

CALCULATION OF THE AMOUNT OF ESTONIAN OIL SHALE PRODUCTS FROM COMBUSTION IN REGULAR AND OXY-FUEL MODE IN A CFB BOILER

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Abstract. *Oxy-fuel combustion is considered as one of the promising carbon capture and storage (CCS) technologies for coal-fired boilers. In oxy-fuel combustion, the combustion gases are oxygen and the recirculating flue gas, and the main components of the combustion gas are O₂, CO₂ and H₂O [1].*

The paper presents the results of the calculation of the flue gas amount during combustion of oil shale using oxy-fuel technology in a circulated fluidized bed (CFB) mode. The calculations were performed for different oil shale heating values and different recycled flue gas (RFG) ratios. Oxy-fuel combustion with flue gas recycling was found to enable the decrease of the extent of carbonate minerals decomposition (ECD), thereby increasing the amount of heat released per 1 kg of fuel. To minimize ECD, the recycled flue gas ratio should be maintained at a level higher than 0.7. This condition allows an increase of the partial pressure of CO₂ over the equilibrium state line of calcite decomposition reaction at the bed temperature. The decrease of ECD was observed up to $k_{\text{CO}_2\text{-min}} = 0.28$. The decrease of k_{CO_2} leads to an additional increase in the amount of heat released during oil shale combustion per 1 kg and, depending on the mean lower heating value (LHV), the heat can be increased up to 0.34 MJ/kg.

A comparison with the bituminous and anthracite coals revealed that the specific emission of CO₂ per input fuel energy for oil shale is expected to be even smaller compared with those of the considered coals.

Keywords: *oil shale, oxy-fuel combustion, extent of carbonate minerals decomposition, CFB, CO₂ emission.*

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1. Introduction

Currently, there seems to be no good alternative to coal power in the near future. Energy demand and CO₂ emissions continue to increase [2]. Coal-fired energy generation, which rose by an estimated 6% from 2010 to 2012, continues to grow faster than non-fossil energy sources on an absolute basis. Approximately half of the coal-fired power plants built in 2011 use inefficient technologies [3].

Improving the performance of coal-fired power plants can significantly reduce the CO₂ emissions [4, 5]. A unit operating at the global average efficiency would emit over 1000 g CO₂/kWh, whereas the best units working with ultra-supercritical steam conditions reduce this to closer to 740 g CO₂/kWh [2].

The next step beyond improving the efficiency is the implementation of carbon dioxide carbon capture and storage (CCS), that is, a set of technologies that can significantly reduce the CO₂ emissions from new and existing coal- and gas-fired power plants [2, 6]. Current available CCS technologies are: post-combustion CO₂ capture, pre-combustion CO₂ capture, chemical looping combustion and oxy-fuel combustion [5, 7, 8]. The captured carbon dioxide can be used for enhanced oil recovery or stored in depleted oil and gas reservoirs, coal beds, deep saline aquifers, etc. [9, 10].

Oxy-fuel combustion is seen as one of the major options for CO₂ capture for future clean coal technologies [6, 11]. Oxy-fuel combustion technology is considered to be the most energy- and cost-efficient of the carbon capture technologies [12–18]. The concept of oxy-fuel technology is the removal of nitrogen from oxidizer to perform the combustion process in an oxygen and recycled flue gas environment to decrease the combustion temperature [19]. As a result, the flue gas formed primarily consists of carbon dioxide and water [9].

Oxy-fuel combustion in a CFB for CO₂ capture has been rarely studied so far [20–28]. Most of those studies considered bituminous coals and lignites, and some of the studies considered biomass fuels. There is only one study dealing with oil shale [29]. The main part of these experimental and theoretical investigations covers the pulverized firing technology.

Estonia has no coal reserves; however, it has an unconventional fuel – oil shale. Oil shale is a sedimentary rock that contains organic matter called kerogen. The organic matter of oil shale contains relatively large amounts of carbon (up to 30%_{dry}), hydrogen (up to 3.8%_{dry}), and oxygen (up to 3.9%_{dry}). Oil shale has high contents of mineral matter, which consists of carbonaceous, sandy-clay-carbonaceous and sandy-clay parts. Oil shale is characterized as a fuel with a high content of sulfur (up to 2%_{dry} including organic and pyritic sulfur), alkali metals and chlorine.

