

CZECH TECHNICAL UNIVERSITY IN PRAGUE

FACULTY OF MECHANICAL ENGINEERING

DEPARTMENT OF ENERGY ENGINEERING

DISSERTATION THESIS STATEMENT

Desulphurization during oxyfuel combustion in a  
fluidized bed

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Doctoral study programme: Mechanical Engineering

Field of study: Power Engineering

Supervisor: *doc. Ing. Jan Hrdlička, Ph.D.*

Dissertation thesis statement for obtaining the academic title of “Doctor”,  
abbreviated as "Ph.D."

Prague

February, 2019

Title in Czech language:

Odsiřování při oxyfuel spalování ve fluidní vrstvě

This dissertation is an outcome of a full-time doctoral study programme at the Department of Energy Engineering, Faculty of Mechanical Engineering, Czech Technical University in Prague.

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The thesis was send out on: .....

The defence of the dissertation thesis will take place on:

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# 1. Introduction

Energy production from the combustion of fossil fuels is accompanied by the formation of gaseous emissions. For several decades, there have been discussions about climate change caused by the production of greenhouse gases, and efforts are being made to reduce their production as much as possible. The most important greenhouse gas being discussed in this time is carbon dioxide  $\text{CO}_2$ , the product of oxidation of carbon from fossil fuels.

The fossil fuels have and in future decades will have the irreplaceable role in an energy mix and the role of coal will stay very important. Coal is the most frequently used source for heat and electricity production. About 47% of electricity produced in the Czech Republic comes from coal combustion. The Czech Republic accepted SET plan in 2007, which is a complex of steps leading to lowering greenhouse emission production in EU in order to start research of new so called clean technologies. The Czech Republic is also committed to the EU Directive known as Strategy 20 20 20, which includes reducing greenhouse gas emissions in 2020 by 20% compared to 1990. [1]

## Motivation and scope of the dissertation

CCS technologies (Carbon Capture and Storage, or Carbon Capture and Sequestration) are one of the main approaches for the reduction of carbon dioxide emissions from stationary energy sources. Oxyfuel combustion belongs to this group of technologies with the potential to become so called near zero  $\text{CO}_2$  emission combustion technology [2]. Oxyfuel combustion is a process, which uses pure oxygen as the oxidant during combustion instead of air for fuel combustion. However, using just pure oxygen would lead to too high combustion temperatures and thus the recirculated flue gas must be used in order to supply sufficient amount of heat carrier and decrease the combustion temperatures. The result is a flue gas with high concentration of  $\text{CO}_2$ .

Due to its relatively simple technology design and operation, the oxyfuel combustion can be considered as one of the most promising CCS technologies [3]. For the same reason, it can be reasonably applied no smaller power production capacities, as opposed to other CCS technologies. Current oxyfuel research focuses mainly on pulverized coal combustion, or circulating fluidized bed combustion. Worldwide, there are several laboratory and pilot experimental facilities aimed at circulating fluidized bed and pulverized coal combustion. A few investigations have been made in the field of bubbling fluidized bed combustion, which is more suitable for lower power capacities and for wider range of fuels including low quality fuels.

One of the main advantages of the fluidized bed combustion is the possibility of sulphur dioxide removal directly in the furnace during combustion in a

relatively easy and cheap way, by infusing an additive – limestone to the combustion chamber [4]. This method of direct flue gas desulphurization is known and well described method in air combustion. However, oxyfuel combustion is characterized by absolutely different combustion conditions and the desulphurization is highly affected. Lowering of  $\text{SO}_2$  concentration is an important factor in the oxyfuel process, because  $\text{SO}_2$  have impacts in the furnace, during ash collection,  $\text{CO}_2$  compression and transport as well as storage.

In a boiler under oxyfuel firing combustion, the concentration of  $\text{SO}_2$  is higher throughout the process and it causes the water wall corrosion in the furnace. Enhanced oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  has an impact on ash deposits in the convective part. Additionally, it negatively affects the SCR, which needs to be installed for  $\text{NO}_x$  reduction, by formation of ammonium bisulphate, thus deactivating the SCR catalyst. In cooler sections, it forms liquid  $\text{H}_2\text{SO}_4$  with high corrosion potential.  $\text{SO}_2$  has negative impact on the  $\text{CO}_2$  compression, and there are discussions about the transport, where the transport type and route will affect required  $\text{SO}_x$  regulations and economics. Some toxicological questions are associated with potential leakages from underground storage. Although no  $\text{SO}_2$  legislation for pipeline or sequestration is currently drawn, it is necessary to know the process of desulphurization and to be able to work within the emissions limits which may be set. It is necessary to consider the risks between pipeline corrosion, toxicological risks of leakage, mineral reactions in sequestration and economic disincentives from over the stringent specifications. [5]

The facts mentioned above present clear evidence for the need to experimentally verify the possibilities of using a direct desulphurisation method for oxyfuel combustion in bubbling fluidized bed boilers and to determine the influences of individual operating parameters on desulfurization efficiency.

