate CO₂ to total CO₂ emission depending on oil shale LHV is presented in Fig. 3. It can be seen that CO₂ emission from decomposition of carbonate minerals formed 14.4% (conventional fuel) and 11.2% (upgraded fuel) from the total CO₂ emission.

Estonian oil shale can be utilized more efficiently increasing electricity production efficiency of power unit applying higher steam parameters. For predicting total CO₂ emission (per MWhₑ) for CFB combustion based power units with electricity production efficiencies of 0.38 and 0.41 additional calculations were made. The calculations are based on the test data (CO₂ emission from CFB boiler per MWhₑ) using the recalculation ratios 0.38/0.90 = 0.422 and 0.41/0.90 = 0.456, accordingly. The results of calculations for upgraded and conventional oil shale are presented in Table 2. There

Fig. 2. Specific CO₂ emissions depending on oil shale LHV.
Fig 3. The ratio of carbonate CO₂ to total CO₂ emission depending on oil shale LHV.

can be seen that if firing conventional oil shale in power units with efficiencies of 0.38 and 0.41, the total CO₂ emission would be 0.93 t/MWhₑ and 0.87 t/MWhₑ, respectively instead of 1.01 t/MWhₑ observed in the tests for current power units with efficiency of 0.35.

**Other emissions**

The results for flue gas components (SO₂, CO, NOₓ, N₂O) are presented for dry flue gas and O₂ = 6%. As the gas analysis showed, carbon monoxide emission varied during the tests in the range of 20–45 mg/nm³ and had no significant correlation with fuel quality. The CO emission depended rather on combustion efficiency than on fuel LHV.

Concentration of nitrogen oxides in flue gas had a slight tendency to increase with higher oil shale LHV. The concentration of NOₓ in flue gas is proportional to the nitrogen content of the fuel [1]. Still, the NOₓ emission for upgraded oil shale stayed below the level of 200 mg/nm³.

SO₂ and N₂O concentration in flue gas during all the tests stayed below 15 mg/nm³. That is below measurement level of the gas analyzer. Due to large amount of free lime available in oil shale (usually molar ratio of Ca/S = 8–10 [1]) and low combustion temperature, the SO₂ formed during combustion is bound totally into ash and therefore practically no SO₂ is emitted.
Concentration of particulates in flue gas after ESP was not measured during the tests. For economic calculations it was assumed that the concentration stayed below 30 mg/m³.

**Fuel consumption and ash mass flow rates**

As it was expected, firing oil shale with higher quality resulted in reduction of fuel consumption rate. Due to higher LHV the fuel consumption decreased by 22% when firing upgraded oil shale instead of conventional one. Even greater reduction of ash mass flow was achieved – up to 25% due to reduced fuel consumption rate and lower ash content of upgraded oil shale. The results for fuel consumption and ash mass flow rates per electric power are presented in Fig. 4. Herewith, the fuel consumption rate is calculated via boiler indirect heat balance. The ash mass flow rate is calculated based on fuel consumption rate and real ash content of fuel (kg/kg). Real ash content takes into account ash mass increase due to reactions occurring in the furnace during combustion process – marcasite (FeS₂) oxidation, calcium sulfate (CaSO₄) formation and incomplete decomposition of carbonate minerals.

![Graph showing fuel consumption and ash mass flow rates](image)

*Fig. 4.* Specific ash mass flow and fuel consumption rate depending on oil shale LHV.

As there is a strong correlation between oil shale characteristic composition and LHV, it is possible to present the test results for CO₂ emission and for ash mass flow (in Fig. 2 and Fig. 4) depending on oil shale LHV.

Major test results for the CFB boiler are presented in Table 2.
Economic aspects

The firing tests with upgraded oil shale indicated significant reduction of fuel consumption and ash mass flow rates as well as air emissions from the CFB boiler. The results of tests described above were used for analyzing the potential extent of cost reduction in Narva power plants. The economic analysis was made for the case of replacing oil shale of 8.4 MJ/kg (LHV) with the one of 10.5 MJ/kg heating value. Cost calculations were made for the CFB units installed in Eesti and Balti power plants for the current capacity: 215 MWₑ CFB units are operated in both power plants. Also, the calculations of potential savings were made for the year 2015, assuming that two units of 215 MWₑ are operating and a new CFB-based capacity of 300 MWₑ or 600 MWₑ will be commissioned resulting in total capacity of 730 MWₑ or 1030 MWₑ as an option. The following annual electricity production was assumed: 2.92 TWhₑ in 2010 and 4.96 TWhₑ or 7.00 TWhₑ in 2015. In economic calculations for the new power units the production costs were taken similar to these of Eesti Power Plant.

The costs analyzed in regard to impact of introducing upgraded oil shale were: fuel costs, transport costs, operational costs and costs related to the environmental impact.

Fuel costs

The fuel cost is an important component of electricity production expenditures. In Estonia, according to the Electricity Market Act the price of the oil shale sold to large (with capacity of at least 500 MWₐ) power plants must be regulated. At present, the Competition Authority has set a price cap of 1.26 EUR/MJ for oil shale (8.4 MJ/kg) supplied to Narva power plants. In the current analysis it is assumed that the price of oil shale is proportional to the heating value. Therefore, as the price of energy in fuel (EUR/MJ) is assumed to be the same for conventional and upgraded oil shale, the prices of fuel are 10.55 EUR/t and 13.24 EUR/t, respectively. Nevertheless, due to the higher combustion efficiency 0.21 EUR per every MWhₑ of produced electricity can be saved.
Transport costs
The use of upgraded fuel enables to reduce oil shale transport costs from mines to power plants. Assuming the current level (2010) of railway tariffs and installed generation capacity of 430 MW, the cost paid for transportation of oil shale to Balti Power Plant and to Eesti Power Plant can be reduced by EUR 0.56 and by EUR 0.26 million a year, respectively. As the result, the total reduction of transportation costs is approximately EUR 0.82 million. By 2015, in the case of total installed capacity of 1030 MW, the annual savings can reach EUR 1.89 million, assuming 5% annual increase of transport costs since 2010.

Operational costs in power plants
In power plants the use of upgraded oil shale enables to reduce the operating costs for oil shale as well as for ash. The consumption of oil shale and the ash flow rates depending on LHV is presented in Fig. 4.

As the introduction of upgraded oil shale results in smaller volumes of fuel, it enables to reduce 22% of the variable part of the fuel and 25% of the ash operational costs. Nevertheless, in Narva power plants the value of savings in absolute terms is rather modest – at the current level (2010) the annual savings can be EUR 0.28 million. In projections of operational costs of handling oil shale and ash for 2015 the annual increase of 6% was assumed. So, in 2015 approximately EUR 0.77 million can be saved annually in the case of installed capacity of 1030 MW.

Environmental impact costs
An impact greater than direct cutting of operational costs is achieved due to substantial reduction of environment costs. According to Estonian legislation the harmful impact on environment has to be compensated following the ‘polluter pays’ principle. Since 1991 the environmental charges have been in use to compensate the use of natural resources and release of waste or pollutants into soil, water or ambient air. The charges together with the relevant rates are stipulated by the Environmental Charges Act. The air pollution charge on the release into ambient air from a stationary source of pollution is applied for emission of:

- sulfur dioxide (SO₂) or other inorganic sulfur compounds;
- carbon monoxide (CO);
- carbon dioxide (CO₂);
- particulates;
- nitrogen oxides or other inorganic nitrogen compounds;
- volatile organic compounds (except methane)°;
- mercaptans°;
- heavy metals or compounds of heavy metals°.

° were not considered in this article
Also, the pollution charge is applied for waste disposal, including oil shale fly and bottom ash landfilled at the ash fields.

In the present study the reduction in emission of carbon dioxide and particulates as well as ash disposal was analyzed and economic effect of these reductions assessed.

In Estonia, the pollution charge for release of carbon dioxide into ambient air was introduced in 2000. As since 1 January 2008 Estonia has introduced excise duty on electricity, from the same date the electricity producers do not have to pay the pollution charge on CO₂ emission. As a result, at present, the CO₂ charge has to be paid by all enterprises producing heat, excluding the ones firing biomass, peat or waste.

According to the Environmental Charges Act, the rates of pollution charges will be increased gradually in the following years up to the 2015. The rates relevant to the present study are presented in Table 3.

The calculations indicated that at the level of CFB-based capacities installed in 2010, the replacing of conventional oil shale (8.4 MJ/kg) with the upgraded one (10.5 MJ/kg) would reduce the pollution charges (for emission of particulates and for ash landfilling) paid by Narva power plants by EUR 0.52 million. In 2015, assuming installed capacity of 1030 MWₑ, the annual savings of pollution charges would be EUR 2.98 million.