Oil shale is Estonia's primary energy resource, with approximately 90% of the electricity consumed is produced from oil shale. Today, the country's oil shale usage is the largest in the world. Most of the oil shale,

approximately 12 million tons yearly, is used for power generation through the use of CFBC and pulverized combustion (PC) technologies [30]. Oil shale burned in power plants has the following proximate characteristics: $W_i^r = 11\text{--}13\%$ (moisture, as received fuel), $A^r = 45\text{--}57\%$ (ash content, as received fuel), $CO_2 = 16\text{--}19\%$ (carbonate CO_2 content, as received fuel), and $Q_i^r = 8.3\text{--}8.7$ MJ/kg (heating value, as received fuel). The molar ratio of Ca/S of 8–10 in oil shale exceeds by over 2–3 times the ratio of Ca/S sufficient to capture SO_2 completely [5]. Oil shale contains many carbonate minerals. Due to decomposition of carbonate minerals, the CO_2 footprint is larger than that of a typical coal firing power plant. The decomposition rate of carbonates in a PC boiler is 0.97, and the rate in a CFB boiler 0.68, depending on the fuel LHV and properties. The specific emission of CO_2 for PC and CFB is 974 g CO_2/kWh and 872 g CO_2/kWh , respectively. The specific emission of SO_2 for PC and CFB is 11.89 g SO_2/kWh and zero, respectively [31, 32].

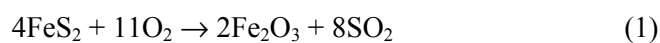
CFB combustion is considered to be one of the best solutions for the use of low grade high ash fuels, such as oil shale. In the CFB boiler, the temperature is controlled using the circulating bed material, which is cooled in an external heat exchanger. The CFB units firing oil shale do not require a sophisticated burner design and management, and they do not require $DeNO_x$ and $DeSO_x$ facilities; therefore, it is considerably easier to retrofit an existing CFB boiler with the oxy-fuel combustion technology.

This study provides the first theoretical preliminary results of oil shale combustion in a CFB boiler applying oxy-fuel technology. The goal of this research was to determine the gas volumes in different parts of the CFB boiler at different recycled flue gas ratios. The comparisons with the bituminous and anthracite coals are also presented.

2. Initial data and the calculation methodology

The combustion calculations were performed for oil shale with varying LHV from 7 to 11.5 MJ/kg. To obtain the corresponding results of the proximate and ultimate analysis data for the oil shale, the method described in [33, 34] was used. The quantitative theoretical analysis method is based on the research experience that has proven to have a statistically significant relationship between the heating value (HV) and the proximate/ultimate analysis data for the Estonian oil shale. Therefore, knowing the oil shale HV, it is possible to calculate the average fuel characteristics, such as the ash and CO_2 contents, the organic part distribution and the average mineralogical composition. The results of the calculation are listed in Table 1. The detailed description of the theoretical methods can be found in [33, 34].

To determine the stoichiometric amount of oxygen required to oxidize inorganic FeS_2 , the following reaction was taken into account:



During oil shale firing, the amount of heat released and the amount of ash formed in combustion per mass unit of fuel is significantly affected by the endothermic and exothermic processes occurring in the mineral matter. The main thermal effects are related to the decomposition of oil shale calcite and dolomite, FeS₂ oxidation, and sulfation of CaO. The extent of these reactions affects the amount of heat released, the amount of ash and combustion products produced and ultimately the flue gas composition. In PC boilers, almost complete decomposition of the oil shale carbonate minerals occurs. The extent of carbonate minerals decomposition (ECD) can be as high as 0.97, $k_{\text{CO}_2} \approx 0.97$ [33], which is mainly due to the high combustion temperature (1400–1500 °C) and certainly due to the low partial pressure of CO₂ and small particle size of the fuel. However, under CFB combustion conditions, incomplete decomposition of carbonates is observed ($k_{\text{CO}_2} \approx 0.6\text{--}0.8$), which is mainly due to the relatively low temperature compared to PC systems, due to the slow kinetics of decomposition in the furnace and due to the coarse particle size of the parent fuel resulting in the decrease of the carbonate originated CO₂ content in the flue gas [34].

An additional decrease of ECD would be expected when applying oxy-fuel combustion technology in CFB boilers. This effect is primarily attributed to the significant increase of the CO₂ partial pressure in the flue gas, which exceeds the equilibrium state line of the calcite CaCO₃ decomposition.

Under these conditions, the thermal decomposition of dolomite would be observed by the following reaction because it is not correlated with the CO₂ partial pressure:



In addition, in oxy-fuel mode, the CO₂ content in the flue gas increases. The sulfur is bound with CaO or most likely directly bound with CaCO₃.

