



Emissions of SO₂, NO and N₂O in a circulating fluidized bed combustor during co-firing coal and biomass

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Abstract

This paper presents the experimental investigations of the emissions of SO₂, NO and N₂O in a bench scale circulating fluidized bed combustor for coal combustion and co-firing coal and biomass. The thermal capacity of the combustor is 30 kW. The setup is electrically heated during startup. The influence of the excess air, the degree of the air staging, the biomass share and the feeding position of the fuels on the emissions of SO₂, NO and N₂O were studied. The results showed that an increase in the biomass shares resulted in an increase of the CO concentration in the flue gas, probably due to the high volatile content of the biomass. In co-firing, the emission of SO₂ increased with increasing biomass share slightly, however, non-linear increase relationship between SO₂ emission and fuel sulfur content was observed. Air staging significantly decreased the NO emission without raising the SO₂ level. Although the change of the fuel feeding position from riser to downer resulted in a decrease in the NO emission level, no obvious change was observed for the SO₂ level. Taking the coal feeding position R as a reference, the relative NO emission could significantly decrease during co-firing coal and biomass when feeding fuel at position D and keeping the first stage stoichiometry greater than 0.95. The possible mechanisms of the sulfur and nitrogen chemistry at these conditions were discussed and the ways of simultaneous reduction of SO₂, NO and N₂O were proposed.

Key words: circulating fluidized bed (CFB); combustion; SO₂; NO; N₂O; co-firing; biomass

Introduction

Coal now contributes 70% of China total energy consumption and this tendency will keep quite a long time in the future (Liu, 2000). Combustion in low capacity, the main manner to use coal in China, leads to the problem of low combustion efficiency and high level pollutant emissions. Emitted SO₂ and NO from combustion is the main reason of acid rain in southwest China (Lin, 2000). Using circulating fluidized bed (CFB) combustor integrated with *in-situ* calcium injection can effectively promote combustion efficiency and reduce NO and SO₂ simultaneously. However, a significant amount of N₂O (20–250 ppm) (Li *et al.*, 1998), which is one of the greenhouse gases and also contributes to the ozone depletion at stratosphere, emitted during CFB combustion (Wojtowicz *et al.*, 1993). So, it is important to control the emissions of NO, N₂O and SO₂ during CFB coal combustion.

Approximate 54×10⁶ t of rice husk, which can generate heat or power as part substitute of coal, are produced every year in China (Armesto *et al.*, 2002; Fang *et al.*, 2004). Among the biomass thermo-chemical conversion

technologies (i.e. combustion, gasification and pyrolysis), combustion is the only proven technology for heat and power production (Nussbaumer, 2003). In general, there is a rapid consumption of oxygen for firing biomass, which takes place in one phase. Whereas, for coal, the oxygen consumption profile exhibits two regions characterizing a short phase for volatile combustion and a long char combustion phase (Werther *et al.*, 2000). So the following phenomena may occur when co-firing coal and biomass: firstly, biomass is easy to be ignited because of higher volatile matter, the quicker oxygen consumption of biomass reduces the oxygen available for coal, and the coal-char concentration at suspension area will be increased during CFB combustion with increasing biomass mass share, the possibility of reduction of NO and N₂O on char surface will increase accordingly; secondly, large amount of biomass will be risen to freeboard quickly when feeding coal and biomass at the same position because of lower terminal velocity of biomass. That is, biomass combustion and coal-char combustion would occur at the same area during co-firing, NH₃ originates from biomass devolatilization will react with NO finally producing N₂ if OH, O radical is available for NH₃ decomposition (Johnsson, 1994).

Devolatilization or gasification solid fuels like coal,

biomass results in forming a fuel gas containing high concentrations of combustible gas with CO, H₂ and CH₄ as its major compounds. At the same time, quite amount of NH₃ and HCN, the major precursors of NO and N₂O, originate from the organic nitrogen in the fuels (Glarborg *et al.*, 2003; Leppalahti and Koljonen, 1995). Basically, there are three principal approaches to decrease the NO and N₂O concentration during solid fuels thermal-chemical conversion process: (1) to find proper pyrolysis/gasification conditions that the fuel-nitrogen would directly react to N₂ (Ohtsuka *et al.*, 1998; Tsubouchi *et al.*, 2003; Wu and Ohtsuka, 1997); (2) to convert the NH₃ and HCN to molecular nitrogen before combustion; (3) to use NH₃ and HCN as reducing agent to reduce NO and N₂O finally producing N₂ at proper operating conditions during combustion (Lin, 1994). Generally speaking, the solid fuel feeding position is always near the distributor during CFB combustion and downer is merely act as return leg, if changing the fuel feeding position to downer, pyrolysis or gasification solid fuels will take place before they enter the riser, the released NH₃ and HCN may be reducing NO to N₂. In principal, the reactions would be the same as in thermal De-NO_x process (Leckner *et al.*, 1991; Miller and Bowman, 1989) or reburning technology (Smoot *et al.*, 1998). By integrating with calcium injection technology, simultaneously retention NO, N₂O and SO₂ will be reached. However, there is still not enough information about reduce emissions of NO and N₂O by co-firing coal and biomass and by changing the solid fuel feeding position.

The objective of this work was to investigate the effect of different parameter such as biomass share, first stage stoichiometry and excess air on the emissions of NO, N₂O, SO₂, and CO during coal combustion and co-firing coal and rice husk in a CFB combustor. In order to find out an *in-situ* pollutant retention measure, the comparison of emission performance of different coal and biomass feeding position with coal combustion and co-firing coal and rice husk has also been studied in this paper. The results obtained from this study could be used to propose a novel *in-situ* simultaneous process to reduce emissions of NO, N₂O, and SO₂.

