

CALCIUM SULFATION CHARACTERISTICS AT HIGH OXYGEN CONCENTRATION IN A 1MW_{TH} PILOT SCALE OXY-FUEL CIRCULATING FLUIDIZED BED

Wei Li¹, Mingxin Xu^{1,2}, Shiyuan Li^{1,2,*}

1 Institute of Engineering Thermophysics, Chinese Academy of Sciences, Beijing 100190, China

2 University of Chinese Academy of Sciences, Beijing 100049, China

*Email: lishiyuan@iet.cn

Abstract – In present study, tests were conducted to investigate the behaviors of sulfur capture by calcium based sorbents during oxy-fuel circulating fluidized bed combustion with high oxygen concentration via a 1MW_{th} pilot-scale oxy-fuel circulating fluidized bed facility. The effects of operating temperature, overall oxygen concentration, and Ca/S molar ratio were taken into consideration. It was determined that the efficiency of sulfur capture during oxy-fuel combustion was higher than that in air combustion. Meanwhile, with increasing the concentration of oxygen, the efficiency of sulfur capture increased. Comparing with the optimum temperature for sulfur capture during air combustion, the optimum temperature during oxy-fuel circulating fluidized bed combustion was about 930°C when the overall oxygen concentration was 50%. In addition, the optimal molar ratio of Ca/S can be set as 3.0 during oxy-fuel combustion with consideration of various factors.

1. INTRODUCTION

The emission of pollutants from fossil fuel combustion has caused lots of different environmental problems, such as greenhouse effect and acid rain. CO₂, the major source of greenhouse gas, is one of the typical pollutants [1]. Currently, new technologies about CO₂ capture, utilization, and storage (CCUS) have been developed widely, among which oxy-fuel combustion is considered as one of the most promising concepts [2]. During oxy-fuel combustion, the mixture of pure oxygen and recycled flue gas, which consists of mainly CO₂, is used as the reactant for fuel combustion. With this technology, the concentration of CO₂ in the flue gas can be enriched up to 95%, which can be directly used for CO₂ recovery or storage.

Although the studies about oxy-fuel combustion are mainly about pulverized coal (PC) boiler, fluidized bed combustion, especially circulating fluidized bed (CFB) combustion, is also one of the common systems which are very appropriate for oxy-fuel combustion. Based on the operating results obtained from a conventional 0.8 MW_{th} pilot plant located in CanmetEnergy, it can be found that oxy-fuel circulating fluidized bed combustion offers all the advantages of air-firing CFB, which strongly supports the superiority of oxy-fuel CFB combustion [3, 4]. Besides, in order to meet the demands for the new power plants which are under construction, the concept named second generation oxy-fuel combustion, in which the inlet oxygen concentration will be as high as 50%, has been established in recent years [5, 6]. Because of the adoption of external heat exchangers in CFB combustion, the inlet oxygen concentration during oxy-fuel combustion can be easily increased to 50% or more by changing the heat flux in the furnace. The research group from Institute of Engineering Thermophysics, Chinese Academy of Sciences (IET-CAS) is one of the representative research groups which concentrate on the investigation about the secondary generation oxy-fuel CFB combustion. Up to now, a 1MW_{th} pilot-scale oxy-fuel CFB combustion unit has been designed and constructed in IET-CAS. The pilot unit can be operated under both air and oxy-fuel combustion modes. Meanwhile, during O₂/RFG tests, the overall oxygen concentration can be regulated in the range from 30% to 50%. Some inspiring results obtained via the pilot-unit have been reported recently [7].

Except for CO₂, SO₂, the direct source for acid rain, is another important pollutant generated from fossil fuel combustion. As all known, comparing with pulverized coal combustion, one of the

unique advantages for CFB combustion is the in-situ sulfur capture [8]. During the CFB combustion, desulfurization of the flue gases can occur inside the bed by feeding calcium based sorbent (limestone) with low costs. Meanwhile, because of the low operating temperature, which fortunately is the optimum reacting temperature for limestone to remove SO₂, during CFB combustion, the efficiency of sulfur capture in CFB combustion is also higher than that in PC combustion.