Accounting for all the above, and assuming that the CO₂ formation from dolomite is approximately 16% of the total mineral CO₂ in the fuel [35], the minimum amount of carbonate CO₂ released during thermal decomposition and sulfur capture was calculated as follows:

$$V_{\text{CO}_2\text{-carb}} = 0.00509k_{\text{CO}_2\text{-min}}(\text{CO}_2)_M^r, \quad (3)$$

$$k_{\text{CO}_2\text{-min}} = 1.375S_p^d k_s / (\text{CO}_2)_M^d + 0.16, \quad (4)$$

where

$V_{\text{CO}_2\text{-carb}}$ – minimum amount of carbonate CO₂ formed by decomposition of carbonates, nm³/kg;

$k_{\text{CO}_2\text{-min}}$ – minimum extent of carbonate decomposition;

$(\text{CO}_2)_M^r$ – carbonate CO₂ content of as received fuel, %;

S_p^d – content of pyrite (marcasite) sulfur in dry fuel, %;

k_s – extent of sulfur binding in the boiler;

$(\text{CO}_2)_M^d$ – carbonate CO₂ content of dry fuel, %.

During the calculation of the specific parameters related to LHV, the sulfur capture was corrected as follows. In the case of oil shale the LHV is a conditional value representing the amount of heat released during the combustion of 1 kg fuel under conditions when carbonate minerals decompose completely ($k_{CO_2} = 1$), the formation of calcium sulfate does not occur ($k_s = 0$) and new minerals are not formed. However, in practice, the conditional heating value is widely used, where the extent of the sulfation is not directly determined by detailed analysis of the ash contained in a calorimetric bomb. In this case, it is assumed that during combustion of oil shale in a calorimetric bomb, $k_s = 0.4$. In the present study, the thermal effects due to both the incomplete decomposition of carbonaceous minerals and the calcium sulfate formation were taken into account.

Table 1. Calculated proximate and ultimate oil shale fuel characteristics

LHV (ar) Q_{is}^r , MJ/kg	7.0	7.5	8.0	8.5	9.0	9.5	10.0	10.5	11.0	11.5
Ash A_d , % _{dry}	53.64	52.78	51.96	51.16	50.40	49.67	48.98	48.32	47.70	47.11
Water W_{tr}^r , % _{ar}	10.60	10.94	11.27	11.60	11.94	12.27	12.61	12.94	13.28	13.61
Content of the organic part R^d , % _{dry}										
C^d	19.69	21.00	22.31	23.63	24.94	26.25	27.56	28.87	30.18	31.49
H^d	2.47	2.63	2.79	2.96	3.12	3.29	3.45	3.62	3.78	3.94
S_o^d	0.45	0.48	0.51	0.54	0.57	0.60	0.63	0.66	0.69	0.72
N^d	0.08	0.09	0.10	0.10	0.11	0.11	0.12	0.12	0.13	0.13
Cl^d	0.19	0.20	0.22	0.23	0.24	0.25	0.27	0.28	0.29	0.30
O^d	2.54	2.71	2.88	3.05	3.22	3.39	3.56	3.73	3.90	4.07
Total, R^d	25.42	27.11	28.81	30.50	32.20	33.89	35.59	37.28	38.97	40.66
Content of the carbonate part K^d , % _{dry}										
CaO^d	23.09	22.56	21.95	21.24	20.44	19.54	18.55	17.44	16.24	14.93
MgO^d	3.17	3.10	3.01	2.92	2.81	2.68	2.54	2.39	2.23	2.05
FeO^d	0.10	0.09	0.09	0.09	0.09	0.08	0.08	0.07	0.07	0.06
Carbonate CO_2^d	21.65	21.16	20.58	19.92	19.17	18.33	17.39	16.36	15.23	14.00
Total, K^d	47.99	46.91	45.64	44.17	42.50	40.63	38.56	36.27	33.76	31.04
Content of the sandy-clay part L^d , % _{dry}										
SiO_2^d	15.90	15.53	15.28	15.15	15.13	15.23	15.46	15.82	16.30	16.92
CaO^d	0.19	0.18	0.18	0.18	0.18	0.18	0.18	0.19	0.19	0.20
$Al_2O_3^d$	4.28	4.18	4.11	4.08	4.07	4.10	4.16	4.26	4.39	4.56
$Fe_2O_3^d$	0.74	0.73	0.72	0.71	0.71	0.71	0.72	0.74	0.76	0.79
TiO_2^d	0.19	0.18	0.18	0.18	0.18	0.18	0.18	0.19	0.19	0.20
MgO^d	0.11	0.10	0.10	0.10	0.10	0.10	0.10	0.11	0.11	0.11
Na_2O^d	0.21	0.21	0.20	0.20	0.20	0.20	0.21	0.21	0.22	0.23
K_2O^d	1.68	1.64	1.61	1.60	1.59	1.60	1.63	1.67	1.72	1.78
FeS_2^d	2.47	2.42	2.38	2.36	2.35	2.37	2.40	2.46	2.54	2.63
Sulfate sulfur, SO_3^d	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.14	0.14
Crystal water, H_2O^d	0.69	0.68	0.66	0.66	0.66	0.66	0.67	0.69	0.71	0.74
Total, L^d	26.59	25.98	25.55	25.33	25.30	25.47	25.86	26.45	27.26	28.30
Total, $R^d + K^d + L^d$	100	100	100	100	100	100	100	100	100	100

