

SPECIFIC INFLUENCE OF BIOMASS ON THE DESULPHURISATION PROCESS IN COMBUSTION OF BROWN COAL AND BIOMASS MIXTURE IN FLUIDISED BED BOILER

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This thesis is focused on specific aspects of the desulphurisation processes of fluidised-bed boilers. The original goal of the study was to analyse the influence of several kinds of biomass on the quality of the desulphurisation process in combustion of the mixture of brown coal, biomass and limestone in fluidised-bed boilers.

Key words: biomass, environment protection, desulphurisation process.

Specifičan utjecaj biomase na proces odsumporavanja pri izgaranju smjese mrkog ugljena i biomase fluidiziranom sloju kotla. Rad je usmjeren na određene aspekte procesa odsumporavanja u kotlovičim fluidiziranim slojem. Cilj studije bio je analizirati utjecaj nekoliko vrsta biomase na kvalitetu procesa odsumporavanja izgaranja smjese od mrkog ugljena, biomase i vapnenca u fluidiziranom sloju kotla.

Ključne riječi: biomasa, zaštita okoliša, desulfurizacija.

INTRODUCTION

Separate boilers combusting biomass, as well as boilers with integrated burning of coal with various sorts of biomass, is considered to be trendy at present. The main “enticement” for the thermal power and heating plants operators at a decision making about installation of new and adaptation of the existing boilers including their accessories for co-combustion process are “green bonuses”, lower operation costs due to coal consumption reduction and saving of emission permits within emissions trading system. There are solved such issues as fuel

storage, increasing demand and thus permanently increasing price of biomass, its delivery, and operation and technological tasks related to the change of technology to co-combustion. For fluidised bed boilers operators, this study is worth to be paid attention due to some specific features of brown coal (lignite) and biomass mixture combustion in fluidised bed relating with an influence of biomass on quality and operation of desulphurisation process based on the dry limestone method.

THEORETICAL PART

Coal-beds are accompanied more or less by sulfur, which transforms during coal burning mostly into sulfur dioxide (SO_2), partly also into sulfur trioxide, remnants of it are further bound to solid waste products – such as ash and slag.

The process of SO_2 formation in flue gas from sulfur contained in fuel can be described by the following chemical reaction:



Concentration of sulfur dioxide in flue gas must not exceed the limit value determined for given source of air pollutants. For SO_2 concentration reduction in flue gas leaving the fluidized bed boilers, the dry additive limestone method is mostly applied. This method is based on dosing of air and finely ground limestone into the boiler furnace or on adding of ground limestone into coal.

FLUE GAS DESULPHURISATION OF FLUIDISED BED BOILERS AT CO-COMBUSTION OF BROWN COAL WITH VARIOUS SORTS OF BIOMASS

On the basis of already performed study [2] that proved a real unfavourable impact of coal ash matters on the desulphurisation capability of calcined limestones it was decided to carry out similar laboratory experiments modelling combustion of a brown coal – biomass mixture.

Influence of added biomass on the desulphurisation process in a technological unit has not been investigated yet. Biomass used for co-combustion (straw, wooden chips, etc.) has in the most cases a negligible content of combustible sulphur, however

If we use the stoichiometric rate $\text{CaCO}_3 : \text{SO}_2$ at values 2-2,5 : 1, then typical achievable desulfurization is in the range of 85-90 % - dependent on sulfur content in coal and limestone reactivity [1-3].

The following reactions are running in this desulfurization process:

Limestone calcination (at temperatures 800-900 °C):



Sulfation reaction (running at higher speed between 600-1000 °C):



Calcination of limestone at temperatures above 1050°C is not already suitable, because formed calcinate overburning occurs due to a porous structure change [1-3].

very often it has a high content of calcium compounds, which in case of favourable conditions in the combustion process could become another source of calcined lime formation and thus in this way it could contribute to increasing of coal flue gas desulphurisation efficiency. On the other hand, biomass contains not negligible amount of sodium, potassium, phosphorus compounds and other elements, which showed in the former studies to be undesirable with negative impact on desulphurisation process efficiency.

Material of samples for experimental work

Choice of used samples was based on presumption of expected application of knowledge gained in technological experience. For the experimental work there were selected two different sorts of biomass: wooden chips (*S2 in the text*) and small

pellets of a plant origin (*S1 in the text*). The basic fuel was brown coal. Limestone with calcium content converted to calcium oxide > 90 % mass. was used as desulphurisation material (Table 1).