As described above, in Estonia the utilities producing electricity are not obliged to pay pollution charge for emitting CO₂ into ambient air. Still, the emission of CO₂ has an increasing impact on the environmental performance as well as on economic results of power plants. Estonia has no problems of meeting targets set by Kyoto Protocol. Nevertheless, the EU has set several challenging climate and energy targets to be met by 2020, among these there is a goal to reduce greenhouse gas (GHG) emissions in the EU member states by at least 20% below 1990 levels. To promote reaching this target in a cost-effective and economically efficient manner the European Parliament and the Council established in 2003 a scheme for greenhouse gas emission allowance trading (EU ETS) within the Community [7].

Estonian enterprises, including Narva power plants, had no problems with meeting GHG emission reduction targets set for the first period (2005–2007) of the EU ETS. The situation during the second period (2008–2012) will be more difficult as the allocated amount of CO₂ allowances is by 47.8% smaller than Estonia had applied for. Data on Narva power plants for the first two periods of EU ETS are presented in Table 4.

As there is a great difference between applied and allocated quantities of emission allowances the lacking allowances must be purchased paying the

<table>
<thead>
<tr>
<th>Table 3. Rates of pollution charges (EUR/t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pollutant</td>
</tr>
<tr>
<td>-------------------------------------------</td>
</tr>
<tr>
<td>Particulates (air emission)</td>
</tr>
<tr>
<td>Oil shale ash (landfilling)</td>
</tr>
</tbody>
</table>
Table 4. CO₂ emission allowances for Narva power plants (2008–2012), 10³ t

<table>
<thead>
<tr>
<th>Power plant</th>
<th>Applied</th>
<th>Allocated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Balti</td>
<td>2 974.8</td>
<td>1 454.3</td>
</tr>
<tr>
<td>Eesti</td>
<td>11 679.2</td>
<td>7 214.5</td>
</tr>
</tbody>
</table>

market price. In the EU it has been decided that full auctioning of allowances shall be the rule for the power sector since 2013, as well no free allocation shall be made in respect of any electricity production by EU ETS new entrants [8]. This means that the CO₂ emission level would be the factor of increasing importance for electricity producers.

In the current analysis the basic cost calculations were made applying the emission allowance price of 15 EUR per ton of CO₂. The use of upgraded oil shale would save EUR 4.2 million (installed capacity of 430 MWₑ), EUR 6.92 million (730 MWₑ) or EUR 9.63 million (1030 MWₑ). Hence, the cost of CO₂ allowance is the main contributor to economic savings in the current analysis. Therefore, the sensitivity analysis was carried out to determine the impact of higher price level of CO₂ emission allowance. The results for 20 EUR/t indicate that the annual savings (in 2015) could reach up to EUR 9.22 million (730 MWₑ) or even to EUR 12.84 million in the case of 1030 MWₑ installed capacity.

The potential specific savings of production costs in Narva power plants are presented by cost elements in Tables 5 and 6. In these tables the savings are calculated per produced electricity (gross).

Today, in Estonia the rates of environment-related charges are at low level, also there is no need to purchase allowances for CO₂ emission. As the result, the share of environment related potential savings is low: in 2010 0.18 EUR per MWhₑ of produced electricity. In Estonia, the gradual increase of pollution charge rates is stipulated in the relevant law. Therefore, in 2015 the level of potential savings is already quite significant.

The major effect of cost reduction can be gained due to smaller emission of CO₂. The sensitivity analysis indicated that raising price on CO₂ emission allowances would increase the relevant specific savings essentially (Table 6).

Table 5. Specific savings of electricity production costs

<table>
<thead>
<tr>
<th>Cost article</th>
<th>EUR/MWhₑ</th>
<th>% of the current price*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel</td>
<td>0.21</td>
<td>0.81</td>
</tr>
<tr>
<td>Transport</td>
<td>0.27</td>
<td>1.05</td>
</tr>
<tr>
<td>Operations</td>
<td>0.10</td>
<td>0.36</td>
</tr>
<tr>
<td>Total</td>
<td>0.58</td>
<td>2.22</td>
</tr>
</tbody>
</table>

* – savings are compared with price cap (29.41 EUR/MWhₑ) set by the Competition Authority for the electricity supplied from Narva power plants.
Table 6. Specific savings of environment related electricity production costs in 2015

<table>
<thead>
<tr>
<th>Cost article</th>
<th>EUR/MWhₑ</th>
<th>% of the current price*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pollution charges</td>
<td>0.43</td>
<td>1.6</td>
</tr>
<tr>
<td>CO₂ allowances</td>
<td></td>
<td></td>
</tr>
<tr>
<td>if 10 EUR/t</td>
<td>0.92</td>
<td>3.5</td>
</tr>
<tr>
<td>if 15 EUR/t</td>
<td>1.38</td>
<td>5.2</td>
</tr>
<tr>
<td>if 20 EUR/t</td>
<td>1.83</td>
<td>6.9</td>
</tr>
<tr>
<td>Total</td>
<td>1.35–2.26</td>
<td>5.1–8.5</td>
</tr>
</tbody>
</table>

*— savings are compared with price cap (29.41 EUR/MWhₑ) set by the Competition Authority for the electricity supplied from the Narva power plants

During the period of 2010–2015 the use of upgraded oil shale in CFB based power units of Narva power plants would enable to avoid 2.04 million tons CO₂ emission and save from EUR 20 million (10 EUR/t CO₂) to EUR 40 million (20 EUR/t CO₂) of allowance purchases. Additionally, EUR 19.1 million could be saved due to lower operational costs and smaller pollution charges.

Conclusions

Firing upgraded (10.5 MJ/kg) oil shale in the CFB boilers would enable to decrease the environmental impact of power production significantly. The main effect was expressed in reduction of CO₂ emission by 7% compared to conventional (8.4 MJ/kg) oil shale. Also, much lower rates of fuel consumption (~22%) and ash mass flow (~25%) were observed. CO₂ emission from decomposition of carbonate minerals formed 14.4% when firing conventional and 11.2% when firing upgraded oil shale from the total CO₂ emission. Total CO₂ emission was 1.01 t/MWhₑ for conventional oil shale and 0.94 t/MWhₑ in the case of upgraded oil shale.

The economic calculations indicate clearly that introduction of upgraded oil shale in power plants has positive effect on electricity production costs, especially on environment-related expenditures. Potential specific saving of production costs (fuel, transport and operations) will be 0.58 EUR/MWhₑ. The significant environmental benefit – avoided emission of CO₂ – would translate into essential economic effect as well. In 2015, 2.26 EUR/MWhₑ of environment related costs can be saved in the case of CO₂ allowance price of 20 EUR/t, the total savings reaching up to 3 EUR/MWhₑ. In the latter case the total annual savings (all costs) in CFB based units of Narva power plants could reach EUR 19.5 million.
Acknowledgements

Authors express their gratitude to Estonian Science Foundation (Grant No. 6661) for financial support and to Narva power plants to technical assistants carrying out firing tests and to Dr. Tõnu Pihu, MSc. Teet Parve, Mr. Rein Rootamm, Mr. Illar Viilmann and Dr. Arvi Prikk for assistance in firing tests.

REFERENCES


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FIRING ESTONIAN OIL SHALE IN CFB BOILERS – ASH BALANCE AND BEHAVIOUR OF CARBONATE MINERALS

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The ash balance and the extent of carbonate decomposition (ECD) for circulating fluidised-bed (CFB) boilers depending on oil shale lower heating value (8.5 and 11.1 MJ/kg) were analysed. As for the ash balance, ash mass flow rates (kg/s) for each ash separation port were determined. In calculations the ECD methodology developed at the Department of Thermal Engineering (DTE) on the basis of ash composition was used. Changes in the boiler ash balance occurred when firing oil shale of different quality. Additionally, the reduction of the CO₂ emission by 7% and of the total ash mass flow by 23% was obtained when firing upgraded oil shale instead of low-grade oil shale.

Introduction

Oil shale is the main energy resource in Estonia. Around 90% of the electricity in the country is produced from oil shale at the Narva Power Plants (NPP). The lower heating value (LHV) of oil shale used for electricity production is 8.3–8.4 MJ/kg. This is a low-grade fuel with a high content of carbonate minerals. Burning that kind of fuel is associated with several problems concerning dissociation of carbonate minerals, high CO₂ emission levels, ash handling and storing. In the context of minimising the environmental impact of power production, the question has arisen about utilisation of oil shale of higher quality. The application of the modern CFB technology at the NPP provides advantages in utilisation of upgraded oil shale with the LHV at up to 11.0 MJ/kg.

Several positive aspects of using oil shale of higher quality can be highlighted: decreased concentration of CO₂ in flue gas, reduction of fuel consumption per kWh of produced power, and the improvements in ash handling and storing. Considering these aspects, the energy unit efficiency increases, which also improves cost efficiency.