## 2. The goals and contributions of the dissertation

The dissertation thesis focuses on oxyfuel combustion in bubbling fluidized bed boilers and **the main goal is to study the process of direct desulphurization during oxyfuel combustion and compare it with the desulphurization process under air combustion.**

The most important contribution and novelty of the thesis is experimental verification of the desulphurization process during oxyfuel combustion in bubbling fluidized bed combustors under real combustion and operation conditions, which is in contrast to the majority of other research which has been made on this topic so far conducted mainly in laboratory conditions or with simulated atmospheres. In order to achieve the main goal of the thesis a suitable experimental facility has to be designed. Moreover the experiments will be run also on the already existing 500 kWt pilot bubbling fluidized bed boiler; this one has to be reconstructed and modified so that it is able to operate under oxyfuel regime. Using two experimental facilities gives another benefit in terms of the possibility of scaling up the results. The results from the experiments should show the pros and cons of the oxyfuel conditions on the desulphurisation process. The main factors influencing the desulphurization process will be defined and optimization of the process will be done.

The individual objectives of the dissertation thesis are summarized in the following points:

- 1) Theoretical analysis of oxyfuel combustion and its mathematical balance model with the specification on combustion in bubbling fluidized bed boilers and comparison with combustion under air conditions.
- 2) Design of the experimental facility with the power output about 30 kWt, suitable for working under air and oxyfuel combustion and modification of the bigger 500 kWt BFBC pilot boiler to be able to operate under oxyfuel regime.
- 3) Experimental validation of the mathematical balance model of oxyfuel combustion.

Previous steps are important and necessary in order to reach the main goal of the dissertation thesis which is defined as:

**Describe and compare the process of SO<sub>2</sub> capture during bubbling fluidized bed combustion under air and oxyfuel conditions and study the effect of scaling up the experiments from lab-scale facility to pilot scale BFBC.**

### 3. Theoretical analysis of the oxyfuel combustion

Oxyfuel combustion and air combustion use different volumes of all streams of gases, which is shown in Figure 1. All streams in this figure corresponds to the ratio of the real flows (normal cubic meters per kg of fuel).

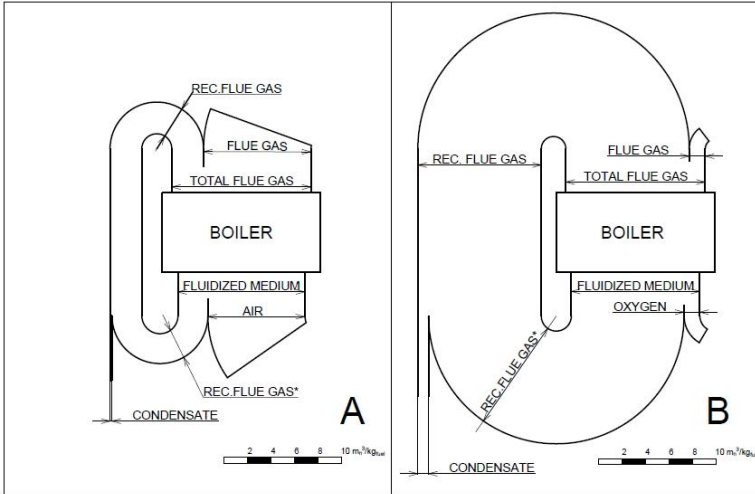


Figure 1: A comparison of the volume flow of all streams of gases for combustion with air (A) and with oxygen (B) [I, II]

#### Methodology for stoichiometric calculations [III, IV]

Stoichiometric calculations are volumetric calculations. They are used to determine the amount of oxidant required to burn a unit amount of fuel, and to determine the volume of the flue gases that arise. Stoichiometric calculations are based on chemical reaction equations and the balance of the amount of substance. In general, we consider two basic models here - a complete combustion model, and an incomplete combustion model. Although the incomplete combustion model is more appropriate, the complete combustion is used in most model technical applications, and it is also used here. [6]

By using this methodology it is possible to calculate the balances of all volume streams – volume of oxidant  $V_{O_2}$ , volume of flue gas  $V_{FG}$ , volume of flue gas recirculation  $V_{REC}$ , total volume of flue gas  $V_{TFG}$  and volume of fluidization medium  $V_{FM}$ . The list of equations used for calculation of the volume flows and balances is stated in Table 1.

Table 1: List of equations for calculation the volume flows in the boiler [III, IV]