The calculations of the flue gas volumes in the oxy-fuel combustion of oil shale were performed for a steady state regime, implementing the process for which the schematic diagram is shown in Figure 1. The recycled flue gas

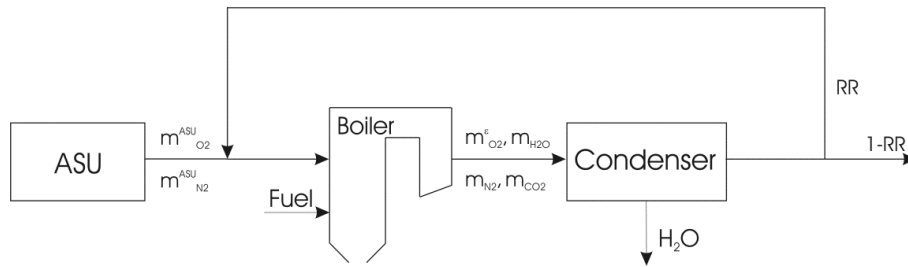


Fig. 1. Schematic of the proposed oxy-fuel combustion process.

(RFG) stream was assumed to be taken after the water vapor condenser. To simplify the calculations, the water content in the gases after the condenser was assumed to be $0.05 \text{ kg}_{\text{H}_2\text{O}} \text{ per kg of fuel burned}$.

The flue gas recycle ratio was defined as the ratio of the mass of the recycled flue gas stream m_{RFG} to the total mass of flue gas at the boiler outlet:

$$\text{RFG ratio} \equiv \text{RR} = \frac{m_{\text{RFG}}}{m_{\text{RFG}} + m_{\text{PFG}}}, \quad (5)$$

where m_{PFG} is the mass of the product flue gas stream.

In addition, based on an overview article [9], the oxygen content in flue gas after the air separation unit was assumed to be $95\%_{\text{vol}}$, with $5\%_{\text{vol}}$ of nitrogen and argon. The oil shale calculations were performed for an excess O_2 constant value of $5\%_{\text{vol}}$ at the boiler outlet. In the steady state regime, the mass CO_2 content per kg fuel m_{CO_2} at the boiler outlet for different RFG ratios was calculated as follows:

$$m_{\text{CO}_2} = \frac{m_{\text{CO}_2}^{\text{F}}}{1 - \text{RR}}, \quad (6)$$

where $m_{\text{CO}_2}^{\text{F}}$ is the total mass of CO_2 occurring during combustion of 1 kg oil shale, including CO_2 from organic carbon combustion and calculated according to Equation (3) CO_2 from carbonate minerals decomposition.

The nitrogen content at the boiler outlet can be determined from:

$$m_{\text{N}_2} = \frac{m_{\text{N}_2}^{\text{ASU}} + m_{\text{N}_2}^{\text{F}}}{1 - \text{RR}}, \quad (7)$$

where m_{N_2} is the specific amount of N_2 from fuel nitrogen, and $m_{\text{N}_2}^{\text{ASU}}$ is the N_2 coming from the air separation unit (ASU), calculated as:

$$m_{\text{N}_2}^{\text{ASU}} = \left(m_{\text{O}_2}^{\text{St}} + m_{\text{O}_2}^{\text{e}} (1 - \text{RR}) \right) \frac{k_{\text{N}_2}^{\text{ASU}}}{k_{\text{O}_2}^{\text{ASU}}}, \quad (8)$$

where $m_{O_2}^{St}$ is the stoichiometric amount of O_2 , $m_{O_2}^e$ is the excess amount of O_2 at the boiler outlet, $m_{N_2}^{ASU}$ is the mass fraction of N_2 at the ASU outlet, and $k_{O_2}^{ASU}$ is the mass fraction of O_2 at the ASU outlet.