For oxy-fuel CFB combustion, since the atmosphere in which coal burns changes typically, the characteristics of sulfur capture by limestone greatly differ from those obtained in CFB air modes.

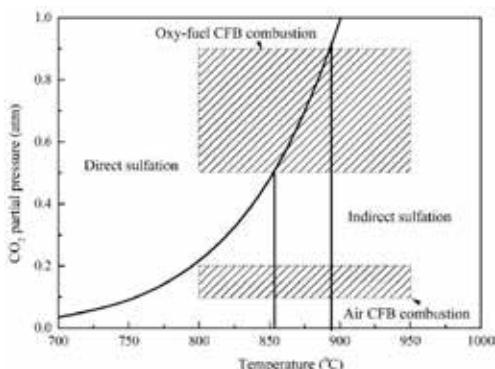


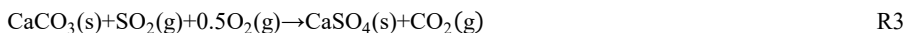
Fig. 1 CaCO₃-CaO thermodynamic equilibrium over limestone[9]

Fig. 1 shows the curve of CaCO₃-CaO thermodynamic equilibrium. Generally, as the temperature and CO₂ partial pressure change, there are two different routes of limestone sulfation, which are indirect and direct sulfation respectively, under oxy-fuel CFB combustion. As shown in Fig. 1, under the equilibrium curve, indirect sulfation of limestone is the dominant. In this zone, the calcination of limestone occurs prior (R1). CaO, product of CaCO₃ calcination, is the reagent for the subsequent reaction of sulfur capture (R2). The chemical equations are as follows [10]:



The desulfuration occurring in CFB air combustion belongs to the indirect sulfation.

However, above the curve, direct sulfation is more important. In this zone, CaCO₃ will react with SO₂ directly, as follows [10]:



Since the concentration of CO₂ in the boiler is higher during oxy-fuel CFB combustion than that during air combustion, the process of sulfur capture by limestone can be either indirect sulfation or direct sulfation, as shown in Fig. 1.

Many studies about the sulfation of limestone during oxy-fuel CFB combustion have been done via TGA and fixed bed [11-13]. Compared with air-firing mode, the sulfur capture efficiency for oxy-fuel combustion is generally higher. However, there has not been in agreement on the optimum temperature of sulfur retention during oxy-fuel CFB combustion, because the results reported varied with the different experimental facilities [14]. More work should be carried out in actual continuous circulating fluidized bed reactors, in order to obtain the universal conclusion about the optimum temperature for the sulfur capture. In addition, most of available results at present were focused on the 1st oxy-fuel combustion [15, 16]. The investigations about the behaviors of sulfur capture by

limestone during 2nd oxy-fuel CFB combustion are rare. Some more studies about the actual behaviors of sulfur retention should also be accomplished to facilitate the development of strategies about desulfurization during oxy-fuel combustion, especially with high oxygen concentration.

The aim of present study is to investigate the characteristics of sulfur capture by limestone and to determine the optimum operating temperature for the maximum efficiency of sulfur capture during oxy-fuel CFB combustion with high oxygen concentration via 1MW_{th} pilot scale oxy-fuel CFB combustor. The effect of oxygen concentration and Ca/S ratios were also taken into consideration.

2. EXPERIMENTAL FACILITY AND METHODS

2.1 1MW_{th} pilot-scale oxy-fuel CFB facility

The schematic diagram of the oxy-fuel CFB pilot facility is shown in Fig. 2. This facility was designed to operate under both air and O₂/RFG combustion modes, in which the overall oxygen concentrations ranges from 21% to 50% via the adjustment of external heat exchangers. The bed temperature of the furnace can be maintained in the range of 850°C to 950°C. A detailed description of this pilot facility has been given in our previous literature [7].