	Volume of oxidant	Volume of flue gas	Volume of recirculated flue gas	Total volume of flue gas in the boiler	Volume of fluidization medium
$V_{\dots O_2}$	$\alpha \cdot 22.39 \cdot \left( \frac{C^r}{12.01} + \frac{H^r}{4.032} + \frac{S^r}{32.06} - \frac{O^r}{32} \right)$	$\frac{\alpha - 1}{\alpha} \cdot \omega_{O_2} \cdot V_{O,D}$	$r \cdot V_{FG,O_2}$	$V_{FG,O_2} + V_{REC,O_2}$	$V_{O,O_2} + V_{REC,O_2}$
$V_{\dots H_2}$	$\alpha \cdot \omega_{H_2} \cdot V_{O,D,min}$	$\frac{22.4}{28.016} \cdot N^r + V_{O,N_2}$	$r \cdot V_{FG,H_2}$	$V_{FG,H_2} + V_{REC,H_2}$	$V_{O,H_2} + V_{REC,H_2}$
$V_{\dots CO_2}$	$\alpha \cdot \omega_{CO_2} \cdot V_{O,D,min}$	$\frac{22.26}{12.01} \cdot C^r + V_{O,CO_2}$	$r \cdot V_{FG,CO_2}$	$V_{FG,CO_2} + V_{REC,CO_2}$	$V_{O,CO_2} + V_{REC,CO_2}$
$V_{\dots Ar}$	$\alpha \cdot \omega_{Ar} \cdot V_{O,D,min}$	$V_{O,Ar}$	$r \cdot V_{FG,Ar}$	$V_{FG,Ar} + V_{REC,Ar}$	$V_{O,Ar} + V_{REC,Ar}$
$V_{\dots SO_2}$	$\alpha \cdot \omega_{SO_2} \cdot V_{O,D,min}$	$\frac{21.89}{32.06} \cdot S^r + V_{O,SO_2}$	$r \cdot V_{FG,SO_2}$	$V_{FG,SO_2} + V_{REC,SO_2}$	$V_{O,SO_2} + V_{REC,SO_2}$
Total volume of dry gas	$\sum_i V_{O,i}$	$\sum_i V_{FG,i}$	$\sum_i V_{REC,i}$	$\sum_i V_{TFG,i}$	$\sum_i V_{FM,i}$
$V_{\dots H_2O}$	$V_{O,W} - V_{O,D}$	$V_{FUEL,H_2O} + V_{D,H_2O} - C$	$V_{REC,W} - V_{REC,D}$	$V_{FUEL,H_2O} + V_{O,H_2O} + V_{REC,H_2O}$	$V_{O,H_2O} + V_{REC,H_2O}$
Total volume of wet gas	$\kappa \cdot V_{O,D}$	$V_{FG,D} + V_{FG,H_2O}$	$\frac{V_{REC,D}}{1 - \omega_{H_2O}}$	$V_{TFG,D} + V_{TFG,H_2O}$	$V_{FM,D} + V_{FM,H_2O}$
Minimum volume of oxidant			$V_{O,min} = \frac{V_{O,O_2}}{\omega_{O_2}} = \frac{22.39 \cdot \left( \frac{C^r}{12.01} + \frac{H^r}{4.032} + \frac{S^r}{32.06} - \frac{O^r}{32} \right)}{\omega_{O_2}}$		
Volume of water vapour arisen only by combustion of the fuel			$V_{FUEL,H_2O} = \frac{44.8}{18.016} \cdot H^r + W^r$		
Coefficient for reduction of water vapour in case of condensation			$C = \frac{r \cdot \left( V_{FUEL,H_2O} + V_{O,H_2O} - \frac{\omega_{H_2O} \cdot V_{FG,D}}{1 - \omega_{H_2O}} \right)}{r + 1}$		
Values $f$			$O_2, N_2, CO_2, Ar, SO_2$		



#### 4. Theoretical application of oxyfuel combustion in a BFB

The methodology of theoretical calculation based on stoichiometric calculation, presented in detail in the doctoral thesis, was used for verification of oxyfuel combustion in BFB. The fuel used for the calculation was the same as was used for the experiments. In order to predict the possibility of usage the oxyfuel combustion in BFB, two main conditions should be met:

- the produced heat in the furnace should be similar to the air combustion in order to ensure the stability and quality of the combustion and reaching the required fluidized bed temperature
- the hydrodynamic characterisation of the fluidized bed should be similar to air combustion in order to ensure stable fluidization regime

The verification of the oxyfuel combustion was thus based on finding such a state, which could be comparable with the reference air combustion in terms of the similar fluidized bed temperature and in terms of ensuring sufficient amount of fluidized medium. This would allow to assume that the oxyfuel combustion is applicable also for the BFB technology. Important assumption for the verification is that we consider constant fuel load for air and for oxyfuel state.

Due to the complicated theoretical calculation of fluidized bed temperature, the adiabatic combustion temperature  $T_{ad}$  was chosen as one of the correlation parameters. Second parameter used for verification was the volume of fluidization medium.

Comparison was made by using two normalized parameters – normalized adiabatic flame temperature  $T_{ad}$  and normalized volume of fluidized medium  $V_{fm}$ :

$$T_{ad} = T_{ad1}/T_{ad0} \quad [ - ] \quad 4-1$$

$$V_{fm} = V_{fm1}/V_{fm0} \quad [ - ] \quad 4-2$$

The calculated reference air state values of  $T_{ad0}$  and  $V_{fm0}$  are  $T_{ad0} = 1180^{\circ}\text{C}$  and  $V_{fm0} = 9,7 \text{ m}_n^3/\text{kg}_{pal}$ . The only parameter which can be used for setting the oxyfuel regime is the amount of flue gas recirculation (FGR) referred by recirculation coefficient  $r$ . The effects of FGR on the studied parameters are stated in Figure 2 considering wet FGR, respectively in Figure 3 considering dry FGR in oxyfuel mode. [IV]