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However, firing of oil shale of higher quality could cause changes in the CFB boiler operating conditions. Considering the fact that the carbonate minerals (mainly limestone) in oil shale are mechanically harder (compressive strength range of 40–80 MPa) and heavier by density (2200–2600 kg/m$^3$) than the organic and sandy-clay part (compressive strength range of 20–40 MPa and density at 1500–1800 kg/m$^3$), firing of oil shale containing reduced amount of carbonate minerals could cause redistribution of the CFB boiler ash mass flows and changes in the behaviour of mineral matter in the furnace during the combustion process.

To investigate the distribution of ash mass flows and the behaviour of the mineral matter depending on oil shale quality, the boiler ash balance was determined and the extent of carbonate decomposition for the boiler ash was calculated. The investigation is based on the full-scale oil shale firing tests carried out by the DTE and the NPP during 2006–2007.

**Experimental part**

**Arrangement of the tests and collection of the process data**

The oil shale firing tests were carried out in the CFB boiler No. 1 of the Balti Power Plant energy unit No. 11. The capacity of the energy unit was 215 MW$e$ and it was commissioned in 2004 by Foster Wheeler Energia OY. The main parameters of the boiler (Fig. 1) used were as follows:

- steam capacity (primary/secondary) – 95/76 kg/s;
- primary/secondary steam pressure – 12.7/2.4 MN/m$^2$;
- steam temperature – 535/535 °C.

The detailed description of the boiler is provided in [1].

Several fuel classes of various composition and the LHV at 8.2–11.5 MJ/kg were fired. A total of 17 tests were carried out in accordance with EVS-EN 12952 – 15:2003 [2]. The upgraded oil shale fuel was specially prepared. The tests were run at boiler loads of 90% of nominal power.

During each test run several process data sets were collected. As regards the investigation of the ash mass balance and the behaviour of carbonate minerals in the CFB boiler, the fuel and ash sampling from the separation ports was performed as described below, followed by averaging and dividing procedures for achieving the representative average sample of the test run. The locations of the ports used to collect solid samples are indicated in Fig. 1. The fuel samples (A) before and (B) after the secondary fuel crusher were taken to determine the granular composition of the fuel fed into the boiler. The secondary fuel crushers are located at the end of each fuel-feeding line before fuel entering the furnace and are used to ensure the most suitable granular composition of the fuel for the CFB boiler. The fuel samples for the ultimate and proximate analysis were taken from the main fuel conveyor (not shown in Fig.1). Additionally, several ash samples were taken. The furnace ash samples were taken from the following collection ports (Fig. 1): C – bottom ash and D – reheater of the second stage.
Small and light ash particles \((d < 50 \, \mu \text{m})\) [1] not separated by the separators of solids comprise fly ash. The fly ash samples were taken from the following collection ports: E – convective cage of superheater and reheater of first stages (SH-RH), F – economizer (ECO), G – air preheater (APH) and from four fields in the electrostatic precipitator (ESP: H, I, J, K). The fuel and ash samples were analysed by the chemistry laboratory of the DTE. The granular composition analyses of the fly ash samples were performed by ENAS OY, Finland.

![Diagram](image)

**Fig. 1.** Oil shale-fired CFB boiler (sample ports).

1 – raw fuel silo, 2 – fuel feeder, 3 – grate, 4 – furnace chamber, 5 – separating chamber, 6 – fluidised bed internal heat exchanger (INTREX), 7 – separator of solids, 8 – convective superheater and reheater, 9 – economizer, 10 – air preheater, 11 – electrostatic precipitator, 12 – secondary fuel crusher

**Processing test data**

**Determination of the ash mass flow rates**

The ash formed during the combustion process is removed from the boiler by several separation ports as shown in Fig. 1 (C to K). For the ash balance, the ash mass flow rates for each separation port were calculated. The ash from the separation ports is directed to the common ash silo by the ash senders via the mechanical and pneumatic conveying lines. The calculation was performed on the basis of the ash senders’ operation frequency (except convective cage (E) and INTREX (D)) and the ash bulk density. The data of the ash senders’ operation frequencies was registered by the data logging.
system of the plant. For the calculation it was assumed that 2/3 of the total ash senders' volumes was effective.

Considering the circumstance that the ash mass flow from the SH-RH (E) is directed to the bottom ash silo, a specially prepared valve was installed on the ash tube under the convective cage to determine the ash mass flow rate from SH-RH (E). The ash mass flow rate (E) was calculated on the basis of the ash bulk volume in the tube and the time spent on the tube fulfilment in the case of the closed valve. The valve was closed cyclically during the tests for measurements. The ash mass flow from the INTREX (D) is included in the bottom ash mass flow (C).

**Determination of the extent of carbonate decomposition**

Regarding CO₂ emissions from the CFB boiler, the behaviour of carbonate minerals during the combustion process plays a significant role. It is well known that calcite and dolomite during the combustion process dissociate according to the following reactions [3]:

\[
CaCO_3 \rightarrow CaO + CO_2 \\
CaMg(CO_3)_2 \rightarrow CaO + MgO + 2CO_2 \\
CaCO_3 + SO_2 + 1/2O_2 \rightarrow CaSO_4 + CO_2.
\]  

(1) \hspace{1cm} (2) \hspace{1cm} (3)

Carbon dioxide formed during the dissociation (reactions 1–3) of such carbonate minerals is added to the amount of CO₂ formed during the burning of carbon. It results in an increased amount of CO₂ in the flue gas. The share of mineral CO₂ in the total CO₂ emission depends on the oil shale mineral CO₂ content and the ECD.

It is possible to determine the ECD for the CFB boiler ash on the basis of the ash composition alone [4]. In order to determine the ECD, it is important to know the CaO and MgO content of the ash. The initial amount of CO₂ bound with CaO and MgO before the decomposition of carbonates occurs can be established using the formulas below:

\[
CO_{2\text{CaO}} = 0.7785 \text{ CaO}_{\text{ash}} \\
CO_{2\text{MgO}} = 1.0555 \text{ MgO}_{\text{ash}} \\
CO_{2\text{sum}} = CO_{2\text{CaO}} + CO_{2\text{MgO}}
\]  

(4) \hspace{1cm} (5) \hspace{1cm} (6)

where CO₂_{CaO} and CO₂_{MgO} – CO₂ bound accordingly with CaO and MgO and calculated in percentages of the ash mass, and CaO_{ash} and MgO_{ash} – CaO and MgO content of ash. If the carbonaceous CO₂ content of ash (CO₂_{ash}) is also determined by the chemical analysis, the ECD is calculated with Eq. 7:

\[
k_{CO_2} = 1 - (CO_{2\text{ ash}} / CO_{2\text{ sum}}).
\]  

(7)
CO₂ emission from the CFB boiler

As mentioned above, the total amount of CO₂ discharged into the atmosphere when firing oil shale depends on these two aspects: burning of carbon and decomposition of carbonates. The calculation of the CO₂ emission per one kilogram of fuel as received is performed according to the formulas below [3]:

The amount of CO₂ arising from the burning of carbon, in nm³/kg:

\[ V_{CO₂,carbon} = 0.01853 \, C'_c \], (8)

where \( C'_c \) – carbon content of oil shale, %.

The amount of the CO₂ arising from the decomposition of carbonates, nm³/kg:

\[ V_{CO₂,carb} = 0.00509 \, k_{CO₂} \, (CO₂)_{c}' , \] (9)

where \( k_{CO₂} \) – extent of carbonate decomposition;

\((CO₂)_{c}'\) – content of mineral CO₂ in oil shale, %.

The total amount of the CO₂ emission from the CFB boiler is calculated as follows, in nm³/kg:

\[ V_{CO₂} = V_{CO₂,carbon} + V_{CO₂,carb} . \] (10)

This is the specific emission of CO₂ from the CFB boiler per produced thermal energy, in t/MWhₚ₉:

\[ CO₂ = 3.6 \, V_{CO₂} \, \rho \, B / \dot{Q}_{heat} , \] (11)

where \( \rho = 1.977 \) – density of CO₂, kg/nm³;

\( B \) – fuel consumption rate, kg/s;

\( \dot{Q}_{heat} \) – boiler heat output, MWₚ₉.

Results and discussion

Investigation of the ash balance

The investigation of the CFB boiler ash balance is based on the tests in which oil shale with the LHV 8.5 MJ/kg (Test 1) and 11.1 MJ/kg (Test 2) were fired. For Test 1 the boiler operated continuously for three days and five days for Test 2. A short characterisation of the fuels is provided in Table 1.

