



The combustion of dry lignite under Oxy-fuel process conditions in a 0.5 MW_{th} test plant

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Abstract

For the testing of the oxy-fuel process, an 0.5 MW_{th} test facility of the technical institute CEBra, Centre for Energy Technology Brandenburg e. V has been in operation within a two-year trial period in cooperation with VE-G and EVN AG. A stable operation under oxy-fuel condition with lignite and hard-coal could be demonstrated. During the operation a high CO₂-concentration of 92 Vol.-% in the dry flue-gas could be achieved. Further a high influence of the variation of the oxygen distribution in front of the furnace on the formation of NO_x was detected.

By the usage of CaCO₃ during the combustion a high reduction of SO₂ could be achieved under Oxy-fuel conditions. The flue gas condenser has a stable operation without slagging. The moisture content of the flue gas was reduced to 3 Ma.-% and a high potential for SO₂-removal by the condensing process was detected.

The burning rate under Oxyfuel-Conditions varies considerably from that of air combustion. Experimental results focused on the influence of gas composition to combustion time and combustion rate of the fuels are presented. They indicate that a substitution of nitrogen by CO₂ in the gas composition yield a reduction of combustion time. High CO₂-concentrations in the combustion gas affect the conditions of the chemical reaction complex so that the Boudouard-reaction becomes more important.

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combustion; oxy-fuel; flue gas condenser; combustion rate; desulphurization; recirculated

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1. Introduction

Due to climatic and political reasons, future coal-fired power plants are to be built on the basis of the CCS (Carbon Capture and Storage) technology. With this technology, the resulting climate-harmful CO₂ from the combustion of fossil fuels is separated and subsequently placed in a suitable storage site or fed for further material use.

The CO₂ separation can be done in three different ways:

- Before combustion (Pre-combustion)
- After combustion (Post-combustion)
- CO₂ enrichment > 90% in the flue gas - followed by separation (Oxy-fuel)

The oxy-fuel process combines the advantages of a simple design process of combustion with the highest CO₂ capture potential. The availability of the oxy-fuel process should be highly similar to conventional power plants. In addition, this technology has a high efficiency potential.

For the testing of the oxy-fuel process, an existing 0.5 MWth test facility of the technical institute CEBra, Centre for Energy Technology Brandenburg e. V. was upgraded in 2005 in cooperation with Alstom Power Boiler, Vattenfall Europe Generation (VE-G) and the Chair of Power Plant Technology (BTU Cottbus) and the key components (oxygen supply, flue gas condenser) for the oxy-fuel processes were enhanced. Subsequently, the process has been investigated within a two-year trial period in cooperation with VE-G and EVN AG. The main findings of this trial period are presented in this article.

2. Research on Oxyfuel Process

2.1. Plant description

The oxy-fuel process is thereby characterized such that, the combustion is realized with a gas mixture of pure oxygen and the recirculated flue gas from the combustion. For that purpose, pure oxygen (99.95 Vol.-%) is supplied from a tank and mixed with dedusted, hot flue gas before the combustion chamber at the test facility. This gas mixture which shows similar oxygen content as air is channelled to the primary and secondary air levels in the combustion chamber.

The high fraction of flue gas which is returned to the combustion chamber leads to an enrichment of CO₂, water vapour and sulphur dioxide in the flue gas.

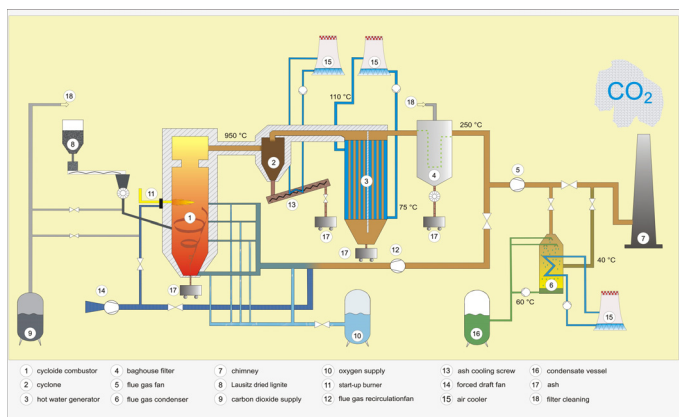


Figure 2.1: Layout of the 0.5 MWth test facility

After the separation of water vapour (and the consequent separation of sulphur dioxide) in a newly developed flue gas condenser (FGC), an exhaust gas from combustion which consists of almost CO₂ exclusively is produced.