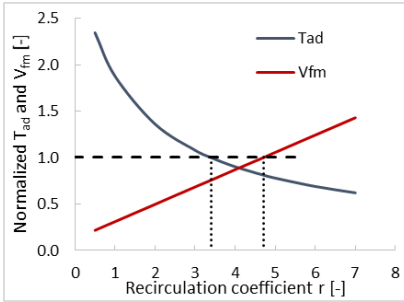


Figure 2: Effect of the amount of recirculated flue gas on adiabatic flame temperature and on volume of fluidized medium considering no condensation of water vapour in FGR [IV]

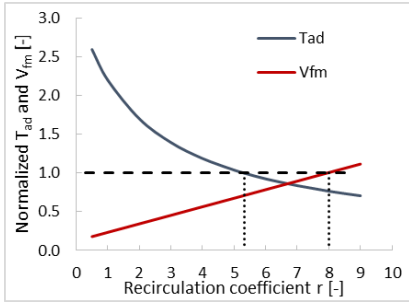


Figure 3: Effect of the amount of recirculated flue gas on adiabatic flame temperature and on volume of fluidized medium considering dry FGR (full condensation of water vapour in FGR) [IV]

Figures 2 and 3 show the inverse effect of the FGR on adiabatic flame temperature and on volume of fluidized medium. With increasing amount of FGR (increasing coefficient  $r$ ) decreases adiabatic flame temperature, while the volume of fluidized medium logically increases. The dash line in figures expresses the reference state of air combustion.

From the theoretical point of view, we can draw a conclusion, that it is impossible to achieve equal oxy-combustion and air-combustion regimes in terms of simultaneously having the same thermodynamic and hydrodynamic parameters. Figures 2 and 3 show the limit cases. For fluidized bed combustion it is necessary to ensure sufficient fluidization – in practice it means to use twice or three times higher velocity than the minimum fluidization velocity. The possible decrease of the temperatures can be minimized by a higher fuel supply, thus increasing power load of the bed.

## 5. Experimental set-up

In order to fulfil the goals of the thesis and proceed the experimental part, it was necessary to design suitable lab-scale experimental facility having the size in order of tens of kW, which would be optimal for easy combustion control and for studying the optimization of the oxy-fuel combustion process. Results from this experimental facility were later validated on bigger pilot plant facility – 500 kW bubbling fluidized bed boiler, which was reconstructed and optimized for oxyfuel combustion.

### 30 kW laboratory bubbling fluidized bed combustor

The experimental facility “MiniFluid” was designed in order to cover relatively large field of various experiments. The facility is made of several modules, which are easily exchangeable and can be optimized for specific purposes. The facility can work both in cold regime without combustion in order to study e.g. fluidization properties of the fluidized bed materials but also in combustion regimes from air to pure oxyfuel combustion. The power output is about 20 to 30 kW depending on fuel load and fuel quality. The basic scheme of the combustor is shown in Figure 4. [VII]

Measured values are volume flow of air supply, volume flow of FGR, volume flow of oxygen supply, volume flow of secondary air supply, mass flow of the fuel, fluidized bed pressure drop and temperature profiles along the whole high of the reactor. Emission monitoring is continuous, flue gases are taken before the flue gas ventilator. Monitored emissions are  $O_2$ ,  $CO$ ,  $CO_2$ ,  $NO_x$  and  $SO_2$ . All the system is driven by LabView software.

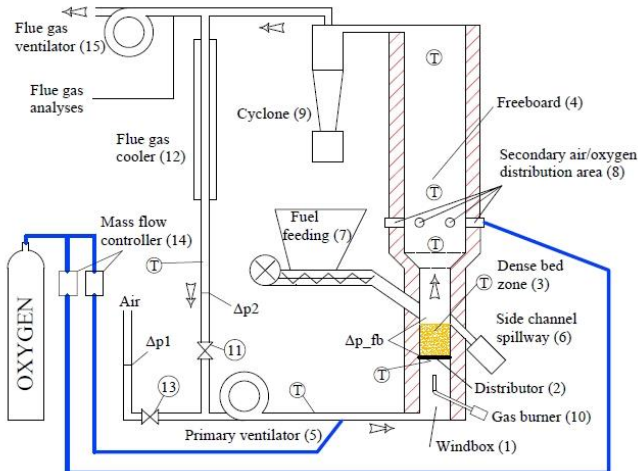


Figure 4: Schematic diagram of the MiniFluid facility

## 500 kW pilot bubbling fluidized bed boiler

Second facility, which was used for the experiments is a pilot scale experimental bubbling fluidized bed boiler having power output around 500 kW marked as “Golem”. Although the maximal power output is 500 kW, majority of experiments was done on lower power output in case of decreasing the oxygen consumption. The boiler is designed as a vertical double pass boiler with a circular cross-section having a cross-over pass that connects the two vertical passes [IX]. The basic scheme is shown in Figure 5, photograph of the boiler is in Figure 6. The boiler is equipped with a V-shaped trough type fluidized bed distributor, and consists of 36 nozzles immersed in the fluidized bed, which are located on two parallel sides and are placed horizontally in three cascade rows. The fluidization medium supply is separated to each parallel sides and to the middle trough, which is made of perforated metal plate. More details about the design of the distributor are given in [X].

The boiler was originally build for the air combustion purposes and it was reconstructed to meet the necessary requirements for oxy-fuel regime. The fuel system was closed and sealed. All the openings, inspection ports and flanges were also sealed in order to avoid air ingress. Oxygen for oxy-fuel regime is supplied into the primary mixture after the primary fan and is controlled by mass flow controller.