The results for the CFB boiler ash balance when firing oil shale of different quality can be viewed in Fig. 2. As it was expected, the firing of oil shale of different quality resulted in changes in the distribution of the ash mass flows. The main difference can be noticed in the bottom ash mass flows.
Table 1. Characterisation of oil shale fuel as received (mass %)

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description, unit</th>
<th>Test 1</th>
<th>Test 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q&lt;sub&gt;h&lt;/sub&gt;</td>
<td>Lower heating value, MJ/kg</td>
<td>8.5</td>
<td>11.1</td>
</tr>
<tr>
<td>W&lt;sub&gt;r&lt;/sub&gt;</td>
<td>Moisture, %</td>
<td>11.1</td>
<td>11.3</td>
</tr>
<tr>
<td>A&lt;sub&gt;r&lt;/sub&gt;</td>
<td>Ash (815 °C), %</td>
<td>44.3</td>
<td>42.3</td>
</tr>
<tr>
<td>C&lt;sub&gt;r&lt;/sub&gt;</td>
<td>Organic carbon, %</td>
<td>21.1</td>
<td>26.1</td>
</tr>
<tr>
<td>(CO&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;r&lt;/sub&gt;</td>
<td>Mineral CO&lt;sub&gt;2&lt;/sub&gt;, %</td>
<td>18.7</td>
<td>14.1</td>
</tr>
<tr>
<td>R[0.5]&lt;sub&gt;L&lt;/sub&gt;</td>
<td>Median size of fuel before crushe (Fig. 1, A), mm</td>
<td>1.2</td>
<td>0.75</td>
</tr>
<tr>
<td>R[0.5]&lt;sub&gt;H&lt;/sub&gt;</td>
<td>Median size of fuel after crushe (Fig. 1, B), mm</td>
<td>0.57</td>
<td>0.41</td>
</tr>
</tbody>
</table>

Fig. 2. Ash balance for CFB boiler.

The shares of bottom and fly ash were 37% and 63% when burning low-grade (8.5 MJ/kg) oil shale, but 30% and 70% in the case of firing upgraded (11.1 MJ/kg) oil shale. This denotes a reduced bottom ash ratio when firing upgraded fuel. One of the reasons for the reduced bottom ash mass flow when firing upgraded oil shale could be in the reduction of the content of carbonate minerals in the fuel. When firing oil shale at 8.5 MJ/kg (higher content of carbonate minerals), carbonate minerals (relatively large limestone particles) during the combustion process in the furnace subside through the fluidised bed due to their substantial density and can be removed from the boiler along with the bottom ash, resulting in a higher share of the bottom ash mass flow. On the other hand, the reduced bottom ash mass flow when firing upgraded fuel can be explained by the granular composition of the fuel. More precisely, as it can be seen in Table 1, the upgraded fuel used in Test 2 was finer, with the median size of particles at \( R[0.5]<sub>H</sub> = 0.41 \) mm. When firing low-grade oil shale, the fuel median size was \( R[0.5]<sub>H</sub> = 0.57 \) mm. The finer granular composition of the upgraded fuel in Test 2 was caused by the finer initial fuel entering the secondary fuel crushe. The finer granular
composition of the initial fuel was caused by the higher crushing rate of the fuel due to better conditions in the primary fuel crusher (not shown in Fig. 1). The primary crusher's new hammers were installed during operation one month before the firing tests with the upgraded fuel. Due to finer fuel particles, limestone decomposes to a larger extent and the organic part burns quicker, resulting in reduction of the bottom ash mass flow rate.

The firing of oil shale of higher quality also affected the boiler total ash mass flow (Fig. 2). To summarise the ash mass flows from the separation ports, the total ash mass flow discharged from the boiler was 16.3 kg/s for Test 1 and 12.6 kg/s for Test 2, meaning a reduction of the total ash mass flow by 23% when firing oil shale of higher quality. The reduction of the total ash mass flow was achieved by the reduction of both fuel consumption due to the increased LHV and ash content of oil shale (Table 1).

**The sulphate- and carbonate-free ash balance**

For estimating the accuracy of the measurements of boiler ash mass flows, the sulphate- and carbonate-free ash balance was composed. The sulphate- and carbonate-free ash balance is based on the ash components which form oxides during the combustion process: SiO$_2$, Fe$_2$O$_3$, Al$_2$O$_3$, CaO, MgO, K$_2$O and Na$_2$O. These components are bound totally into the ash and they do not proceed partly or totally into the combustion gases such as SO$_2$, CO$_2$ and Cl. The boiler ash which contains only these elements is called sulphate- and carbonate-free ash.

For composing the sulphate- and carbonate-free ash balance, the flow rate of sulphate-free ash mass into the boiler with the fuel was calculated. The calculation is based on the laboratory data on ash content of the fuel, fuel consumption rate (calculated via boiler heat balance) and chemical composition of the fuel ash. The sulphate- and carbonate-free ash mass flow discharged from the boiler is calculated on the basis of the ash composition and the measured ash mass flows. If the ash balance is correct, the sulphate-free ash mass flow fed into the boiler with the fuel should be equal to the sulphate- and carbonate-free total ash mass flow discharged from the boiler.

The calculation showed that the sulphate- and carbonate-free total ash mass flow discharged from the boiler was 8% greater than the sulphate-free ash mass flow fed into boiler when firing oil shale with the LHV 8.5 MJ/kg and 16% greater when firing oil shale with the LHV 11.1 MJ/kg (see also Table 2).

**Investigation of the behaviour of carbonate minerals and CO$_2$ emissions**

The results of the analyses of the ash samples and determined $k_{CO_2}$ values are presented in Table 3. It can be seen in Table 3 that median sizes and densities of the fly ash samples (E-K) are quite similar when firing oil shale (8.5 MJ/kg or 11.1 MJ/kg). Determined $k_{CO_2}$ values for the fly ash samples are also quite similar, being in the range of 0.70–0.88.
However, concerning the $k_{\text{CO}_2}$ value for the bottom ash samples, it can be seen in Table 3 that when firing low-grade (8.5 MJ/kg) oil shale it is 0.47 and when firing upgraded (11.1 MJ/kg) oil shale it is 0.68. The reason for the lower $k_{\text{CO}_2}$ value when firing low-grade fuel could be explained by the coarser granular composition of the ash. As it can be seen in Table 3, the bottom ash median size when firing the low-grade fuel is 1.13 mm and when firing the upgraded fuel it is 0.43 mm. The coarser granular composition of the bottom ash when firing low-grade fuel was caused by the coarser fuel (coarser limestone particles in the fuel) fired.

While the CFB boiler is equipped with a separator of solids, the granular composition of fly ash leaving separator does not depend on the fuel granular composition. Coarser and heavier fuel and ash particles are captured by the separator and directed to the circulating medium for burnout.

Taking into account the ash mass flow rates (kg/s) for each separation port (Fig. 2), the $k_{\text{CO}_2}$ for the CFB boiler total ash is calculated (weighted average). It can be seen from Table 3 that the total $k_{\text{CO}_2}$ for the CFB boiler when burning upgraded oil shale (Test 2) is 0.78 and when firing low-grade oil shale (Test 1) it is 0.69. As the boiler was operated at the same load and furnace temperatures, the reason for the higher $k_{\text{CO}_2}$ value when firing upgraded fuel can be explained by the fuel granular composition. As mentioned above, the upgraded fuel used was finer. Indeed finer limestone particles in the fuel during the combustion process can be heated up quickly and thus decompose to a larger extent.

The specific CO$_2$ emission results for the CFB boiler's useful heat rate are presented in Table 2. According to the test results, the total CO$_2$ emission when firing low-grade oil shale was 0.384 t/MWh$_{\text{th}}$ and when firing upgraded oil shale it was 0.356 t/MWh$_{\text{th}}$. When firing oil shale of higher quality, a reduction of the CO$_2$ emission by ~7% was achieved as compared to firing of low-grade oil shale. As regards the CO$_2$ emission from the decomposition of carbonates when firing low-grade fuel, it was 14.1%, and when firing upgraded fuel, it was 10.4% of the total CO$_2$ emission.