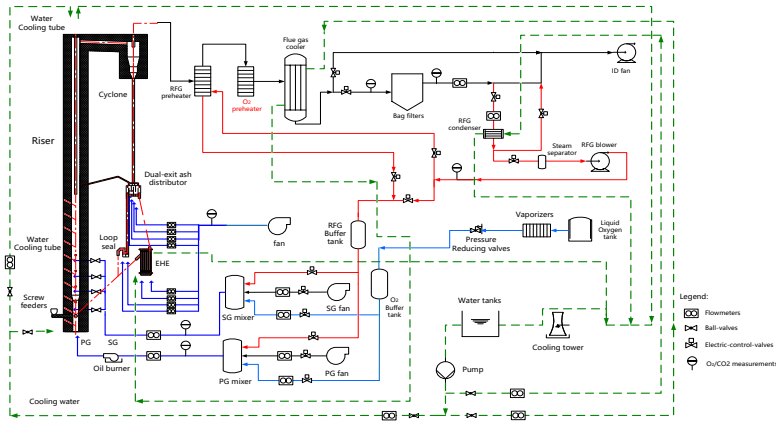


Fig. 2 Schematic of the 1MW_{th} pilot-scale oxy-fuel CFB facility

2.2 Materials

Datong (DT) coal, a typical Chinese bituminous coal, was used in present study. The ultimate and proximate analysis of DT coal are listed in Table 1 and the ash analysis is given in Table 2. The coal was crushed and double sieved to less than 8 mm size before testing. Sand with a diameter less than 1 mm was used as the start-up bed material. For sulfur capture, limestone with a composition as shown in Table 3 was used. The particle size of the limestone was less than 1 mm.

Table 1 Proximate and ultimate analyses of DT coal

LHV/(MJ·kg ⁻¹)	Proximate analysis /(wt.%)					Ultimate analysis /(wt.%)			
	Q _{net,ar}	FC _{ar}	M _{ar}	A _{ar}	V _{ar}	C _{ar}	H _{ar}	O _{ar}	S _{ar}
22.61	44.38	2.20	26.05	27.37	58.08	3.73	8.58	0.32	1.04

Table 2 Ash components of DT coal

Components	CaO	MgO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	TiO ₂	SO ₃	Na ₂ O
Ash /(wt.%)	6.31	0.23	50.40	34.60	1.56	0.44	1.25	2.40	0.10

Table 3 Components of limestone

Components	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	TiO ₂	Cr ₂ O ₃	SO ₃
Limestone /(wt.%)	96.25	1.90	0.69	0.60	0.29	0.12	0.06	0.04

2.3 Start-up and oxy-transition process

The oxy-CFB pilot facility was started in the air-combustion mode. When the bed temperature reached to the specific experimental temperature, an air based test was carried out first with a period of 2.5h. Upon the completion of the air baseline test, the switch from air combustion to O₂/RFG combustion started. The process of oxy-transition has been introduced in detailed in our previous study [7]. The transition was accomplished smoothly with a period of approximately 4 hours. After the process of transition from air mode to O₂/RFG mode, tests under oxy-fuel combustion started.

2.4 Test conditions

The tests in present study were under air and O₂/RFG combustion respectively. The detailed parameters and results of each condition are listed in Table 4 and Table 5 respectively. During the tests, the external heat exchangers was adopted when the oxygen concentration was 40% or 50% during O₂/RFG combustion. Each test was kept for at least 2.5h of steady-state operation. The concentration of CO₂, CO, SO₂, NO, and N₂O in the flue gas was continuously monitored online via a FTIR gas analyzer (Gasetm DX4000, Finland), which was located at the outlet of bag filter. The measurement of all the pollutants was less than ±5%. The efficiency of sulfur capture is calculated based on the following formula:

$$\eta_{\text{sulfur}} = \left(1 - \frac{|\text{SO}_2|_{\text{fg}}}{10^4 (|\text{CO}_2|_{\text{fg}} - |\text{CO}_2|_{\text{in}}) + |\text{CO}|_{\text{fg}}} \right) * 100\% \quad \text{R4}$$

Where, η_{sulfur} is the efficiency of sulfur capture; $|\text{SO}_2|_{\text{fg}}$, $|\text{CO}_2|_{\text{fg}}$, and $|\text{CO}|_{\text{fg}}$ are the concentrations of SO₂, CO₂, and CO in the flue gas respectively; $|\text{CO}_2|_{\text{in}}$ is the concentration of CO₂ in the feeding gas; S_{fuel} , C_{fuel} are the molar ratio of S and C in the fuel respectively.