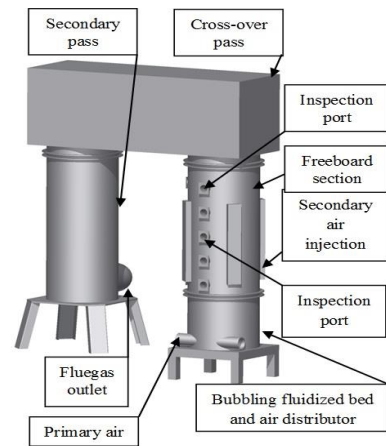


Figure 5: Schematic diagram of the FBC boiler Golem [IX]



Figure 6: Photograph of the FBC boiler Golem

## Fuel

In order to keep stable combustion characteristics and good combustion quality and ensure the comparable results from the experiments, a single type of the fuel was chosen for all of the test. The used coal is marked Bílina, type hp1 originating in the north-west Czech coal basin. Along the whole period of experiments, several samples of coal were taken and proximate and ultimate analyses were done. The results are presented in Table 2. It was determined, that the coal did not change in elemental composition, but was changed in water content, due to the progressive drying. The coal composition stated here shows the average values, but the differences in water content were covered in each evaluation of the measurement. The own ash of the used coal forms the fluidized bed.

Table 2: Proximate and ultimate analysis of the used coal

		Properties “dry ash free”				Properties “as received”			
		C	O	H	S	N	A	W	LHV
		[%]	[%]	[%]	[%]	[%]	[%]	[%]	[MJ/kg]
Coal	for	72.3	18.9	6.3	1.33	1.13	9.3	25	18.5
Golem									
Coal	for	72.3	18.9	6.3	1.33	1.11	10.6	14.9	21.8
Minifluid									

## Limestone

Two sorts of limestone from different mines in the Czech Republic were used for the experiments with SO<sub>2</sub> capture. Their characteristics are shown in Table 3. The characteristic dimensions were got from the sieving analysis and the CaCO<sub>3</sub> content was got from the producers of the limestone. Limestones are marked as Limestone 1 and Limestone 2, later presented as L1 and L2.

Table 3: Properties of limestone additives

	Mean diam. $d_p$	Mode diam. $d_{mod}$	Median diam. $d_{med}$	CaCO <sub>3</sub>
	[mm]	[mm]	[mm]	[%]
Limestone L1	0.29	0.22	0.31	99
Limestone L2	0.27	0.18	0.55	74

Both experimental facilities do not have any special part for separate limestone addition. The process of limestone addition was done before each measurement by manual premixing the fuel with the given amount of limestone.

## 6. Results from experiments

### Sulphur self-retention

The first investigated behaviour was to determine the effect of self-retention of sulphur on the coal ash. The measurements were done using pure ash of the coal as the inert material of fluidized bed without limestone addition. Sulphur self-retention is possible in case of the presence of calcium in the ash. The used fuel contains about 0.8% of Calcium as an element and about 80% is in the form, which can be calcined to CaO. This amount of Calcium corresponds to inert  $\text{Ca/S} = 0.65$ . Comparison of sulphur self-retention in air and oxyfuel mode is shown in Figure 7. The figure clearly shows that the sulphur self-retention is significantly enhanced under oxyfuel combustion. The difference can be attributed to the higher  $\text{SO}_2$  concentrations in oxyfuel mode, allowing a higher conversion of the sulphation reaction. It is quite interesting that there is just weak temperature dependence on the sulphur self-retention in the studied temperature interval.

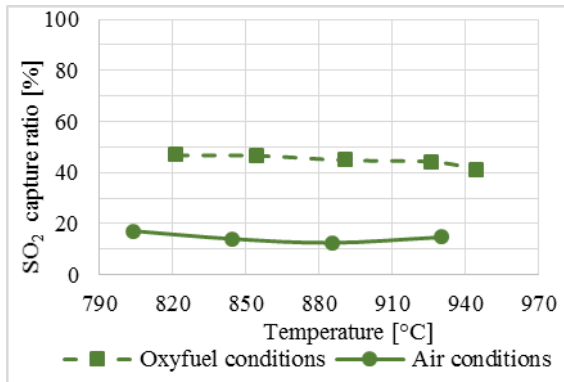


Figure 7: Comparison of sulphur self-retention under oxyfuel and air conditions [XIV]

### Effect of Ca/S ratio

The most important parameter affecting the  $\text{SO}_2$  direct capture is the stoichiometry of the added sorbent. With increase of Ca/S ratio, the  $\text{SO}_2$  capture ratio increases inversely exponentially. Figure 8 shows the difference between air and oxyfuel mode for both used sorbents, Figure 9 then represents the results in limestone/coal weight ratio.

It can be seen that under oxyfuel regime, the  $\text{SO}_2$  capture is significantly enhanced. For example, in order to reach 80%  $\text{SO}_2$  capture in air mode we need to set the Ca/S ratio to 3.75 for limestone L2, and nearly to 5 for limestone L1.