<table>
<thead>
<tr>
<th>Indicator</th>
<th>LHV 8.5 MJ/kg</th>
<th>LHV 11.1 MJ/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total CO$<em>2$ emission, t/MWh$</em>{\text{th}}$</td>
<td>0.384</td>
<td>0.356</td>
</tr>
<tr>
<td>CO$<em>2$ emission from burning of carbon, t/MWh$</em>{\text{th}}$</td>
<td>0.330</td>
<td>0.319</td>
</tr>
<tr>
<td>CO$<em>2$ emission from decomposition of carbonates, t/MWh$</em>{\text{th}}$</td>
<td>0.054</td>
<td>0.037</td>
</tr>
<tr>
<td>Sulphate-free ash mass flow fed into the boiler with fuel, kg/s (1)</td>
<td>12.42</td>
<td>8.94</td>
</tr>
<tr>
<td>Sulphate- and carbonate-free total ash mass flow from the boiler, kg/s (2)</td>
<td>13.51</td>
<td>10.68</td>
</tr>
<tr>
<td>Difference between (1) and (2), %</td>
<td>8.1</td>
<td>16.3</td>
</tr>
</tbody>
</table>

Table 2. Results for CFB boiler CO$_2$ emissions and sulphate- and carbonate-free ash balance
Table 3. Characteristics of the ash samples and results of ECD calculation

<table>
<thead>
<tr>
<th>Separation port (Fig. 1)</th>
<th>LHV 8.5 MJ/kg</th>
<th>LHV 11.1 MJ/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Density g/cm³</td>
<td>R[0.5] µm</td>
</tr>
<tr>
<td>Bottom (C)</td>
<td>1.483</td>
<td>11.33</td>
</tr>
<tr>
<td>INTREX (D)</td>
<td>1.280</td>
<td>108.76</td>
</tr>
<tr>
<td>SH-RH (E)</td>
<td>0.787</td>
<td>20.77</td>
</tr>
<tr>
<td>ECO (F)</td>
<td>0.668</td>
<td>–</td>
</tr>
<tr>
<td>APH (G)</td>
<td>0.841</td>
<td>–</td>
</tr>
<tr>
<td>ESP 1 (H)</td>
<td>0.652</td>
<td>10.99</td>
</tr>
<tr>
<td>ESP 2 (I)</td>
<td>0.666</td>
<td>7.93</td>
</tr>
<tr>
<td>ESP 3 (J)</td>
<td>0.564</td>
<td>–</td>
</tr>
<tr>
<td>ESP 4 (K)</td>
<td>0.431</td>
<td>–</td>
</tr>
</tbody>
</table>

k_CO₂ for CFB boiler total ash (weighted average), – 0.69 0.78

Conclusions

The following general conclusions can be drawn from the investigation of the CFB boiler ash balance and of the mineral matter behaviour when firing oil shale of different quality:

1. When firing low-grade oil shale, the share of the bottom ash mass flow in the total ash was 37% instead of 30% when firing upgraded oil shale. The reduced bottom ash mass flow when firing upgraded oil shale could be explained by the reduced content of the carbonate minerals in the fuel and by the finer granular composition of such fuel.

2. The k_CO₂ value for the CFB boiler’s total ash when firing upgraded oil shale was 0.78, and 0.69 when firing low-grade oil shale. The reason for the higher k_CO₂ value when firing upgraded fuel could be explained by the finer granular composition of the fuel used in the test.

3. In the context of the environmental impact of power production, we should note the reduction of the CO₂ emission by ~7% achieved when firing upgraded oil shale. As CO₂ emissions depend on the k_CO₂ value and the latter depends on the fuel granular composition, theoretically, taking the boiler k_CO₂ value for the boiler total ash at 0.69 as it was when low-grade oil shale was fired, an additional reduction of the total CO₂ emission by more than 1% can be achieved when firing upgraded fuel.
Acknowledgements

The authors express their gratitude to the Estonian Science Foundation (Grant No. 6661) for the financial support, to the Narva Power Plants for the technical assistance with performance of the firing tests and to Mr. Teet Parve, Mr. Rein Rootamm, Mr. Illar Viilman and Mr. Arvi Prikk for their help during the firing tests.

REFERENCES


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PAPER III
COMBUSTION OF BALTIC OIL SHALES IN BOILERS WITH FLUIDIZED BED COMBUSTION

D. Neshumayev, A. Ots, T. Parve, T. Pihu, K. Plamus, and A. Prikk

Translated from Šveikirgeskije Stantsii, No. 8, August 2010, pp. 23 – 26.

This is a study of the combustion of Baltic oil (bituminous) shales with different heats of combustion in a boiler with fluidized bed combustion (CFB). The minimum heat of combustion was varied over 8.5 – 11.5 MJ/kg in the experiments. The behavior of the mineral part of the shales during combustion was taken into account in determining the boiler efficiency, CO2 emissions, and amount of ash production.

Keywords: Baltic oil shales, mineral part of shales, correction of heats of combustion, fluidized bed boilers, thermal efficiency, estimating CO2 emissions, fuel consumption, ash content.

The heat released during combustion of 1 kg of oil (bituminous) shale depends strongly on the endothermic and exothermic processes taking place in the mineral part of the fuel [1]. These processes include the following: decomposition of calcite and dolomite

$$\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \ (179 \text{ kJ/mole})$$

$$\text{CaMg(CO}_3)_2 \rightarrow \text{CaO} + \text{MgO} + 2\text{CO}_2 \ (-315 \text{ kJ/mole});$$

oxidation of marcasite FeS2

$$4\text{FeS}_2 + 11\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 + 8\text{SO}_2 \ (+871 \text{ kJ/mole});$$

sulfating of CaO

$$\text{SO}_2 + \frac{1}{2}\text{O}_2 + \text{CaO} \rightarrow \text{CaSO}_4 \ (+502 \text{ kJ/mole});$$

and, the formation of new minerals

$$2\text{CaO} + \text{SiO}_2 \rightarrow 2\text{CaO} \cdot \text{SiO}_2 \ (+139 \text{ kJ/mole});$$

$$\text{CaO} + \text{Al}_2\text{O}_3 \rightarrow \text{CaO} \cdot \text{Al}_2\text{O}_3 \ (+70 \text{ kJ/mole});$$

$$\text{CaO} + \text{Fe}_2\text{O}_3 \rightarrow \text{CaO} \cdot \text{Fe}_2\text{O}_3 \ (+79 \text{ kJ/mole}).$$

(The thermal effects of the reactions are given in parentheses.)

The extent to which these reactions proceed to completion and produce changes in the amount of heat released during combustion are mainly determined by the fuel combustion technology.

In the case where oil shale dust is burnt, essentially complete decomposition of the carbonates is observed (degree of dissociation $k_{\text{CO}_2} \approx 0.97$ [1]), mainly because of the relatively high temperature in the furnace chamber (1400 – 1500°C), a low partial pressure of CO2 lying below the equilibrium line for reaction (1) at that temperature, and the small size of the fuel particles. On the other hand, for combustion in circulating fluid bed conditions, incomplete decomposition of the carbonates ($k_{\text{CO}_2} \approx 0.60 – 0.85$) is observed because of the low temperature in the furnace and the large size of the fuel particles.

Despite a high molar ratio of calcium and sulfur in the Baltic oil shales (Ca/S = 8 – 10; at least a factor of 2 – 3 higher than necessary for rapid mass exchange with complete bonding of SO2), when the dust is burnt the bonding efficiency for sulfur is only 0.70 – 0.85. This is because at relatively high temperatures 60 – 70% of the CaO is involved in the formation of new minerals and combines with the sand-clay part of the fuel where the CaO is less active with respect to SO2 than free CaO; at the same time, in fluidized bed combustion the formation of new minerals containing CaO proceeds more slowly owing to the low combustion temperature, so that a large part of the CaO formed as a result of the decomposition of carbonates remains free, which leads to essentially complete bonding of the SO2.

Thus, depending on the shale combustion technology, the degree of completion of reactions (1) – (4) will be different, so that there will be a different amount of heat release per 1 kg of fuel. In addition, the extent of chemical transforma-
tion of the mineral part of shales affects the amount of ash formed during combustion, the required (stoichiometric) volume of air, and the composition of the smokestack gases.

This behavior of oil shales during combustion must be taken into account when determining the actual amount of heat released in a furnace, both with dust combustion and with fluidized bed combustion. In the existing European standard EN 12952-15:2003 [2] on determining the thermal efficiency of boilers, there is no provision for taking the thermal effects of reactions (1) – (4) during burning of shales into direct account. However, in principle, several of these thermal effects, in particular the decomposition of calcite and the sulfatization of CaO, can be evaluated on the basis of this standard if the shale is nominally divided into two parts, main (not containing CaCO₃) and carbonate (consisting of CaCO₃), and the equations given in the standard are used to determine the change in the theoretically required volume of air, the composition of the flue gases, heat of combustion, and amount of ash using the CaCO₃ as the additive in a direct sulfur capture process.

In general, the corrected heat of combustion, $Q'_{i,\text{cond}}$, or the actual amount of heat released through combustion of 1 kg of oil shale is given by the sum of the thermal effects,

$$Q'_{i,\text{cor}} = Q'_{i,\text{cond}} + \Delta Q_1 + \Delta Q_3 + \Delta Q_4,$$

(5)

where $Q'_{i,\text{cond}}$ is the nominal heat of combustion (reduced to conditions corresponding to complete decomposition of the carbonates ($k_{CO_2} = 1$) and the absence of sulfatization ($k_{SO_2} = 0$) and new mineral formation processes); $\Delta Q_1$ is the thermal effect with incomplete decomposition of the carbonates via reactions (1); $\Delta Q_3$ is the thermal effect resulting from the formation of calcium sulfate via reaction (3); and, $\Delta Q_4$ is the thermal effect owing to the formation of new minerals via reactions (4).