Table 4 Detailed parameters about oxy-fuel CFB combustion via 1MW_{th} pilot scale facility

Conditions	Atmosphere	O ₂ %	Rate _{fuel} kg/h	v _{dense} m/s	v _{dilute} m/s	T _{riser} °C	Ca/S
1	air	21	86	4.9	4.4	877	2.5
2	air	21	151	6.4	6	890	2.5
3	air	21	142	6.4	5.9	896	3.5
4	air	21	139	6.5	5.8	899	4
5	air	21	163	6.9	6.5	933	2.5
6	O ₂ /RFG	30	123	4.2	3.7	907	2.5
7	O ₂ /RFG	40	161	4.1	3.7	890	2.5
8	O ₂ /RFG	50	185	4.4	3.8	889	2.5
9	O ₂ /RFG	50	180	4	3.5	900	2.5
10	O ₂ /RFG	50	183	4.1	3.8	932	2.5
11	O ₂ /RFG	50	167	4.2	3.7	950	2.5
12	O ₂ /RFG	50	193	4.1	3.8	906	3
13	O ₂ /RFG	50	183	4.3	3.7	908	4

Note: O₂ is the overall oxygen concentration; Rate_{fuel} is the fuel feeding rate; v_{dense} is the gas velocity in the dense zone; v_{dilute} is the gas velocity in the dilute zone; T_{riser} is the average riser temperature; Ca/S is the Ca/S molar ratio;

Table 5 Detailed results about oxy-fuel CFB combustion via 1MW_{th} pilot scale facility

Condition	CO ₂ %	SO ₂ mg/MJ	CO mg/MJ	NO mg/MJ	N ₂ O mg/MJ	η_{sulfur} %
1	14.8	60.8	59.3	111.9	62.5	80.3
2	15.4	133.1	42.3	85.0	42.1	31.8
3	15.5	80.7	42.4	98.6	28.2	60.2
4	15.2	10.0	39.5	100.3	34.0	95.4
5	16.1	154.2	32.2	97.3	19.6	17.8
6	90.7	99.0	186.0	116.0	63.0	83.3
7	90.4	78.0	128.0	124.0	63.0	84.6
8	91	65.0	71.0	147.0	41.0	85.4
9	91	43.1	22.9	203.2	15.6	83.6
10	91.6	28.8	22.5	193.2	11.2	89.3
11	92.2	59.9	22.5	182.5	11.4	78.4
12	91.8	8.0	20.8	210.4	10.8	97
13	91.9	3.0	21.4	213.7	10.9	98.9

Note: CO₂ is the concentration of CO₂ in the flue gas (dry base); SO₂ is the concentration of SO₂ in the flue gas (dry base); CO is the concentration of CO in the flue gas (dry base); NO is the concentration of NO in the flue gas (dry base); N₂O is the concentration of N₂O in the flue gas (dry base); η_{sulfur} is the efficiency of sulfur capture;