In the case of oxyfuel mode, the required Ca/S ratio decreases to 1.85 and 2 for limestone L2 and limestone L1 respectively. In practice, this means a saving of about 90 kg of limestone L1 or around 75 kg of limestone L2 per ton of coal. As for the sulphur self-retention, the higher SO<sub>2</sub> capture can be possibly attributed to generally higher SO<sub>2</sub> relative concentration.

It can be seen, that in case of oxyfuel combustion, there are just small differences in limestone performance. Higher differences can be seen in air combustion, where limestone L1 shows significantly lower performance, however after recalculation from Ca/S ratio to the weight ratio the difference nearly disappears. [XIV]

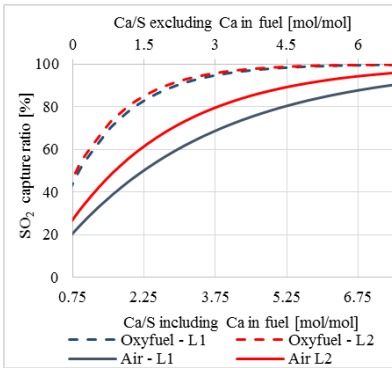


Figure 8: Effect of Ca/S molar ratio on SO<sub>2</sub> capture ratio – comparison of air and oxyfuel conditions

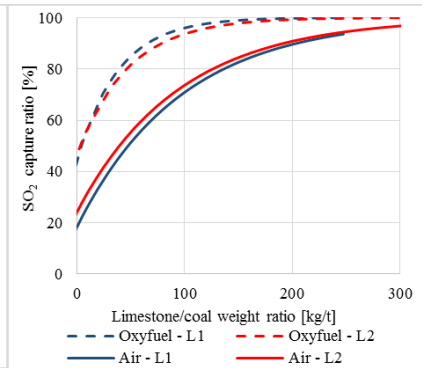


Figure 9: Effect of limestone/coal weight ratio on SO<sub>2</sub> capture – comparison of air and oxyfuel conditions

### Effect of fluidized bed temperatures

In terms of temperature dependence, it has been observed that in the case of air combustion, the optimum temperature for desulphurization is in a range from 800°C to 840°C, which corresponds to the general knowledge about dry additive desulphurization method. In case of oxyfuel combustion, the optimum temperatures are higher, particularly around 880°C. The temperature correlations with f SO<sub>2</sub> capture are shown in Figure 10.

Higher optimal temperatures in oxyfuel regime correspond to a higher limestone calcination temperature due to higher partial pressure of CO<sub>2</sub> in the flue gas. Especially in the case of using limestone L1, the SO<sub>2</sub> capture ratio significantly decreases in the zone where no calcination proceeds. Oppositely limestone L2 has much flatter dependence on combustion temperatures. It was

found that limestone L2 works in oxyfuel regime also in the zone of direct sulphation, thus in the zone where calcination of limestone is suppressed. This L2 behaviour can be particularly attributed to a higher BET surface of this sorbent, which contributes to a higher reaction rate of the indirect sulphation.

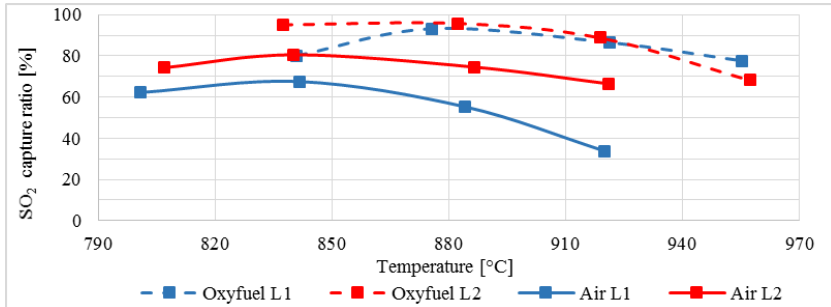


Figure 10: Correlation of SO<sub>2</sub> capture ratio with temperature – comparison of air and oxyfuel combustion

## 7. Effect of the scale up on desulphurization

This chapter evaluates the effect of scale up from laboratory (MiniFluid 30 kW) to pilot scale combustor (Golem 500 kW). Naturally, there are significant differences in operation of the combustors, mainly due to the different design of them. The larger facility Golem suffers more from air ingress, resulting in lower CO<sub>2</sub> concentration at the outlet from the combustor, associated with higher presence of nitrogen as a result. However, the concentration of CO<sub>2</sub> does not drop under 75% in dry flue gas. Also the fluidization velocity is slightly higher in Golem (around 20% in general) and the dimensions of the combustion chamber and freeboard are proportionally different in both facilities. However, it can be concluded that the effect of the monitored parameters on SO<sub>2</sub> capture has the same trends in both facilities, and generally the transfer of experimental results between the scales is possible.

### Effect of sulphur self-retention

In comparison with the results from MiniFluid, we can see a slightly higher SO<sub>2</sub> capture ratio reaching up to 55% just by the sulphur self-retention. In order to identify the reason of such behaviour, the samples of fly ash, which were taken during the measurements, were taken on the XRF analyses. The results from the XRF analyses showed that the coal that was delivered in different time and was used in Golem contains slightly higher Calcium content,



increasing the inner Ca/S ratio to 0.85. Such a difference could explain the reason of slightly higher sulphur self-retention compared to the MiniFluid experiments, which does not exceed 7 percentage points. Concerning the sulphur self-retention, the scale-up differences are shown in Figure 11.