Table 1. Chemical composition of limestone [% mass]

Tablica1. Kemijski sastav vapnenca[% mase]

Oxide	CaO	MgO	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	Na ₂ O	SiO ₂
Value	95.2	0.778	0.874	0.32	0.111	0.058	2.17

Table 2. Contents of various elements in samples of investigated coal and biomass sorts

Tablica 2. Elementarni sastav ispitanih uzoraka pepela - % mase

Element	Ash		
	Coal	Wooden chips (S2)	Plant origin pellets (S1)
Na	0.97	0.799	0.104
Mg	0.771	4.22	10.51
Al	26.5	0.612	0.06
Si	48.4	1.36	1.09
P _x	0.215	1.42	31.97
S _x	0.575	0.642	0.074
Cl		0.0348	
K	2.61	13.45	49.05
Ca	3.14	74.1	5.4
Fe	12.1	0.478	0.548

Experimental part

The subject of the research – limestone – was screened up to particles size 0.3-0.6 mm in advance. This process was followed by formation of a mixture consisting of limestone, ground coal and determined quantity of biomass. This

mixture was then burnt in the laboratory muffle furnace heated to 850°C. The treated mixture in the quantitative way was inserted into the reactor. The figure 1 shows experimental installation.

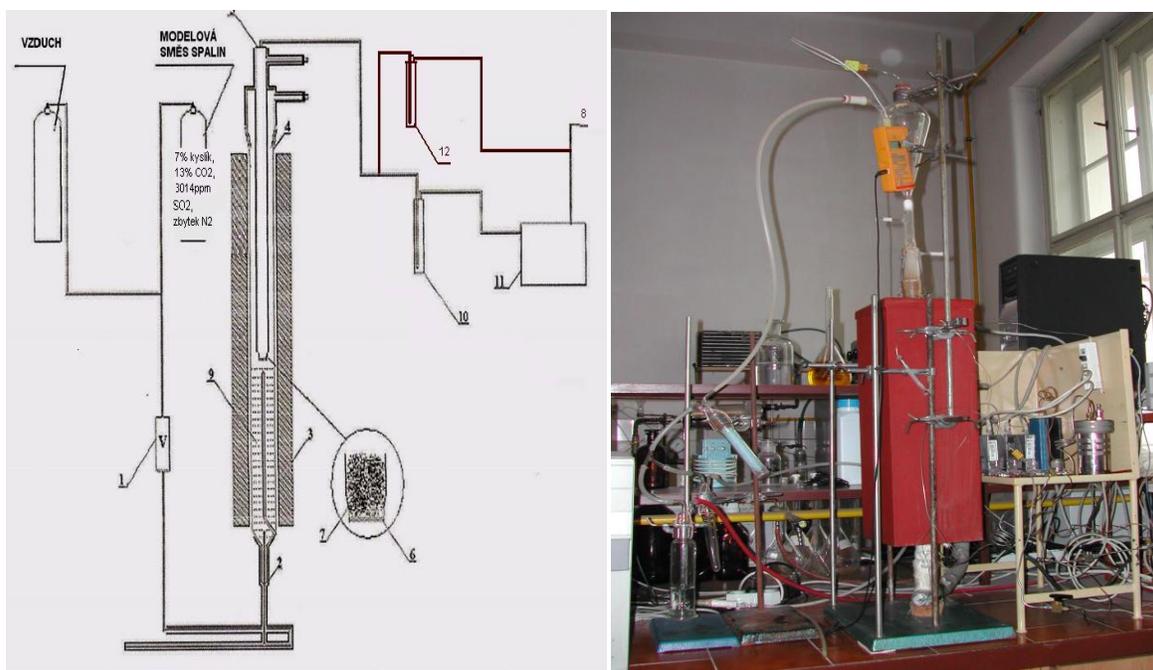


Figure 1. Experimental installation: 1-valve, 2-heating wire, 3-oven, 4-lower part of reactor, 5-upper part of reactor, 6-silica glass frit, 7-sample, 8-exhaust to digester, 9-crushed quartz (5-7 mm), 10-filter, 11-analyser, 12-washing apparatus

Slika 1. Eksperimentalna instalacija: 1-ventil, 2-grijanje žice, 3-pećnica, 4-donji dio reaktora, 5-gornji dio reaktora, 6-silicijsko staklo, 7-uzorak, 8-ispuh prema digestoru, 9-usitnjeni kvarc (5-7 mm), 10-filter, 11-analizator, 12-aparat za pranje

Gaseous mixture simulating flue gas composition with in advance defined SO_2 concentration came into already preheated reactor (temperature $t=850\text{ }^\circ\text{C}$). Sulfur dioxide concentration at the reactor outlet was continually measured by means of the analyzer.

Resulting curves of SO_2 concentration at the reactor outlet on desulfurization time provide characteristics of the desulfurization process and amount of captured SO_2 in a specific time at constant temperature. It means, that the SO_2 outlet concentration is at first at lower values level

in the period during which it is sufficient amount of free CaO . With decrease of free CaO amount, SO_2 outlet concentration is increasing up to exceeding of determined limit (threshold) values.