The combustion (of Lusatian dry brown coal or Polish hard coal) is carried out in an adiabatic combustion chamber (1) after the cycloid firing principle at temperatures between 950°C and 1.000°C. The hot flue gas is cooled down to about 250°C in a heat exchanger (3) after dedusting in a cyclone (2). After the subsequent ash removal in the externally heated bag house filter (4), the flue gas flow is split into part of the combustion chamber (75%) and part of the FGC (6). In the FGC, which is built between the induced draft (ID) fan (6) and the stack (7), the flue gas is cooled down from 250°C to about 40°C whereby the water vapour condenses out.

2.2. Research program

For the characterization of the oxy-fuel process, a research program was developed in cooperation with VE-G and EVN in which the key process parameters,

- Mass flow rate of flue gas and oxygen,
- Flue gas composition (O₂, CO₂, H₂O, CO, NO, SO₂),
- Flue gas temperature and pressure

were to be determined and evaluated.

The main focus of the research program at the 0.5 MW test facility were to:

- achieve highest possible CO₂ concentration in the flue gas,
- minimise the formation of emissions (NO, SO₂, CO) through primary firing technique measures,
- minimise SO₂ concentration by the addition of desulphurization additives in the combustion chamber,
- determine the operating parameters of the FGC.

The investigations were carried out with the Lusatian dry lignite (water content = 19%) and the Polish hard coal.

3. Execution of the tests and tests results

The execution of the tests and the test results of the research program as described in chapter 2 are introduced and discussed below.

3.1. Execution of the tests

The execution of the measurement campaigns was carried out on daily tests with the duration of about 12 h. After heating up of the combustion chamber by means of the 200 kW liquid-gas burner the lignite fire was ignited and than shifted to oxy-fuel operations. The duration of the shift on the interim operating condition - fresh air and flue gas operations (50% FA und 50% FG) amounts to approximately 1.5 h.

To test on the effect of different oxidants composition (OC) and the distribution of oxygen (OD) in primary air (PA) and secondary air (SA) on the formation and reduction of emissions NO, SO₂ and CO, the appropriate desulphurization of the ash and dry desulphurization with Calcium Carbonate (CaCO₃) the following settings are taken:

- | | | |
|--|----------------|----------|
| 1. O ₂ content in combustion chamber | 3 – 4 Vol.-% | (OC 1), |
| 2. O ₂ content in combustion chamber | 7 – 8 Vol.-% | (OC 2), |
| 3. O ₂ content in combustion chamber | 10 – 11 Vol.-% | (OC 3). |
| a. without O ₂ distribution | | (w. OD), |
| b. O ₂ content in PA and in the SA1 same size | | (OD 1), |
| c. O ₂ content in PA greater than in the SA1 | | (OD 2), |
| d. O ₂ content in PA smaller than in the SA1 | | (OD 3). |

The distribution of the oxidation substance to PA and SA is carried out with the aim of achieving a homogenous temperature profile in the combustion chamber in the range between 950°C and 1.000°C.

For the testing of dry desulphurisation, CaCO₃ is mixed with the lignite in the fuel transport system. The amount can be adjusted exactly through a separate additive-metering system.

3.2. Flue gas composition

3.2.1. Flue gas constituents CO₂, O₂, H₂O

To keep the energy input for flue gas cleaning and accumulation of CO₂ for subsequent use as low as possible, the CO₂ concentration has to be maximised and the emissions minimised during the combustion process. Determining for the oxy-fuel process is a maximum CO₂ concentration in the flue gas. This value is influenced by two factors during a stationary plant operation. Firstly, by an oxygen excess and secondly by part of the leakage air which leads to the unwanted dilution of the flue gas with atmospheric nitrogen. High CO₂ concentrations are there only to achieve minimal oxygen excess (OC 1). The ratio of the infiltrated air on the leakages in the test facility (e.g. rotary seal for the fuel gas and the combustion chamber) is to be reduced and is dependent on the low-pressure in the test facility.