3. RESULTS AND DISCUSSION

3.1 Effect of oxygen concentration on limestone sulfation in oxy-fuel CFB combustion

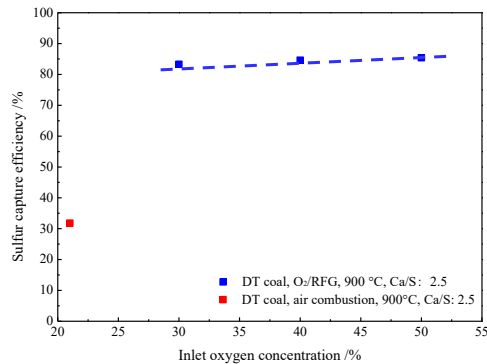


Fig. 3 Effects of oxygen concentration on the sulfation of limestone

Fig. 3 gives the tendencies of sulfur capture efficiency with increasing the inlet oxygen concentration during DT coal air and oxy-fuel CFB combustion at 900°C. The tests were condition 2, 6, 7, and 8. As is shown, it is obvious that the sulfur capture efficiency is higher under O₂/RFG combustion than that under air combustion, even when the oxygen concentration is 30%. This can be attributed to higher utilization of limestone during oxy-fuel CFB combustion. Based on the thermodynamic equilibrium curve of CaCO₃ calcination (Fig. 1), the sulfuration of limestone under both air and O₂/RFG (condition 6) combustions are indirect sulfuration. The calcination of limestone proceeds first. CaO becomes the dominant reagent for the desulfurization. As is known to all, the rate of sulfation reaction of limestone is dually controlled by chemical reaction and diffusion. In the initial stage, chemical reaction is the major factor in controlling the sulfation reaction [17]. However, after reacting for a long time, as CaSO₄, the product of desulfurization, accumulates, the micro pores generated during the process of calcination are blocked by CaSO₄. The reaction turns to be mainly

controlled by diffusion in this stage. The layer of CaSO_4 becomes the major constraint which impedes the diffusion of SO_2 . As a result, the unreacted CaO under the layer of CaSO_4 cannot continue to react with SO_2 and the utilization of limestone decreases obviously. However, under the oxy-fuel combustion in which there is high concentration of CO_2 in the furnace, comparing with that under air combustion, the rate of limestone calcination decreases. The period of initial stage in which the sulfation is controlled by chemical reaction is prolonged. As a result, the utilization of limestone is higher under oxy-fuel combustion, leading to the higher efficiency of sulfur capture than that under air-combustion. Meanwhile, as the concentration of oxygen in the feeding gas increases from 30% to 50%, the efficiency of sulfur slightly increases from 83.4% to 85.4%. This can be due to the changes in concentrations of oxygen and CO_2 in the furnace. During the tests, the operating temperature was kept at about 900°C . With increasing the concentration of inlet oxygen from 30% to 50%, the concentration of CO_2 in the feeding gas is accordingly considered decreasing from 70% to 50%. It is obvious that the sulfation of limestone in these conditions can be regarded as indirect sulfation. The increase of oxygen concentration in the feeding gas has positive effects on reaction R2, leading to the higher efficiency of sulfur capture. The results are enlightening. In order to keep the utilization of limestone acceptable during actual oxy-fuel CFB combustion, operation with high oxygen concentration (50%) will be a good option for high efficiency of in-situ sulfur retention.

3.2 Effect of reacting temperature on limestone sulfation in oxy-fuel CFB combustion

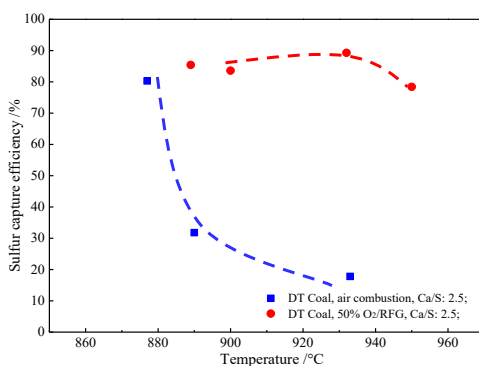


Fig. 4 Effect of reacting temperature on the efficiency of sulfur capture

Fig. 4 shows the tendencies of sulfur capture efficiency with increasing the operating temperature during air and O_2/RFG combustion. The tests were condition 1, 2, 5, 8, 9, 10, and 11. The ratio of Ca/S was kept as 2.5. The concentration of oxygen in the feeding gas during O_2/RFG combustion was 50%. Comparing the efficiencies in the tests, it is obvious that the temperature which corresponds with the highest efficiency of sulfur capture is different. In air combustion mode, the optimum temperature is about 880°C while it is about 930°C in oxy-fuel combustion mode. It indicates that the optimum temperature for sulfur capture by calcium sorbents is much higher in O_2/RFG combustion than that in air combustion. Since indirect sulfuration is dominant during air combustion, as shown in Fig. 1, the limestone is calcined to CaO initially. However, as analyzed in Part 3.1, the sintering of CaO can be promoted with increasing the temperature, leading to the decreasing of the sulfur capture efficiency. On the contrary, during oxy-fuel combustion, since the concentration of CO_2 is much higher than that during air combustion, the calcination of limestone slows down at low temperature. While it is chemical reaction that mainly controls the process of sulfation during this stage, reaction R1 is the rate-determining step which affects the efficiency of sulfur capture. As the operating temperature increases, the calcination of limestone is accelerated, leading to the further formation of CaO [18]. As a result, the efficiency of sulfur capture increases to the maximum with increasing the operating temperature. However, if the temperature continues to