The calculated gas characteristics at the boiler outlet and inlet for different LHV values are presented in Tables 2, 3 and 4. In the tables to each RFG ratio there corresponds a different amount of circulating ash, used to

Table 2. Gas characteristics at the boiler outlet and inlet for LHV = 8.4 MJ/kg

RFG ratio	kg/kg	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
At the boiler outlet										
Excess O_2 content	Nm ³ /kg	0.03	0.03	0.03	0.04	0.05	0.06	0.08	0.12	0.23
CO ₂ content	Nm ³ /kg	0.45	0.51	0.58	0.68	0.82	1.02	1.36	2.04	4.08
Nitrogen content	Nm ³ /kg	0.03	0.04	0.04	0.05	0.06	0.08	0.10	0.15	0.31
H ₂ O content	Nm ³ /kg	0.45	0.45	0.46	0.46	0.47	0.47	0.48	0.48	0.49
Flue gas amount, dry	Nm ³ /kg	0.51	0.58	0.66	0.77	0.92	1.16	1.54	2.31	4.62
Excess O_2 content	%	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
CO ₂ content	%	47.13	49.47	52.11	55.13	58.61	62.65	67.39	73.05	79.90
Flue gas amount, wet	Nm ³ /kg	0.96	1.03	1.12	1.23	1.39	1.63	2.02	2.80	5.11
CO ₂ amount	t/MWh	0.027	0.031	0.035	0.041	0.049	0.062	0.082	0.124	0.247
At the boiler inlet										
CO ₂ content	Nm ³ /kg	0.05	0.10	0.18	0.27	0.41	0.61	0.95	1.63	3.68
N ₂ content	Nm ³ /kg	0.03	0.04	0.04	0.05	0.06	0.08	0.10	0.15	0.31
H ₂ O content	Nm ³ /kg	0.01	0.01	0.02	0.02	0.03	0.03	0.04	0.04	0.05
O ₂ content	Nm ³ /kg	0.56	0.56	0.56	0.57	0.58	0.59	0.61	0.65	0.76
Total gas amount	Nm ³ /kg	0.64	0.71	0.80	0.91	1.07	1.31	1.70	2.47	4.79
CO ₂ content	%	7.08	14.38	21.94	29.83	38.11	46.84	56.12	66.05	76.74
O ₂ content	%	86.92	78.90	70.76	62.44	53.89	45.05	35.83	26.16	15.92

Table 3. Gas characteristics at the boiler outlet and inlet for LHV = 7.0 MJ/kg

RFG ratio	kg/kg	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
At the boiler outlet										
Excess O_2 content	Nm ³ /kg	0.02	0.02	0.03	0.03	0.04	0.05	0.07	0.10	0.20
CO ₂ content	Nm ³ /kg	0.39	0.44	0.50	0.59	0.71	0.88	1.18	1.76	3.53
Nitrogen content	Nm ³ /kg	0.03	0.03	0.04	0.04	0.05	0.07	0.09	0.13	0.26
H ₂ O content	Nm ³ /kg	0.39	0.40	0.40	0.41	0.41	0.42	0.42	0.43	0.43
Flue gas amount, dry	Nm ³ /kg	0.44	0.50	0.57	0.67	0.80	1.00	1.33	2.00	3.99
Excess O_2 content	%	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
CO ₂ content	%	46.87	49.18	51.80	54.80	58.26	62.31	67.08	72.79	79.75
Flue gas amount, wet	Nm ³ /kg	0.84	0.90	0.97	1.07	1.21	1.42	1.75	2.42	4.42
CO ₂ amount	t/MWh	0.028	0.031	0.036	0.042	0.050	0.063	0.084	0.125	0.251
At the boiler inlet										
CO ₂ content	Nm ³ /kg	0.04	0.09	0.15	0.24	0.35	0.53	0.82	1.41	3.17
N ₂ content	Nm ³ /kg	0.03	0.03	0.04	0.04	0.05	0.07	0.09	0.13	0.26
H ₂ O content	Nm ³ /kg	0.01	0.01	0.02	0.02	0.03	0.03	0.04	0.04	0.05
O ₂ content	Nm ³ /kg	0.48	0.48	0.48	0.49	0.50	0.51	0.52	0.56	0.65
Total gas amount	Nm ³ /kg	0.55	0.61	0.69	0.79	0.93	1.13	1.47	2.14	4.14
CO ₂ content	%	7.12	14.44	22.01	29.88	38.14	46.85	56.11	66.03	76.74
O ₂ content	%	86.76	78.63	70.42	62.08	53.53	44.72	35.57	25.97	15.83