In a full-load operation, CO₂ concentrations from 92.15 Vol.-% with an oxygen concentration of 3.24 Vol.-% in dry flue gas could be reached. Taking into consideration the concentrations of the gas components SO₂, NO and CO results to a residual-N₂ concentration of about 4 Vol.-%. This value corresponds to a leakage air mass flow of 10 kg/h and a leakage air ratio of 1.1 Ma.-% in relation to re-circulated flue gas mass flow.

Besides CO₂, water vapour is the second largest component in the flue gas and depending on the fuel moisture accounts for up 30 Vol.-%. To achieve high CO₂ concentrations, the water vapour fraction has to be reduced by cooling of the flue gas in the FGC. In the FGC, the flue gas is dried to about 5.5 Vol.-% of moisture. A further cooling and drying of the flue gas is not possible under current or existing designs.

The changes in oxygen concentration in the combustion chamber (3 to 10 Vol.-%) has a large influence on the operation of the test facility under air and flue gas conditions on the formation and reduction of emissions of NO and SO₂. The oxy-fuel process is associated with a high oxygen surplus, high energy for oxygen supply and the subsequent separation of oxygen from the flue gas and should be minimized for to save energy. The effects of the changes in oxygen concentration and distribution on the emissions are discussed in the following chapter.

3.2.2. Flue gas components NO, SO₂ and CO

When considering measured concentrations of SO₂ and NO in the flue gas in the combustion chamber (Fig. 3.2.1 and 3.2.2), there is a dependency on the set oxidants composition OC 1 to OC 3 without detecting OD. With increasing oxygen concentration, the concentrations of NO and SO₂ also increase.

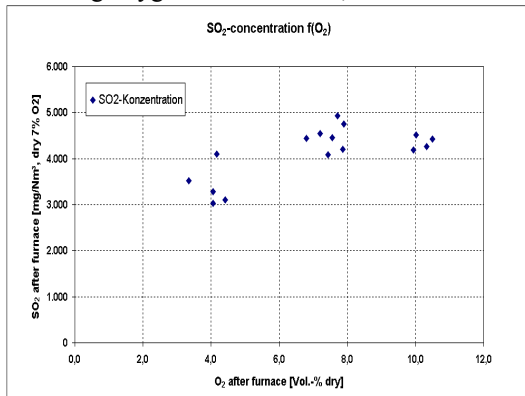


Fig. 3.2.1 SO₂ emission

Furthermore, there is a clear noticeable dependency between the ratio of the oxygen concentration in the primary and secondary air levels (OD 1 to OD 3) and the NO concentration. A lower O₂ concentration in the PA as in the SA1 works to reduce the formation of NO. The formation of CO does not depend as far as possible on the realized oxygen surplus and oxygen distribution (Fig. 3.2.3). The drop in oxygen concentration in the PA and the joint reduction in NO concentration can be realized up to a minimum concentration of 14 Vol.-%. Below this value no stable plant operation is possible.

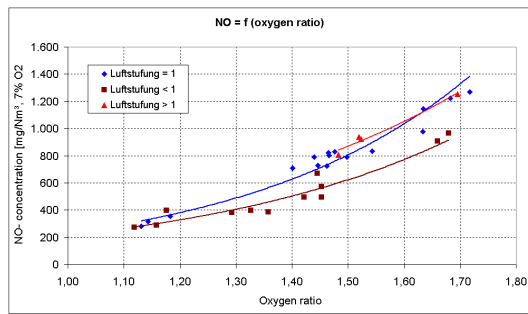


Fig. 3.2.2: NO emissions

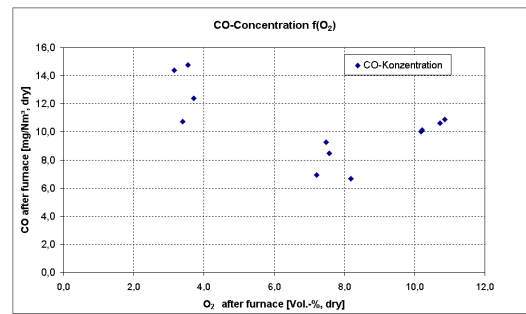


Fig. 3.2.3: Emissions behavior of CO

The changes in oxygen concentration and oxygen distribution are optically and clearly observable from the picture of the flame (Fig. 3.2.4). By the setting to OC 1, a flameless burning can be realized. By changing-over to OC 2 and OC 3 an increase in the formation of flame spikes is visible. At high oxygen concentrations in the primary air, vigorous flame spikes can be seen. By reducing the oxygen to lower concentrations, the flame spikes reduce to a flameless combustion. The combustion behaviour develops independent of the driven oxygen concentration in the combustion chamber. The known low-emission, flameless combustion from fresh-air combustion could also be realized under oxy-fuel conditions.