The measurement was performed at dosing of various quantity of biomass into the basic mixture (20 g of coal and 4 g of limestone). The biomass quantities were as follows: 10, 20 and 30 g which correspond to 50, 100 and 150% of coal mass in the basic mixture.

Figures 2 and 3 show the threshold curves of single samples.

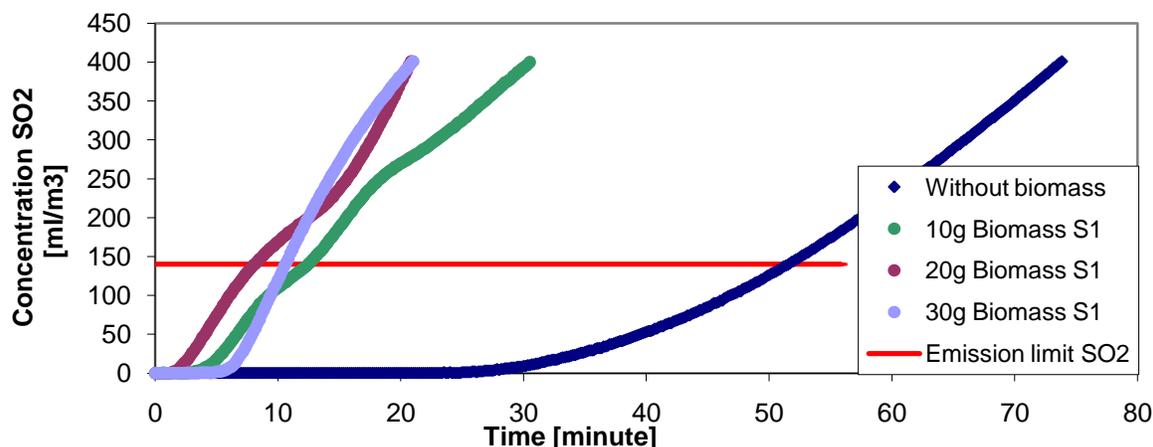


Figure 2. Impact of plant origin small pellets (S1) addition into the basic mixture of coal and limestone on calcined limestone desulphurisation capacity at 850°C

Slika 2. Utjecaj dodavanja malih peleta (S1) biljnog podrijetla u osnovnu smjesu ugljena i vapnenca na kapacitet odsumporavanja kalciniranog vapnenca na 850°C

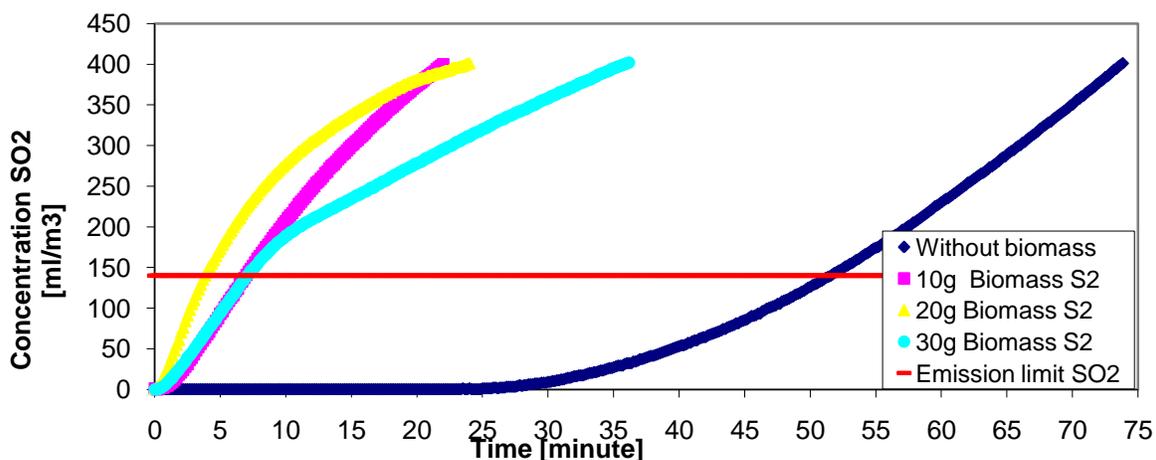


Figure 3. Impact of wooden chips (S2) addition into the basic mixture of coal and limestone on calcined limestone desulphurisation capacity at 850°C

Slika 3. Utjecaj dodavanja drvenih žetona (S2) biljnog podrijetla u osnovnu smjesu ugljena i vapnenca na kapacitet odsumporavanja kalciniranog vapnenca na 850°C

The basic criterion applied for comparison of measured results was the time elapsed from the start of measurement up to achieving of the emission limit defined by legislation, i.e. content of SO_2 $400 \text{ mg}\cdot\text{m}^{-3}$ ($140 \text{ ml}\cdot\text{m}^{-3}$) in flue gas related to normal conditions (dry gas, 6% O_2 vol.) [4].