Table 4. Gas characteristics at the boiler outlet and inlet for LHV = 10.5 MJ/kg

RFG ratio	kg/kg	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
At the boiler outlet										
Excess O ₂ content	Nm ³ /kg	0.03	0.03	0.04	0.05	0.06	0.07	0.09	0.14	0.28
CO ₂ content	Nm ³ /kg	0.54	0.61	0.70	0.82	0.98	1.22	1.63	2.45	4.89
Nitrogen content	Nm ³ /kg	0.04	0.05	0.05	0.06	0.07	0.09	0.12	0.19	0.37
H ₂ O content	Nm ³ /kg	0.53	0.54	0.54	0.55	0.55	0.56	0.56	0.57	0.57
Flue gas amount, dry	Nm ³ /kg	0.62	0.69	0.79	0.92	1.11	1.39	1.85	2.77	5.54
Excess O ₂ content	%	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
CO ₂ content	%	47.38	49.74	52.42	55.46	58.94	62.98	67.70	73.30	80.03
Flue gas amount, wet	Nm ³ /kg	1.15	1.23	1.33	1.47	1.66	1.94	2.41	3.34	6.11
CO ₂ amount	t/MWh	0.027	0.030	0.035	0.041	0.049	0.061	0.081	0.122	0.243
At the boiler inlet										
CO ₂ content	Nm ³ /kg	0.05	0.12	0.21	0.33	0.49	0.73	1.14	1.96	4.40
N ₂ content	Nm ³ /kg	0.04	0.05	0.05	0.06	0.07	0.09	0.12	0.19	0.37
H ₂ O content	Nm ³ /kg	0.01	0.01	0.02	0.02	0.03	0.03	0.04	0.04	0.05
O ₂ content	Nm ³ /kg	0.67	0.68	0.68	0.69	0.70	0.71	0.74	0.78	0.92
Total gas amount	Nm ³ /kg	0.77	0.86	0.96	1.10	1.29	1.57	2.04	2.96	5.74
CO ₂ content	%	7.02	14.28	21.84	29.73	38.02	46.78	56.08	66.02	76.71
O ₂ content	%	87.11	79.22	71.16	62.88	54.32	45.44	36.15	26.39	16.04

control the furnace temperature, as the adiabatic combustion temperature depends on both the heating value of the fuel and the concentration of O₂ and CO₂. In the current study, the amount of circulating ash was not calculated.

3. Results and discussion

The temperature in the CFB boiler furnace is maintained at 750–850 °C. Between those temperature limits, the sulfur binding process is at its maximum intensity. The bed temperature in a CFB boiler is mainly controlled by adjusting the cyclone ash recirculating ratio. The external solid heat exchanger(s) is(are) used to extract heat from the combustion process/recirculating ash. This extraction allows a significant reduction of the amount of recycled flue gas required for combustion temperature control in the case of oxy-fuel combustion. This feature can be used to reduce the RFG ratio in the CFB during the retrofitting to oxy-mode combustion [24].

Applying the assumed initial conditions, the calculated contents of CO₂ and O₂ in the gas at the inlet of the boiler at different RFG ratios are shown in Figure 2. The oil shale was found to contain a large fraction of carbonate minerals, mainly calcite CaCO₃. The reduction of the carbonate mineral decomposition increases the conditional heating value of oil shale and reduces the CO₂ emission. The calcite decomposition is suppressed when the CO₂ partial pressure exceeds the equilibrium state line of the calcite decomposition reaction at a given temperature [36]. For a bed temperature of 850 °C, the equilibrium pressure of CO₂ is ca. 60 kPa. According to Figure 2

the RFG ratio should be maintained at a level higher than 0.7 to achieve the partial pressure of CO_2 over equilibrium. Under these conditions, ECD decreases, and it is defined by Equation (4) $k_{\text{CO}_2-\text{min}}$ minimum. According to Equation (4) $k_{\text{CO}_2-\text{min}}$ minimum, the decrease of ECD would be observed from $k_{\text{CO}_2} = 0.7$ (the mean value in CFB in air mode) down to $k_{\text{CO}_2-\text{min}} = 0.28$, depending on LHV. The decrease of k_{CO_2} leads to an additional increase in the amount of heat released during oil shale combustion per 1 kg and, depending on the mean LHV, it can amount up to 0.34 MJ/kg. The calculations and estimations are based on the calculation method by Arro et al. [33, 34].