Fig. 3.2.4: Photo of oxy-fuel flame, OC 1, OC 2, OC 3 (f. r t. l)

For an optimal operation of the test facility i.e. maximum CO₂ concentration with minimum concentrations of SO₂ and NO, there is a staged combustion (OD 3) with an oxygen surplus of 3 Vol.-% (OC 1) to be realized.

3.3. Dry Desulphurization with calcium carbonate in the combustion chamber

In addition to technical combustion measures (e.g. oxygen distribution), is the use of desulphurization additives during firing for an effective possibility to reduce SO₂. By removing SO₂ during combustion, the corrosion problem in the subsequent reduced flue gas path and the FGC in which SO₂ among others are been washed-out will be balanced.

The flow guide, the lower combustion chamber temperature of 950°C to 1.000°C, the long residence time of the flue gas and the ash in the combustion chamber are favourable for the desulphurization. That is how the dry desulphurization with calcium carbonate (CaCO₃) is been carried out with combustion on fresh air and air/flue gas conditions for the desulphurization efficiency of up to 60% with Ca/S ratio of 1.9.

It could be proven that, under oxy-fuel conditions through the addition of CaCO₃ the SO₂ concentration is reduced by a factor of 4 with a Ca/S ratio of 2 (Fig. 3.3.1). The high desulphurization efficiency by oxy-fuel operations as opposed to fresh air operation is justified by the fact that, the pollutants which are removed before recirculation cannot be augmented in the process.

3.4. Flue gas condenser

With the help of the FGC the contained water vapour is liquefied and removed by cooling of the flue gas. The following 2 processes run in the flue gas condenser.

1. Cooling and saturation of the flue gas with recirculated condensate after entry in the condenser (Quenching).
2. Cooling of the flue gas and condensate over a cooled tube heat exchanger to < 40°C.

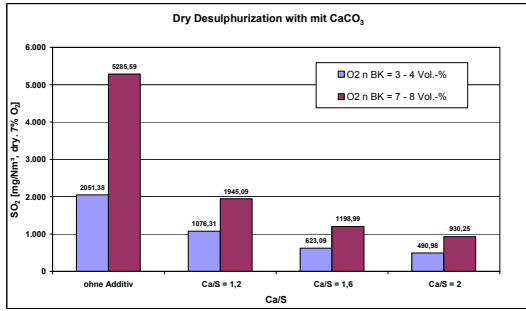


Fig. 3.3.1: Dry desulphurization under oxy-fuel conditions

3.4.1. Flue gas humidity

The flue gas humidity is determined at the inlet and outlet of the flue gas condenser. At the inlet of the flue gas condenser, humidity of up to 30.5 Vol.-% is measured. Humidity of 53 Vol.-% occurs at the outlet. Through condensation, about 50 kg/h of condensate accrues. The composition of the condensate for further use and disposal of great interest and is examined separately in chapter 3.4.3.

3.4.2. Desulphurization efficiency

By the condensation of the water vapour contained in the flue gas, part of the sulphur dioxide from the flue gas is washed out. In connection with the condensed water vapour a sour condensate is formed, which is highly corrosive on the materials of condenser. For the neutralization of this sour condensate and thereby the reduction of corrosion, sodium hydroxide (30 %) is continuously added to the condensate. The pH value to be regulated is preset through the control system. By the addition of sodium hydroxide, the SO₂ in the flue gas reacts with it to form sodium sulphate. In addition to this reaction, CO₂ also reacts with the sodium hydroxide to form sodium carbonate. This undesired reaction leads to the consumption of sodium hydroxide.