It has been shown [3] that the combined thermal effect of the processes taking place in the mineral part of oil shales in fluidized bed combustion can be as high as 6% of the nominal heat of combustion, with the fractions of the thermal effect in $\Delta Q_1$, $\Delta Q_3$, and $\Delta Q_4$ being roughly 0.9, 2.4, and 2.6%, respectively.

The actual amount of ash formation, $\gamma_{A',\text{cor}}$ (as a mass fraction relative to the amount of initial shale), can be calculated using the formula [1]

$$\gamma_{A',\text{cor}} = \gamma_{A',\text{cond}} + 0.375(1 - \beta_{P,A}) + \beta_{P,A} \frac{S'_{P}}{100} +$$

$$+ 2.5 \frac{(S'_{P,A} - S'_{P})}{100} + (1 - k_{CO_2})(CO_2)^{\gamma},$$

(6)

where $\gamma_{A',\text{cond}}$ is the nominal ash content (for $k_{SO_2} = 1$ and $k_{SO_2} = 0$); $\beta_{P,A} = S'_{P,A} / S'_{P}$ is the coefficient of retention of sulfur as sulfide; $S'_{P}$ and $S'_{P,A}$ are the amounts of pyrite (sulfide) sulfur in the fuel and ash, respectively (%); $\gamma_{CO_2}$ and $S'_{P,A}$ are the amounts of sulfated sulfur in the fuel and ash, respectively; and, $(CO_2)^{\gamma}$ is the amount of mineral CO₂ in the fuel (%).

The last three terms on the right of Eq. (6) take into account the increase in the amount of ash formed during combustion through the oxidation of marcasite, formation of calcium sulfate $CaSO_4$, and incomplete decomposition of the carbonates, respectively.

Then the ratio of the fuels in the ash to the design fuel consumption can be calculated using the equation

$$I_u = \frac{\gamma_{A',\text{cor}}}{\gamma_{A',\text{cond}} - \gamma_{W',\text{cor}} - \gamma_{\text{W'\text{, cond}}} - \gamma_{S'_{P}} + \gamma_{S'_{P,A}}}{m_{SL} + m_{FA}U_{FA} / m_{FA} (1 - U_{FA})},$$

(7)

where $\gamma_{W',\text{cor}}$ is the hydrate moisture in the fuel; $\gamma_{S'_{P}}$ is the amount of sulfided sulfur in the fuel; $\gamma_{\text{CO}_2}$ is the amount of mineral CO₂ in the fuel; $m_{SL}$ and $m_{FA}$ are the mass flow rate of shale and fly ash, respectively; and, $u_{SL}$ and $u_{FA}$ are the amounts of flammables (including sulfided sulfur) in the slag and in the exhaust, respectively.

We have made an experimental study of the effect of burning oil shales with different heats of combustion in a fluidized bed boiler on the boiler operating efficiency and exhaust gases.

Full-scale tests were conducted on a boiler with fluidized bed combustion (CFB) with a thermal power of 250 MW in unit No. 11 of the Baltic Electric Power Plant (Estonia) (Fig. 1). A more detailed technical description of this boiler is given elsewhere [4].

The major technical characteristics of the boiler are as follows: primary and secondary steam flow rates 95/76 kg/sec; primary and secondary steam pressures 12.7/2.4 MPa; and, primary and secondary steam temperatures after the boiler 535/535°C. During this work we carried out 17 full-scale tests with live steam loads of 70 – 75 kg/sec on the boiler.

The ranges of the major parameters of the tested oil shales (relative to the working mass of fuel) are the following:

- Minimum heat of combustion $Q'_{i}$, MJ/kg . . . . . . . . . . . . 8.5 – 11.5
- Amount of mineral carbon dioxide (CO₂) % . . . . . . . . . . . . . . . 13.3 – 19.5
- Moisture content $W'$ % . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 9.3 – 12.7
- Nominal ash content $A'_\text{cond}$ % . . . . . . . . . . . . . . . . . . . . . 37.9 – 41.8
- Amount of organic carbon $C'_P$ % . . . . . . . . . . . . . . . . . . . . . 20.1 – 27.4
- Amount of organic sulfur $S'_P$ % . . . . . . . . . . . . . . . . . . . . 0.39 – 0.60
- Amount of pyritic sulfur $S'_{P,A}$ % . . . . . . . . . . . . . . . . . 0.76 – 1.16
In each test the fuel and ash were sampled at different points (Fig. 1) in the fuel-air loop, and repeatedly at each point. The results of the several measurements were then averaged as a representative estimate. The major engineering parameters of the boiler and unit as a whole were recorded using the standard data acquisition system. The temperatures and compositions of the exhaust gases were measured after the air preheater ahead of the electrostatic precipitator (position L in Fig. 1).

The thermal balance and thermal efficiency of this boiler were determined in accordance with the European standard [2], which was modified in order to introduce corrections incorporating the features of oil shale combustion. The efficiency of sulfur bonding was calculated from gas analysis data. Since the concentration of SO$_2$ in the flue gases is essentially zero, $k_{SO_2} = 1$.

Figure 2 shows the experimental data on the change in thermal efficiency of the fluidized bed boiler, as well as the calculated results assuming complete decomposition of the carbonates ($k_{CO_2} = 1$), as functions of the minimum heat of combustion of the shales. The graph indicates an increase of roughly 1.7% in the boiler thermal efficiency as the heat of combustion is raised from 8.5 to 12 MJ/kg. The rise in thermal efficiency is mainly caused by a reduction in heat losses with the flue gases and as physical heat of slag.

One of the economic indicators characterizing the operating efficiency of fluidized bed boilers is the amount of fuel components in the fly and residue ash. Complete combustion of the carbon takes place in this boiler. A tendency toward higher amounts of fuel components in the form of pyritic sulfur was observed in both the residue and fly ash with increasing heat of combustion of the shale (Fig. 3).

As expected, an increase in the heat of combustion of oil shales is accompanied by a reduction in the mass flow rates of burnt fuel and ash, but 25 and 30%, respectively, for the

---

Fig. 1. The boiler with fluidized bed combustion operating with shale: 1, fuel bunker; 2, fuel feed; 3, mesh; 4, furnace chamber; 5, separator chamber; 6, inner heat exchanger with boiling layer (INTREX); 7, solid particle separator; 8, convective steam superheater; 9, economizer; 10, air preheater; 11, electrostatic precipitator; 12, fuel mill; A–L, sampling sites.

Fig. 2. Boiler thermal efficiency for burning of shales with different minimum heats of combustion in a circulating fluidized bed: 1, calculated data ($k_{CO_2} = 1$); 2, experimental data ($k_{CO_2} = 0.58 – 0.77$).

Fig. 3. The degree of retention of sulfided sulfur, $S_{Res}/S_{p}$, as a function of the minimum heat of combustion of shale fuels: 1, residue ash; 2, fly ash.
Fig. 4. Specific flow rate of shale fuel as a function of minimum heat of combustion.

Fig. 5. Specific flow rate of ash as a function of the minimum heat of combustion of shale fuel.

Fig. 6. Specific carbon dioxide emissions of organic (1) and mineral (2) origin as functions of the minimum heat of combustion of shale fuel.

range of variation in the heat of combustion examined here (Figs. 4 and 5).

Figure 6 shows the variation in the CO₂ emission of organic and inorganic origin during combustion of these shales (relative to the useful heat yield in the boiler) calculated using data from elemental analyses of the fuel. This shows that an overall increase in the heat of combustion of the shales by 3.0 MJ/kg leads to a reduction in the specific CO₂ emissions by roughly 7% on average.

CONCLUSION

17 test firings of oil shales with different heats of combustion have been carried out on a 250 MW boiler with fluidized bed combustion.

As the minimum heat of combustion was increased with stable operation of the boiler, it was found that:

- the thermal efficiency of the boiler increases,
- there is a significant reduction in the mass flow rates of fuel and ash,
- the carbon dioxide emissions are reduced, and
- there is a slight increase in the amount of sulfided oxide in both the residue ash and fly ash.

We thank the Estonian Science Foundation for financial support through Grant 6661.