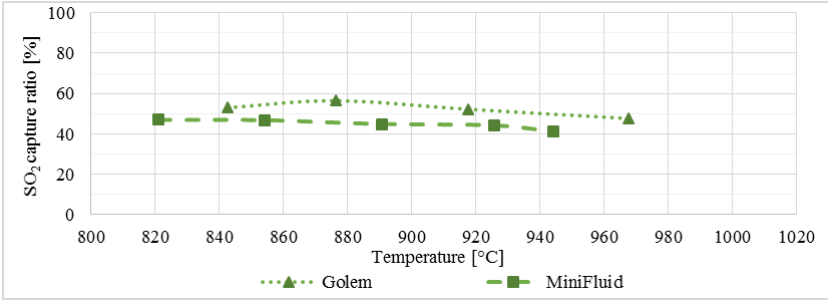


Figure 11: Comparison of the results of sulphur self-retention

### Effect of different Ca/S ratios

Figure 12 compares the effect of Ca/S ratio for both facilities. It can be seen that limestone L2 has very similar results in both facilities, the curves in Figure 12 are nearly the same and covers each other. On the contrary, in case of using limestone L1, bigger differences are seen. In general, limestone L1 achieves lower SO<sub>2</sub> capture efficiency when used in larger scale combustor Golem.

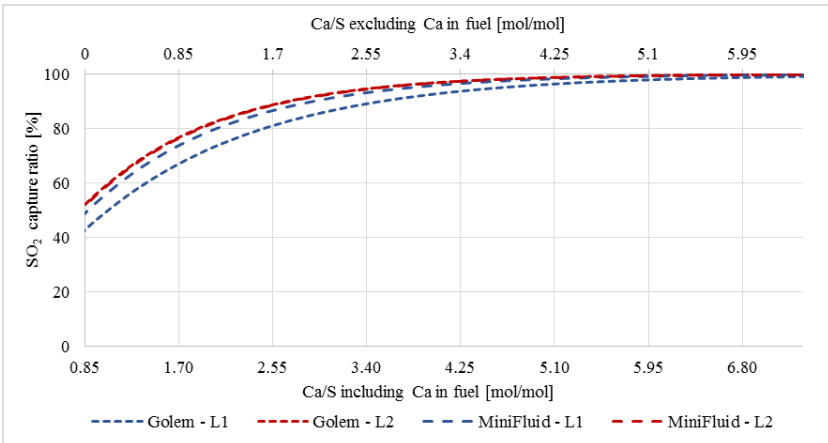


Figure 12: Comparison of the effect of Ca/S molar ratio on SO<sub>2</sub> capture ratio

On the contrary, in case of using limestone L1, bigger differences are seen. In general, limestone L1 achieves lower SO<sub>2</sub> capture efficiency when used in larger scale combustor Golem.

## Effect of bed temperatures

The results from the experiments studying the effect of bed temperatures on SO<sub>2</sub> capture ratio in Golem shows different behaviour compared to the same experiments carried out in the MiniFluid. The maximum SO<sub>2</sub> capture ratio is at about 30°C lower than in case of the measurements in MiniFluid. In case of comparing the results in correlation with temperature, we can see lower SO<sub>2</sub> capture ration for measurements on Golem. The example is shown in Figure 13, where the correlation of temperature influence at Ca/S=3 is compared.

The maximal SO<sub>2</sub> capture ratio was at the similar level as for MiniFluid combustion but it was achieved at a lower combustion temperatures, particularly about 850°C. The difference between the two devices was in CO<sub>2</sub> concentration, which was about 10 percentage points lower in the case of combustion in Golem. Such a decrease of CO<sub>2</sub> concentration causes, that limestone can calcine already at temperature 850°C. This is opposite to MiniFluid combustion, where the calcination was suppressed at this temperature. Another difference is the significantly decreasing SO<sub>2</sub> capture ratio with rising temperature. The reason is probably given by the fact that in the case of combustion in Golem, there was a significantly higher concentration of CO, which in combination with the high temperature causes the reduction of CaSO<sub>4</sub>.

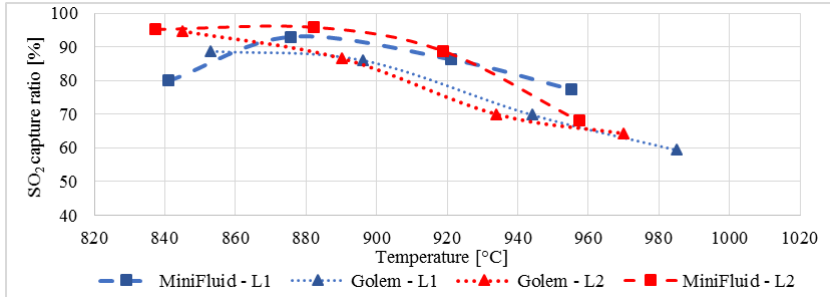


Figure 13: Comparison of the effect of fluidized bed temperatures for T-wall temperature in Golem

## 8. Conclusions

This thesis summarizes the knowledge about oxyfuel combustion in bubbling fluidized bed boilers and specially focuses on the issue of lowering concentration of SO<sub>2</sub> in flue gas. The thesis contains theoretical analysis of oxyfuel process and balance model describing the oxyfuel combustion process. This model is further verified experimentally. Two experimental facilities were developed in order to experimentally study the behaviour of dry additive method of desulphurization under oxyfuel conditions.