To determine the effect of the pH value on the flue gas composition, the pH values are varied as follows during the series of measurement:

- operation without the addition of NaOH,
- pH value between 2 and 4,
- pH value between 5 and 6.

When switching on the condenser without the addition of NaOH a huge drop in the concentration of SO₂ and the pH value could be detected (Fig. 3.4.1).

When operating the condenser with a pH value of 2 to 3, there is almost no separation of SO₂ from the flue gas to be noticed. With a pH of 4.0 to 4.3, the SO₂ concentration drops to less than 2000 mg/Nm³. A further decrease in the pH value to 5-6 leads to an almost complete separation of SO₂ from the flue gas (Fig. 3.4.2).

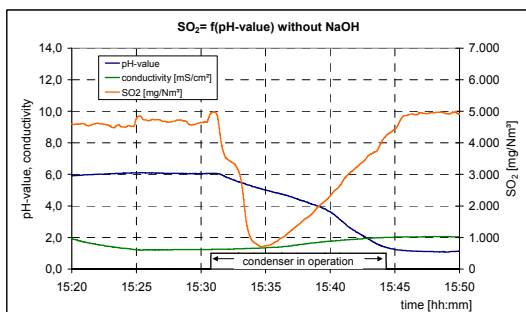


Fig. 3.4.1: SO₂ in the FGC without NaOH addition

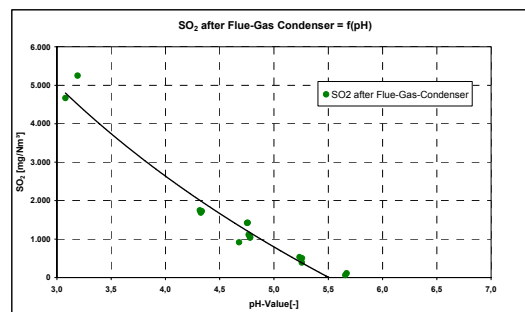


Fig. 3.4.2: SO₂ concentration in the FGC vs. pH value condensate

The influence of the FGC on the CO₂ concentration cannot be determined through gas analysis because the amount of CO₂ which is attached through the condensate will lie within the variation limit of the gas analyzer. The amount of attached CO₂ can only be determined through a condensate analysis (Fig. 3.4.3).

3.4.3. Condensate analysis

High concentrations of sodium, calcium and sulphate very are measured in the condensate which can be explained through the addition of sodium hydroxide and the separation of gaseous SO₂. The high concentration of calcium is ordinated from the ashes that will be separated in the condenser. Furthermore, cations which are not to be expected in brown coal are measured. For that purpose, chromium and nickel are used which exhibit a concentration of 2.9 and 2.0 mg/l respectively.

It was also investigated over a test period of 6 hours how the concentrations of sodium, sulphate, hydrogen carbonate (HCO₃) and dissolved CO₂ change. The pH value for the test period is set to 4-5. The results of the laboratory investigations show a continuous increase of all the investigated ions with an exception of HCO₃ ions (Table 3.4.1 and Fig. 3.4.3).

Table 3.4.1: Condensate analysis

time	pH-value	Na [mg/l]	CO ₂ [mg/l]	SO ₄ [mg/l]	Ca [mg/l]	HCO ₃ [mg/l]
12:00	5,23	2622	53	6200	305,6	9,2
14:00	4,11	3424	869	8544	584,4	< 1,0
16:00	5,12	4325	1241	11000	878,4	27,5
18:00	4,18	5363	1522	13890	1144,4	< 1,0

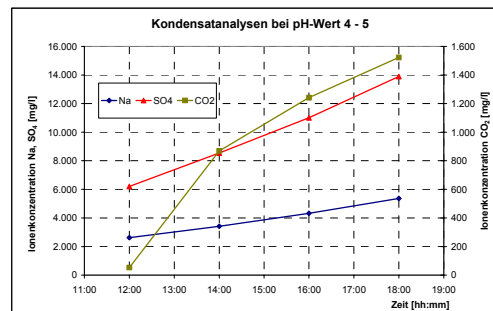


Fig. 3.4.3: Concentration of sodium, sulfate and dissolved CO₂

After two hours a complete saturation of the condensate with CO₂ is reached. Due to high CO₂ partial pressure in the condenser, CO₂ is further dissolved. After four hours of the test period an over saturation of CO₂ is detected the condensate.