REFERENCES

THERMAL EFFECTS BY FIRING OIL SHALE FUEL IN CFB BOILERS

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Abstract: It is well known that during firing of oil shale fuel the amount of heat released during its combustion per kg of fuel is significantly affected by the endothermic and exothermic processes taking place in mineral matter. These thermal effects are calcite and dolomite decomposing, marcasite FeS₂ oxidising, CaO sulphation and formation of the new minerals. The given paper deals with the experimental study of the influence of these thermal effects of oil shale fuel having different heating value on total amount of heat released during combustion in calorimetric bomb, circulating fluidized bed (CFB) and pulverized-firing boiler (PFB). The large-scale (250 MWth) experiments were performed in the K11-1 CFB boiler of the Balti Power Plant. During experiments low heating value of a fuel varied within the range 8.5 – 11 MJ/kg. At the end some conclusions were drawn.

Keywords: oil shale, thermal effects, CFB, CO₂ emissions

INTRODUCTION

It is well known that during firing of oil shale fuel the amount of heat released during its combustion per kg of fuel is significantly affected by the endothermic and exothermic processes taking place in mineral matter (Ots, 2006). These thermal effects are calcite and dolomite decomposing:

\[
\begin{align*}
\text{CaCO}_3 & \rightarrow \text{CaO} + \text{CO}_2 - 179 \text{kJ/mole} \\
\text{CaMg(CO}_3)_2 & \rightarrow \text{CaO} + \text{MgO} + \text{CO}_2 - 315 \text{kJ/mole}
\end{align*}
\]  

(1)

marcasite FeS₂ oxidising

\[
4 \text{FeS}_2 + 11 \text{O}_2 \rightarrow 2 \text{Fe}_2\text{O}_3 + 8 \text{SO}_2 + 871 \text{kJ/mole}
\]

(2)

CaO sulphation

\[
\text{SO}_2 + ½ \text{O}_2 + \text{CaO} \rightarrow \text{CaSO}_4 + 502 \text{kJ/mole}
\]

(3)

formation of the new minerals

\[
\begin{align*}
2 \text{CaO} + \text{SiO}_2 & \rightarrow 2 \text{CaO-SiO}_2 + 139 \text{kJ/mole} \\
\text{CaO} + \text{Al}_2\text{O}_3 & \rightarrow \text{CaO-Al}_2\text{O}_3 + 70 \text{kJ/mole} \\
\text{CaO} + \text{Fe}_2\text{O}_3 & \rightarrow \text{CaO-Fe}_2\text{O}_3 + 79 \text{kJ/mole}
\end{align*}
\]

(4)

The extent of these reactions causing variation in the amount of heat released is determined mainly by fuel combustion technology.

In case of oil shale combustion in calorimetric bomb and pulverized-firing boilers (PFB) practically complete decomposition of carbonate minerals occurs, the extend of carbonate decomposition \( k_{\text{CO}_2} \approx 0.97 \) (Ots, 2006), which mainly resulting from relatively high temperature in furnace \((1400 - 1500 \degree \text{C})\), low partial pressure of \( \text{CO}_2 \) which is below of equilibrium state line of reaction Eq.(1) at given temperature and small particle size of fuel. Instead, at combustion condition in CFB the incomplete decomposition of carbonates is observed \((k_{\text{CO}_2} \approx 0.75-0.85)\) due to low temperature in furnace and coarse fuel particle size.

Despite high molar content of Ca relatively to molar content of S in oil shale equaled \( \text{Ca/S} = 8 – 10 \) exceeding more than 2-3 times ratio of \( \text{Ca/S} \) sufficient at extensive mass transfer to completely capture of \( \text{SO}_2 \) in accordance with reaction Eq.(3), in PFB case desulfurization efficiency is equalled only 0.70 - 0.85. This could be attributed to the fact, that at relatively high temperatures 60 - 70% of \( \text{CaO} \) participating in formation of new minerals Eq.(4) combines with sandy-clay minerals in which \( \text{CaO} \) is less active toward \( \text{SO}_2 \) compared to free \( \text{CaO} \). Whereas during CFB combustion formation of new minerals containing calcium oxide is slower due to low combustion temperature and hence most part of \( \text{CaO} \) released from carbonate minerals decomposition stays in free form resulting in practically complete capturing of \( \text{SO}_2 \).

Thus, depending on combustion technology of oil shale the extent of above stated reactions would be
different resulting in different amount of heat released during combustion of 1 kg oil shale fuel. In addition, depending on extend of these reactions amount of ash occurring during combustion would be also different. These peculiarities of oil shale combustion behavior should be taken into account in determining both heating value (HV) in calorimetric bomb and actual amount of heat released in furnace either in CFB or PFB.

The given paper deals with the experimental study of the influence of these thermal effects of oil shale fuel having different heating value on total amount of heat released as well as on CO₂ and SO₂ emissions during combustion in calorimetric bomb, CFB and PFB.

EXPERIMENTAL

The large-scale (250 MWₑ) experiments were performed in the K11-1 CFB boiler of the Balti Power Plant (Fig. 1). Detailed description of the structure and boiler concept could be found in (Hotta et al. 2005).

The main parameters of the boiler used were as follows: steam capacity – 95/76 kg/s; primary/secondary steam pressure – 12.7/2.4 MPa; steam temperature – 535/535 °C. 17 full test runs were carried out in total.

The variation of main parameters during experiments of the studied oil shale is provided in Table 1. The tests were run at loads of 70-75 kg/s of primary steam.

During each test run regular fuel and ash sampling from separation ports was performed, followed by averaging and dividing procedures for achieving the representative average sample of the test run. In addition, the plant’s own data logging system was used to register the basic data of the boiler operation and the whole power unit. To estimate the boiler thermal efficiency, the flue gas composition and parameters at the cap after the boiler and before the ESP were measured (position L in Fig. 1).

The heat balance and thermal efficiency estimations of the CFB boiler were performed on the basis of the EN 12952-15:2003 standard by the indirect method taking into account the peculiarity of the oil shale fuel (Loosaaar et al. 2008).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Value</th>
</tr>
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<tbody>
<tr>
<td>Low Heating Value, LHVₑ</td>
<td>MJ/kg</td>
<td>8.5 – 11.5</td>
</tr>
<tr>
<td>Mineral CO₂ₑ</td>
<td>%</td>
<td>13.3 – 19.5</td>
</tr>
<tr>
<td>Moisture, Wₑ</td>
<td>%</td>
<td>9.3 – 12.7</td>
</tr>
<tr>
<td>Corrected ash content, Aₐₑ</td>
<td>%</td>
<td>37.9 – 41.8</td>
</tr>
<tr>
<td>Carbon, Cₑ</td>
<td>%</td>
<td>20.1 – 27.4</td>
</tr>
<tr>
<td>Organic sulphur, Sₒₑ</td>
<td>%</td>
<td>0.39 – 0.60</td>
</tr>
<tr>
<td>Pyritic (maccasite) sulphur, Sₚₑ</td>
<td>%</td>
<td>0.76 – 1.16</td>
</tr>
</tbody>
</table>

Since the extend of the reactions Eq.(1) - Eq.(4) as it was shown above during combustion in a calorimetric bomb and in a boiler is different, a common practice of using as a heating value of oil shale so called conditional heating value (HV) as the heat released during its combustion under such circumstances when carbonates are decomposing completely (Eq.(1)) and neither sulphation nor new minerals’ formation from CaO is taking place (Eqs.(3) and (4)). Knowing conditional HV the corrected HVₑₑ or actual amount of heat released during combustion per 1 kg of oil shale in boiler could be determined as the algebraic sum of the thermal effects in accordance with the aforementioned reactions:

\[ HV_{ₑₑ} = HV + \Delta Q_e + \Delta Q_{S-T} + \Delta Q_{NM} \]  

(5)

where \( HV \) – conditional heating value, \( \Delta Q_e \) – thermal effect due to incomplete decomposition of carbonaceous minerals (Eq.(1)), \( \Delta Q_{S-T} \) – thermal effect due to calcium sulphate formation (Eq.(3)), \( \Delta Q_{NM} \) – thermal effect due to new minerals formation (Eq.(4)).
RESULTS AND DISCUSSION

In Fig. 2 and Fig. 3 the thermal effects corresponding to reactions Eq.(1) - Eq.(4) occurring during oil shale combustion in calorimetric bomb and CFB, respectively, in dependence of conditional LHV are depicted. In case of calorimetric bomb (Fig. 2) the thermal effect due to incomplete oxidation of marcasite additionally plotted. Instead in CFB (Fig. 3) marcasite is burning out practically entirely and therefore is not shown.

From the Fig. 2 could be seen that during combustion in calorimetric bomb the thermal effect due to incomplete decomposition of carbonaceous minerals and calcium sulphate formation sharply decreases at increasing of conditional LHV. During combustion of oil shale in CFB (Fig. 3) thermal effects had weak dependence from conditional LHV, here thermal effect due to calcium sulphate formation slightly increases and others had a tendency towards decrease.