As it is obvious from the presented figures, addition of both kinds of biomass (S1 and S2) to the basic calcination mixture (20 g of coal, 4 g of limestone) caused

substantial decrease of desulphurisation capacity. The emission limit of calcined mixture with 10 mg biomass S1 addition was reached 40 minutes sooner than that one in case of sole mixture of coal and limestone. 20 g and 30 g dose of biomass resulted into even higher decrease of desulphurisation capacity of relevant mixture.

Addition of biomass S2 into the coal and limestone mixture had also similarly negative effect.

The worst result at reaching of target SO_2 limit was registered for the variant with identical mass of biomass and coal.

With respect to the fact, that the biomass used in tests contains a negligible quantity of combustible sulphur ($<0.01\%_{\text{mass}}$), decrease of adsorption capacity of calcined limes is not caused by SO_2 capture from biomass on CaO at calcination of given sample, but obviously by reaction of calcium oxide with oxides present in ash matter from coal and biomass.

Undesirable reactions result into formation of various types of vitreous substances and clinker [5], possibly also further crystalline matters. Some arising crystalline structures were found in exposed samples by means of RTG analysis and they are stated with their mass portion in Table 3 (addition 30 g of plant biomass S1 and for a mixture containing 30 g of wooden chips S2).

Table 3. RTG analyses results of coal, limestone and biomass (S1, S2) mixture after exposition by SO_2 in the reactor at temperature 850°C

Tablica 3. Rezultati RTG analize rezultata smjese ugljena, vapnenca i biomase (S1, S2) nakon izlaganja SO_2 u reaktoru pri temperaturi 850°C

Crystalline phase	Chemical formula	Content, %mass	
		S1	S2
Anhydride	CaSO_4	25	28
Calcium oxide	CaO	15	16
Quartz	SiO_2	2	15
Alpha-iron trioxide	Fe_2O_3	3	3
Gehlenite	$2\text{CaOAl}(\text{Al}_{1.22}\text{Si}_{0.78}\text{O}_{0.78})(\text{OH})_{0.22}$	12	19
Calcium-disilicon aluminate	$\text{CaO}*\text{Al}_2\text{O}_3*2\text{SiO}_2$	5	7
Calcium silicate	$\text{CaO}*\text{SiO}_2$	-	12
Calcium-magnesium diphosphate	$\text{Ca}_{2.71}\text{Mg}_{0.29}(\text{PO}_4)_2$	17	-

In both cases it was determined by means of diffraction RTG application presence of a number of crystalline substances limiting quantity of free CaO entering into reaction with sulphur dioxide from the model flue gas. In the exposed SO_2 calcined limes it was found presence of both the final product of sulphating (CaSO_4 , 25 - 28 % $_{\text{mass}}$ in the mixture) and the undesirable compounds (gehlenite, bedded calcium-disilicon aluminate) decreasing reaction capacity.

Due to the fact, that ash matters of plant origin biomass (S1) contain substantially higher portion of phosphorus pentoxide (P_2O_5), in case of the stated calcined lime it was detected formation of considerable high quantity of calcium-magnesium diphosphate (17 % $_{\text{mass}}$).

A great part of found compounds is inert against sulphating reactions and it is able to embed easy free CaO particles and in this way thus prevent their reactions with SO_2 .

CONCLUSION

The results of this study show clearly, that addition of selected biomass to coal in case of co-combustion has negligible impact on the desulphurisation process and its quality.

From the gained knowledge it is obvious, that addition both of wooden chips and plant origin pellets in any tested ratio to researched sort of brown coal decreases very significantly adsorption capacity of the applied type of limestone. As the consequence of this fact it means, that co-combustion of coal and biomass in fluidised bed boilers for the purpose of CO₂ emission rate reduction increases consumption of desulphurisation additives needed for meeting of SO₂ emission limits.

It is thus task a of economical calculations to compare the effect of CO₂ emissions reduction by co-combustion of coal and biomass with increased rate of operation costs caused by a higher limestone

consumption required for meeting of SO₂ emission limits, as well as disposal of a higher amount of waste coming from desulphurisation together with environmental aspects of such waste storage at dumps.

It is the fact that the above mentioned undesirable effects come into existence at a specific combination of coal and limestone containing specific oxides and admixtures forming in the course of calcination process various types of vitreous compounds and clinker. That is why it is necessary to stress, that for optimisation of dry desulphurisation process it is needed to carry out separate testing of each considered type of coal, moreover with using of given sorts of limestone and biomass. For each type of industrial coal, a suitable combination of limestone (possibly also biomass) can be found in order to minimise influence of the above stated factors.

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