The experiments were focused mainly on study the stoichiometry of used additives (Ca/S ratio), influence of operating parameters such as fluidized bed temperature and oxygen concentration, everything for two different sorts of limestone. One of the benefits of the thesis is scale up of the experiments on pilot size combustor – Golem. Altogether more than 180 experiments were carried out, each of them lasting approximately about one hour at stabilized combustion conditions.

In conclusion, the desulphurization under oxyfuel conditions is more efficient than in the case of air combustion at equal process conditions. By this method of desulphurization it is possible to continuously maintain a concentration of SO<sub>2</sub> below 100 ppm using both technologically and economically acceptable conditions (Ca/S not exceeding 4).

The goals of the thesis set above were met in all aspects and their detail analysis and discussion of the results are outlined in the previous chapters. The results of the work have been continuously published at scientific conferences and in scientific journals (see the list of own publications) and were the part of several research projects.

## Authors own publications related to the dissertation topic

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## Anotace

Tato dizertační práce se zabývá technologií „oxyfuel“ spalování, což je jedna z možností snižování emisí oxidu uhličitého ze spalovacích procesů. Proces „oxyfuel“ spalování spočívá v nahrazení vzduchu, jakožto oksyličovadla, čistým kyslíkem. Výsledkem jsou spaliny obsahující z převážné většiny oxid uhličitý a vodní páru. Důležitou otázkou CCS technologií je čistota  $\text{CO}_2$ , která hraje důležitou roli v ekonomické bilanci celého procesu. Jednou ze složek, snižujících čistotu oxidu uhličitého, je oxid siřičitý, který vzniká oxidací síry přítomné v palivu. Práce se zaměřuje na „oxyfuel“ spalování v bublinkové fluidní vrstvě a jejím cílem je ověřit a optimalizovat proces suché aditivní metody odsířování vedoucí ke snížení koncentrace této látky ve spalínách.

V práci je nejdříve podrobně rozebrán proces „oxyfuel“ spalování, je vytvořen matematický model „oxyfuel“ spalování, který je validován s výsledky měření. Tato část práce je nezbytnou pro pochopení samotného procesu fungování „oxyfuel“ spalování a definuje specifika „oxyfuel“ spalování ve fluidních kotlích.

Suchá aditivní metoda odsíření spočívá v přidavku vhodného aditiva, v tomto případě vápence, do spalovací komory. K záchytu  $\text{SO}_2$  tedy dochází ještě v ohništi a produkty odsíření odcházejí v tuhé formě spolu s popelovinami. V práci je uveden současný stav poznání z hlediska snižování emisí  $\text{SO}_2$  v bublinkující fluidní vrstvě a to ve vzduchovém i „oxyfuel“ režimu.

Samotné experimenty byly provedeny na dvou zařízeních o různých výkonech (30 kW a 500 kW), které byly navrženy tak aby byly schopné pracovat jak v režimu vzduchového, tak i v režimu „oxyfuel“ spalování. Byly provedeny experimenty zabývající se hlavními aspekty ovlivňujícími proces odsíření. Mezi zkoumané aspekty patří vliv přebytku vápence, vliv teploty fluidní vrstvy a přebytek oksyličovadla.

## Summary

Presented dissertation thesis deals with oxyfuel combustion, which is one of the possible methods for decreasing emissions of carbon dioxide from combustion process. Oxyfuel combustion is based on substitution of air as an oxidant by pure oxygen. Resulting flue gas contains mainly carbon dioxide and water vapour. Important requirements in the CCS technologies is the purity of  $\text{CO}_2$ , which plays an important role in the economical balance of the whole process. Sulphur dioxide formed by oxidation of sulphur in a fuel is one of the substances lowering the purity of  $\text{CO}_2$ . This thesis focuses on the oxyfuel combustion in bubbling fluidized bed and the main focus is to verify and optimize the process of dry additive desulphurization method leading to lowering the final  $\text{SO}_2$  concentration in flue gas.

The oxyfuel combustion process is analysed in detail and a mathematical oxyfuel combustion model is created and is validated with the measurement results. This part of the work is necessary to understand the process of oxyfuel combustion itself and defines the specifics of oxyfuel combustion in fluidized bed boilers.

The dry additive desulphurization method is based on addition of a suitable sorbent, in this case limestone, to the combustion chamber. Sulphur dioxide is captured directly in combustion chamber and the product of desulphurisation reaction mechanism (calcium sulphate) leaves the combustion process together with ash. The current state of the art of  $\text{SO}_2$  emission reduction in fluidized bed boilers under air and oxyfuel mode is presented in this thesis.

The experiments were carried out in two facilities with different power outputs – 30 kW and 500 kW, which were designed to be able to operate in both air and oxyfuel combustion modes. Experiments were focused on the main aspects influencing the desulphurization process. Among the examined aspects belong the effect of limestone excess, effect of fluidized bed temperature and the excess of oxidant.