Thus, it could be seen that actual amount of heat liberated during combustion of oil shale is differing from conditional HV. In Fig. 4 cumulative thermal effects behavior expressed in percent relative to conditional HV for various combustion technologies including PF is presented. Here, for PF case thermal effects were calculated taking into account $k_{CO_2} \approx 0.97$, desulfurization efficiency $\approx 0.75$ and CaO in free from $\approx 30\%$ in accordance with (Ots, 2006). From given figure could be found that cumulative thermal effects in case of burning of oil shale in CFB depending on LHV can reach up to $\approx 6\%$ of conditional HV. Comparing two combustion technologies CFB and PF as appears from figure the thermal effects more substantial in CFB case, as a result mainly of greater thermal effect due to incomplete decomposition of carbonaceous minerals.
Fig. 3 Thermal effects during oil shale combustion in a CFB

Fig. 4 Sum of the thermal effects of different combustion technologies depending on conditional LHV

Therefore, neglecting during calculation by these thermal effects could result in underestimation of actually amount of heat liberated in furnace and as a consequence of it in overestimation of fuel mass flow and related to the last others parameters like CO₂ emission, amount of ash and etc.

Specific emissions of CO₂ and SO₂ per useful heat of a boiler obtained on the base of fuel ultimate analysis taking into account actual amount of heat released in furnace for CFB and PF technologies depending on conditional LHV are depicted in Fig. 5 and Fig. 6. SO₂ emissions in case of CFB are not plotted on Fig. 6 since as it was discussed early and was also confirmed by present study there is practically complete capturing of SO₂. From these figures could be seen, that specific emissions of CO₂ and SO₂ during combustion of oil shale in CFB are much lower as compared with PFB and this effect is stronger for lower HV values of fuel.

Fig. 5 Specific emissions of CO₂ per useful heat
CONCLUSIONS

The influence of thermal effects occurring during oil shale fuel combustion on total amount of heat released in furnace as well as on CO₂ and SO₂ emissions in calorimetric bomb, CFB and PFB depending from heating value was experimentally investigated. During combustion in calorimetric bomb the thermal effects due to incomplete decomposition of carbonaceous minerals and calcium sulphate formation sharply decrease at increasing of conditional LHV. In case CFB thermal effects had weak dependence from conditional LHV, and thermal effect due to calcium sulphate formation slightly increases and others have a tendency towards decrease. It was found that cumulative thermal effects in case of burning of oil shale in CFB depending on LHV could reach up to ~6% of conditional HV. The thermal effects more substantial in CFB case, as a result mainly of greater thermal effect due to incomplete decomposition of carbonaceous minerals. Specific emissions of CO₂ and SO₂ per useful heat of a boiler during combustion of oil shale in CFB are much lower as compared with PF and this effect is stronger for lower HV values of fuel.

REFERENCES

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3. Education

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<td>Tallinn University of Technology</td>
<td>2004</td>
<td>bachelor's degree</td>
</tr>
<tr>
<td>Nõo Secondary School</td>
<td>1999</td>
<td>secondary education</td>
</tr>
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4. Language skills

<table>
<thead>
<tr>
<th>Language</th>
<th>Level</th>
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</thead>
<tbody>
<tr>
<td>Estonian</td>
<td>native language</td>
</tr>
<tr>
<td>English</td>
<td>average</td>
</tr>
<tr>
<td>Russian</td>
<td>basic skills</td>
</tr>
<tr>
<td>German</td>
<td>basic skills</td>
</tr>
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</table>

5. Professional employment

<table>
<thead>
<tr>
<th>Period</th>
<th>Organisation</th>
<th>Position</th>
</tr>
</thead>
<tbody>
<tr>
<td>2009- present</td>
<td>Tallinn University of Technology, Thermal Engineering Department</td>
<td>research scientist</td>
</tr>
<tr>
<td>2005-2009</td>
<td>Tallinn University of Technology, Thermal Engineering Department</td>
<td>engineer</td>
</tr>
<tr>
<td>2000-2005</td>
<td>Tallinn University of Technology, Thermal Engineering Department</td>
<td>employee of Science Foundation</td>
</tr>
</tbody>
</table>
6. Special courses

<table>
<thead>
<tr>
<th>Period</th>
<th>Educational or other organisation</th>
</tr>
</thead>
<tbody>
<tr>
<td>2012</td>
<td>Computer training course of Moodle, TUT</td>
</tr>
<tr>
<td>2010</td>
<td>Computer training course of MathCad, TUT</td>
</tr>
<tr>
<td>2007</td>
<td>Computer training course of CorelDraw, TUT</td>
</tr>
<tr>
<td>2002-2003</td>
<td>Certificated course of renewable energies and hydrogen technology. Fachhochschule Stralsund (University of Applied Sciences), Germany.</td>
</tr>
</tbody>
</table>

7. Scientific work

Sustainable utilization of energy resources and process improvement in combustion facilities;

Joint master study program of TUT and TU – Nuclear Power Plants;

Heat engineering and environmental problems of oil shale power plants.

8. Defended thesis


9. Main areas of scientific work

Natural sciences and engineering, energetic research
ELULEKIRJELDUS

1. Isikuandmed

   Ees- ja perekonnanimi  Kristjan Plamus
   Sünnaaeg ja -koht     07.02.1981, Tallinn
   Kodakondsus          Eesti
   Perekonnaseis        Abielus

2. Kontaktandmed

   Aadress               Kopli 116, 11712 Tallinn, Eesti
   Telefon               +372 620 39 07
   E-posti aadress       kristjan.plamus@ttu.ee

3. Hariduskäik

<table>
<thead>
<tr>
<th>Õppeasutus</th>
<th>Lõpetamise aeg</th>
<th>Haridus</th>
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</thead>
<tbody>
<tr>
<td>Tallinna Tehnikaülikool</td>
<td>2006</td>
<td>tehnikateaduste magistrikraad</td>
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<tr>
<td>Tallinna Tehnikaülikool</td>
<td>2004</td>
<td>bakalaureuse kraad</td>
</tr>
<tr>
<td>Nõo Reaalgümnaasium</td>
<td>1999</td>
<td>keskharidus</td>
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4. Keelteoskus

<table>
<thead>
<tr>
<th>Keel</th>
<th>Tase</th>
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<tbody>
<tr>
<td>Eesti keel</td>
<td>emakeel</td>
</tr>
<tr>
<td>Inglise keel</td>
<td>kesktase</td>
</tr>
<tr>
<td>Vene keel</td>
<td>algtaise</td>
</tr>
<tr>
<td>Saksa keel</td>
<td>algtaise</td>
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5. Teenistuskäik

<table>
<thead>
<tr>
<th>Töötamise aeg</th>
<th>Tööandja nimetus</th>
<th>Ametikoht</th>
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<tbody>
<tr>
<td>2009-käesoleva ajani</td>
<td>Tallinna Tehnikaülikool,</td>
<td>teadur</td>
</tr>
<tr>
<td></td>
<td>Soojustehnika Instituut</td>
<td></td>
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<tr>
<td>2005-2009</td>
<td>Tallinna Tehnikaülikool,</td>
<td>insener</td>
</tr>
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<td></td>
<td>Soojustehnika Instituut</td>
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</tr>
<tr>
<td>2000-2005</td>
<td>Tallinna Tehnikaülikool,</td>
<td>grandi täitja</td>
</tr>
<tr>
<td></td>
<td>Soojustehnika Instituut</td>
<td></td>
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</tbody>
</table>
6. Täiendusõpe

<table>
<thead>
<tr>
<th>Öppimise aeg</th>
<th>Täiendusõppe läbivitja nimetus</th>
</tr>
</thead>
<tbody>
<tr>
<td>2012</td>
<td>Arvutikoolitus, kursus e-õppekeskkond Moodle, TTÜ</td>
</tr>
<tr>
<td>2010</td>
<td>Arvutikoolitus, kursus MathCad, TTÜ</td>
</tr>
<tr>
<td>2007</td>
<td>Arvutikoolitus, kursus CorelDraw, TTÜ</td>
</tr>
</tbody>
</table>

7. Teadustegevus

Energiaressursside säästlik kasutamine ja protsesside täiustamine põletusseadmetes;
TTÜ ja TÜ ühismagistriõppekava Tuumaelektrijaamad;
Põlevkivielektrijaamade käiduga seotud soojustehnilised ja keskkonnaalased probleemid.

8. Kaitstud lõputööd


9. Teadustöö põhisuunad

Loodusteadused ja tehnika, energeetikaalased uuringud.
DISSEPTIONS DEFENDED AT
TALLINN UNIVERSITY OF TECHNOLOGY ON
MECHANICAL AND INSTRUMENTAL ENGINEERING


63. **Peeter Ross.** Data Sharing and Shared Workflow in Medical Imaging. 2011.

64. **Siim Link.** Reactivity of Woody and Herbaceous Biomass Chars. 2011.