increase, the sintering of CaO occurs as well. The layer of CaSO₄ accumulates and covers the unreacted CaO. The sulfation turns to be mainly controlled by diffusion rather than chemical reaction. As a result, the efficiency of sulfur capture decreases at high temperature and the utilization of limestone is also decreased. Comparing with the optimum temperature for sulfur capture during CFB air combustion, it is expected that the operating temperature for sulfur capture during CFB oxy-fuel combustion, especially with high oxygen concentration, should be incremented up to about 930°C, in order to keep the efficiencies of both sulfur capture and coal combustion acceptable.

3.3 Effect of Ca/S molar ratio on limestone sulfation in oxy-fuel CFB combustion

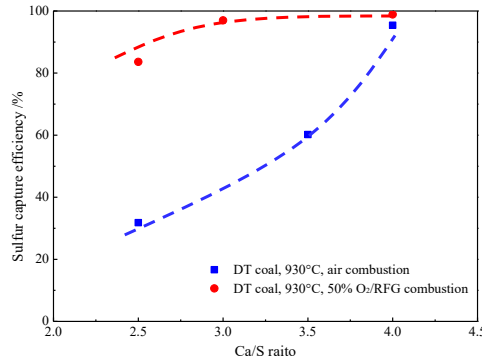


Fig. 5 Effect of Ca/S molar ratio on the efficiency of sulfur capture

As analyzed previously, because of the formation of CaSO₄ during the sulfur capture process, the external pores of reagent solids (CaO or CaCO₃) will be plugged. As a result, the ratio of limestone utilization cannot reach up to 100%. In order to keep the efficiency of sulfur capture during coal combustion high, the amount of limestone used during actual CFB combustion should be excess. The molar ratio of calcium in limestone and sulfur in fuel (Ca/S) is defined to evaluate the amount of calcium sorbents fed during coal CFB combustion.

Fig. 5 shows the tendencies of sulfur capture efficiency with increasing Ca/S ratio during air and O₂/RFG combustion. It is obvious that the efficiencies during both air and O₂/RFG increased with increasing the Ca/S ratio from 2.5 to 4.0. When the ratio of Ca/S is 4.0, the sulfur capture efficiency can reach up to 100%. However, during O₂/RFG combustion, although the efficiency of sulfur capture increases continuously, the increasing trend slows down gradually when Ca/S ratio is more than 3.0. Meanwhile, the utilization of limestone decreases if Ca/S is too high, leading to the waste of limestone. Besides, some previous results have proved that the emission of NO_x increases with increasing the amount of CaO in the furnace because of the effect of CaO on the conversion from NH₃ to NO_x [19]. As a result, there is an optimum molar ratio of Ca/S during actual coal CFB combustion. For oxy-fuel combustion, especially with high oxygen concentration in the feeding flow, Ca/S can be set as 3.0.

4. CONCLUSION

The characteristics of sulfur capture during oxy-fuel combustion were studied in an oxy-CFBC pilot-scale facility. The following conclusions can be drawn from the investigation:

The efficiency of sulfur capture during O₂/RFG combustion is higher than that in air-combustion in the temperature range of 900-950°C because of the existence of high CO₂ in the furnace during oxy-fuel combustion. Besides, with increasing the concentration of oxygen, the efficiency of sulfur capture increases slightly. Operation with high oxygen concentration can be one of useful choices for in-situ sulfur capture during oxy-fuel CFB combustion.

The optimum operating temperature for sulfur capture in oxy-fuel combustion is different from that in air-combustion. Comparing the temperature which is about 880°C during air-combustion, the optimum temperature is about 930°C during O₂/RFG combustion in which overall oxygen concentration is 50%. In order to keep the sulfur retention, the operating temperature should be increased as high as 930°C during actual oxy-fuel combustion with high oxygen concentration.

The efficiency of sulfur capture during both air and oxy-fuel combustion increases with increasing the Ca/S ratio. With consideration of various factors, the optimal ratio of Ca/S can be set as 3.0 during oxy-fuel combustion with high oxygen concentration.