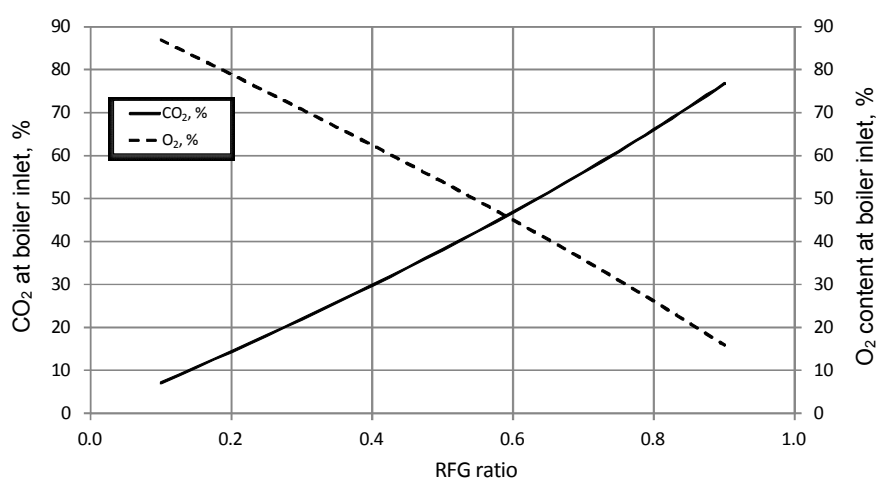


Fig. 2. CO_2 and O_2 content at the boiler inlet at different RFG ratios.

The specific flue gas volume per 1 kg oil shale for different values of LHV and different RFG ratios is shown in Figure 3. On the same plot, the specific gas volumes occurring during air mode combustion are depicted. From Figure 3 it is clear that to obtain in oxy mode the same gas volume as in the conventional mode, the RFG ratio should be maintained at 83.

Figures 4 and 5 depict the specific content of CO_2 per 1 kg oil shale and per fuel energy of oil shale at the boiler outlet for different LHV values and RFG ratios, respectively. For comparison, on the same plot, the calculations of the specific content of CO_2 per fuel energy for bituminous coal and anthracite are shown. These calculations were performed using the proximate and ultimate fuel analysis found in [37, 38]. From Figure 5 it can be seen that the specific CO_2 for selected coals is slightly higher than that for oil shale. This behavior could be explained by the high hydrogen-to-carbon ratio in oil shale and the additional reduction of carbonate minerals decomposition in oil shale due to the increased partial pressure of CO_2 . The

difference of the specific CO_2 could be additionally increased due to the addition of lime to the coal in the direct desulfurization process.

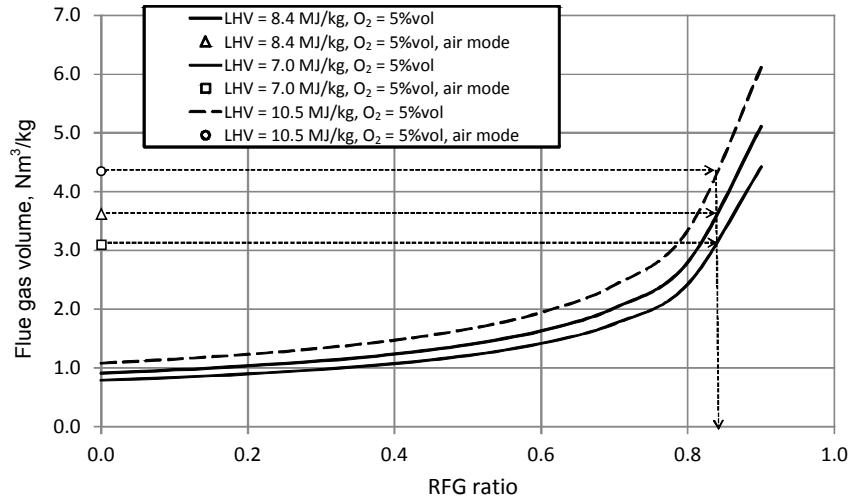


Fig. 3. Flue gas volume per 1 kg oil shale at different RFG ratios in oxy mode.