The formation of HCO₃ from CO₂ and condensate is like the formation of SO₄ dependent on pH value. HCO₃ is formed at a pH value > 5 and leads to an increased consumption of NaOH for the adjustment of a constant pH value.

For an optimized operation of the FGC with respect to a high separation of SO₂ and a lower separation of CO₂ (dissolved as HCO₃), a pH value of about 5.0 should be used.

3.4.4. Soiling tendency of the flue gas condenser

The condenser is located behind the bag house filter. Therefore, a lower ash load is anticipated during operation. Furthermore, the condenser comes with a self cleaning function. For the cooling of the flue gas condensate is injected in the flue gas by nozzles at the head of the condenser. A liquid film is formed, which solves the possible disposal on the underneath lying heat exchanger pipes. This liquid flow is increased in the flow direction through additional occurring condensate. In the region between the condensate nozzles and the process tank no soiling could be detected.

4. Comparison of the Combustion Time of char in air and O₂/CO₂-atmospheres

The gas composition under Oxyfuel-Conditions varies from the combustion with air. Hence experimental tests using a thermo gravimetric analysis reactor were carried out. The combustion behavior of a predried lignite (water: 10,7%, ash: 12,1%, volatiles 49,0%, carbon: 28,2%) was investigated. Beside air a gas consisting of 21/79 Vol.-% O₂/CO₂ was used. In order to realize high heating rates the probe was given directly into the preheated combustion

reactor. For comparison the measured combustion times were normalized to 100 mg. The resulting standardized combustion times are shown in figure 4.

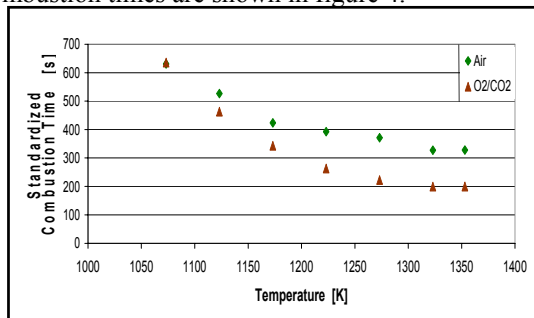


Fig. 4: Standardized Combustion Time at different Temperatures for air and O₂/CO₂ atmospheres

With increasing combustion temperatures the combustion time decreases. Despite the same oxygen concentrations in the combustion gas the combustion time in an O₂/CO₂-atmosphere is apparently shorter than in air for temperatures higher than 1100K. Whereas in air only oxygen acts as a reactant in an O₂/CO₂-atmosphere the carbon dioxides reacts with the carbon as well. Especially in oxygen lean atmospheres as occurring on the bottom of the combustion crucible the Boudouard reaction increases the mass lost of char as registered.

These results show that the reaction mechanism are affected by the O₂/CO₂ atmosphere. Thus, the combustion behavior will be examined under close to reality conditions in a new laboratory test rig (ALVA 20) so that either high heating rates and turbulent gas flows are considered.

5. Conclusion and prospects

In the past two years extensive research was carried out with the application of DBC and hard coal under oxy-fuel conditions. In regards to the reduction of emissions NO and SO₂ consistent positive impacts are made of the staged combustion and the addition of dry desulphurization additives in the combustion chamber. By the implementation of staged combustion the reduction of NO concentration also under oxy-fuel conditions is realizable.

The addition of calcium carbonate as a desulphurization additive leads to a reduction of SO₂ by a factor of 4 during combustion under oxy-fuel conditions. The test results obtained for DBC are transferable to hard coal by trend on the combustion.

The used FGD conforms to the test facility - reliably the task to separate the water vapour to an absolute humidity of approximately 5 Vol.-% and at the same time an almost complete separation of SO₂ by the addition of sodium hydroxide for the necessary neutralization of the condensate. Through the self cleaning effect of the condensate injection at the head of the condenser no soiling as well as slagging of the interior has been detected up till now.

With regards to the realization of commercial power plants after the oxy-fuel process a FGD from the above described design in combination with a continuous dry desulphurization within the steam generator could reduce consistently high SO₂ concentrations and the associated corrosion properties of the flue gas.