ACKNOWLEDGEMENTS

This study is supported by the Strategic Priority Research Program of the Chinese Academy of Sciences (Grant No. XDA07030200), the International Science & Technology Cooperation Program of China (Grant No. 2014DFG61680).

REFERENCES

- [1] Wall T, Liu Y, et al. An overview on oxyfuel coal combustion—State of the art research and technology development. *Chemical Engineering Research and Design*. 2009;87:1003-16.
- [2] Buhre BJP, Elliott LK, et al. Oxy-fuel combustion technology for coal-fired power generation. *Progress in Energy and Combustion Science*. 2005;31:283-307.
- [3] Tan Y, Jia L, et al. Experiences and results on a 0.8 MW_{th} oxy-fuel operation pilot-scale circulating fluidized bed. *Applied Energy*. 2012;92:343-7.
- [4] Jia L, Tan Y, et al. Commissioning of a 0.8 MW_{th} CFBC for oxy-fuel combustion. *International Journal of Greenhouse Gas Control*. 2012;7:240-3.
- [5] Escudero AI, Espatolero S, et al. Minimization of CO₂ capture energy penalty in second generation oxy-fuel power plants. *Applied Thermal Engineering*. 2016;103:274-81.
- [6] Saastamoinen H, Pikkarainen T. Development of 2nd generation oxyfuel CFB technology—laboratory and pilot scale combustion experiments in high oxygen concentration. *VII Liekkipäivä, Tampere (Finland)*. 2014.
- [7] Li H, Li S, et al. Experimental Results for Oxy-fuel Combustion with High Oxygen Concentration in a 1MW_{th} Pilot-scale Circulating Fluidized Bed. *Energy Procedia*. 2014;63:362-71.
- [8] Basu P. Combustion of coal in circulating fluidized-bed boilers: a review. *Chemical Engineering Science*. 1999;54:5547-57.
- [9] de Diego LF, de las Obras-Loscertales M, et al. Characterization of a limestone in a batch fluidized bed reactor for sulfur retention under oxy-fuel operating conditions. *International Journal of Greenhouse Gas Control*. 2011;5:1190-8.
- [10] Hu G, Dam-Johansen K, et al. Review of the direct sulfation reaction of limestone. *Progress in energy and combustion science*. 2006;32:386-407.
- [11] Chen C, Zhao C, et al. Calcination and sintering characteristics of limestone under O₂/CO₂ combustion atmosphere. *Fuel Processing Technology*. 2007;88:171-8.
- [12] Garcia-Labiano F, Rufas A, et al. Calcium-based sorbents behaviour during sulphation at oxy-fuel fluidised bed combustion conditions. *Fuel*. 2011;90:3100-8.
- [13] Liu H, Katagiri S, et al. Sulfation behavior of limestone under high CO₂ concentration in O₂/CO₂ coal combustion. *Fuel*. 2000;79:945-53.
- [14] De Diego L, Rufas A, et al. Optimum temperature for sulphur retention in fluidised beds working under oxy-fuel combustion conditions. *Fuel*. 2013;114:106-13.
- [15] Lupiáñez C, Guedea I, et al. Experimental study of SO₂ and NO_x emissions in fluidized bed oxy-fuel combustion. *Fuel processing technology*. 2013;106:587-94.
- [16] Liémans I, Alban B, et al. SO_x and NO_x absorption based removal into acidic conditions for the flue gas treatment in oxy-fuel combustion. *Energy Procedia*. 2011;4:2847-54.
- [17] Zheng J, Yates J, et al. A model for desulphurisation with limestone in a fluidised coal combustor. *Chemical Engineering Science*. 1982;37:167-74.
- [18] Li W. Study on SO₂ emission and removal characteristics for oxy-fuel circulating fluidized bed combustion: The University of Chinese Academy of Sciences; 2015.
- [19] Hansen PFB, Dam-Johansen K, et al. Catalytic reduction of NO and N₂O on limestone during sulfur capture under fluidized bed combustion conditions. *Chemical Engineering Science*. 1992;47:2419-24.