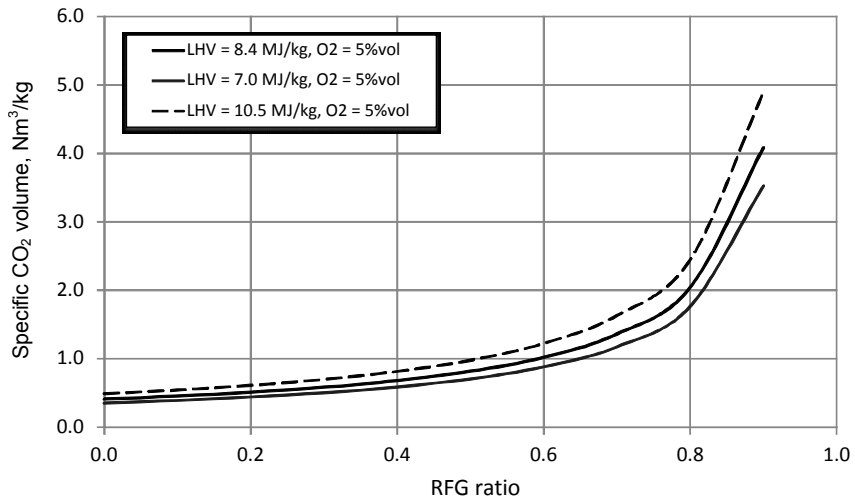


Fig. 4. Specific CO_2 volume at the boiler outlet for different oil shale LHV values and RFG ratios in oxy mode.

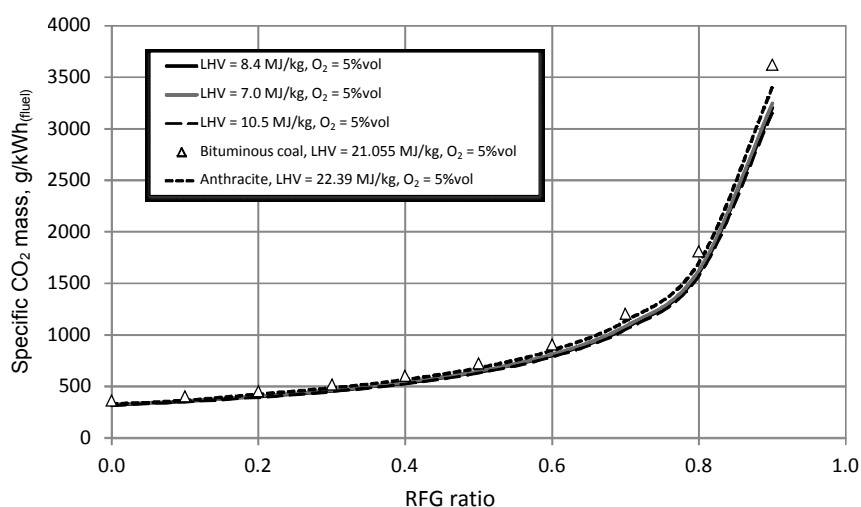


Fig. 5. Specific CO₂ emission per fuel energy at the boiler outlet for different oil shale LHV values and RFG ratios in oxy mode.

4. Conclusions

The gas volume calculations for oil shale combustion applying oxy-fuel technology in a circulated fluidized bed environment for different oil shale LHV values and different recycled flue gas ratios were performed. It was found that to minimize ECD, the recycled flue gas ratio should be maintained at a level higher than 0.7. This condition allows for an increase of the partial pressure of CO₂ over the equilibrium state line of the calcite decomposition reaction at the bed temperature. The decrease of ECD would be observed down to $k_{\text{CO}_2-\text{min}} = 0.28$. The decrease of k_{CO_2} leads to an additional increase in the amount of heat released during oil shale combustion per 1 kg and, depending on the mean LHV value, it could be as high as 0.34 MJ/kg.

The calculations indicated that to obtain in oxy mode the same gas volume as in the conventional mode, the RFG ratio should be maintained at 83.

The comparison with the bituminous and anthracite coals indicates that the specific emission of CO₂ per input fuel energy for oil shale could be expected to be even smaller than that of the considered coals.

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