1 Experimental

1.1 Apparatus

The experiments were carried out in a 30-kW (thermal) CFB combustor as schematically illustrated in Fig.1. The apparatus consists of a riser, with a height of 7 m and an i.d. of 0.86 m, and a downer with a height of 3 m and an i.d. of 0.39 m. Both reactors are made of high temperature resistant stainless steel and are externally heated by six electric heating elements, which can be independently controlled.

The combustion air can be divided into two streams: preheated primary air is introduced below the gas distributor and the secondary air is tangentially introduced to the combustor via a port located 1.66 m above the gas distributor. Thus, the two stage combustion can be realized.

6 K-type thermocouples are installed on the riser to

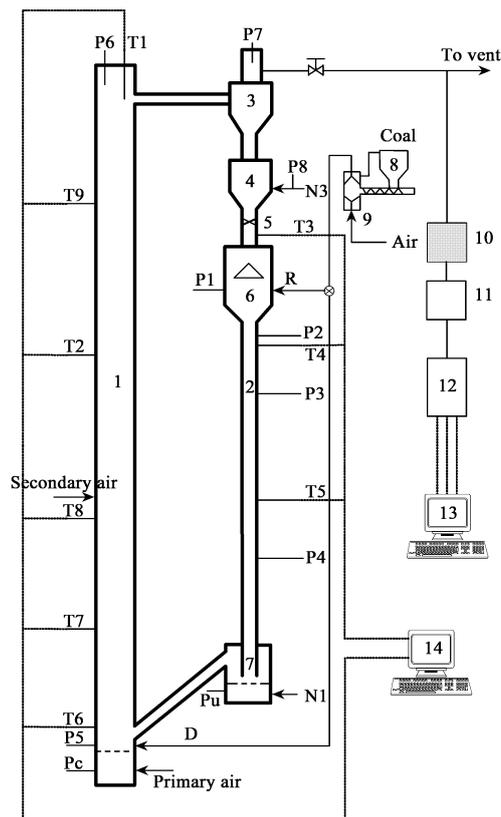


Fig. 1 Schematic diagram of applied CFB combustor. (1) combustor; (2) downer; (3) cyclone; (4) particles hopper; (5) butterfly valve; (6) solid-solid mixer; (7) U-type valve; (8) screw feeder; (9) pneumatic feeder; (10) filter; (11) water trap; (12) gas analyzer; (13) gas concentration acquisition station; (14) temperature acquisition station.

measure the temperature and they are located 0.15 m (T6), 1.6 m (T7), 2.8 m (T8), 4.0 m (T2), 5.2 m (T9) and 6.43 m (T1) above the gas distributor respectively. However, only 3 K-type thermocouples are used to measure the temperature in the downer. The pressures in the CFB combustor are measured by 10 U-type manometers, 4 for the riser and 6 for the downer.

There are 2 feeding ports for coal and biomass particles: one is located at 20 mm above the gas distributor in the riser (position R), the other is designed at the lower part of solid-solid mixer in the downer (position D). A two-stage feeding system, which is composed of a screw feeder and a pneumatic transportation feeder, was specially designed to introduce fuel particles or silica sand particles into the CFB combustor. Coal or biomass particles was firstly screwed by the screw feeder and then transported pneumatically into the CFB combustor by compressed air. The feeding rate of coal or biomass particles was easily controlled by varying the motor rotation speed of the screw feeder. The feeding coal and biomass particles were well mixed in the transportation pipe before introduced into the CFB combustor.

The concentrations of O₂, CO, CO₂, SO₂, NO, and N₂O in flue gas are on-line measured by an ABB-AO2020 continuous gas analyzer. The gas sampling pipes from the CFB combustor to the ABB-AO2020 continuous gas analyzer are made of stainless steel and Teflon. All measured

temperatures and gas concentrations were logged into a computer by a data acquisition system at set time intervals. To compare the experimental data with other references, all gas concentrations have been converted to 6% O₂ basis.

1.2 Raw materials

The coal and rice husk were from Datong, Shanxi Province, and Heibei Province of China. The proximate and ultimate analysis of bituminous coal and rice husk are listed in Table 1. Both coal and rice husk are milled and sieved into 0.154–0.600 mm and then dried in an oven at 383 K for at least 4 h before experiments. The size distributions of these particles are shown in Fig.2. The silica sand with the size of 0.224–0.280 mm is used as bed material in the CFB combustor.

1.3 Experimental procedure

Coal is introduced into the CFB combustor at a rate of about 3 kg/h at position R or D when temperature at gas distributor is higher than the ignition temperature of the coal.

To compare with the emissions of SO₂, NO and N₂O during coal combustion and co-firing of coal and rice husk, two sets of experiments have been performed. Coal firing experiments are firstly carried out by changing excess air and the primary air/secondary air ratio at a 2.68 kg/h coal feeding rate; then coal and biomass co-firing experiments are performed with rice husk mass share as 13 wt%, 22 wt%, 27 wt% and 30 wt%, whereas coal feeding rate is kept at 2.68 kg/h.

The fuel particles introduced at position D can be quickly heated up to 1023–1093 K by heat exchange between fuel and silica sand particles in the downer. Gasification reactions of introduced fuel particles occurred in the downer where the atmosphere is isolated from the

riser by the U-valve, and the air ratio is about 0.15–0.20. The char and gas together with circulated solid in the downer will be transported through the U-valve to the riser, where combustion reactions are performed. Silica sands, ash and incompletely burned char particles are transported to the top of the riser, then separated from the flue gas by a cyclone and entered into the hot media hopper while the clean flue gas is exited from the vent.

Each experiment run is performed more than one or two hours under specified operating conditions when the temperature and the flue gas concentrations only fluctuate in a very narrow range. The results presented in this paper are the mean values. The operation conditions are listed in Table 2.

2 Results and discussion

2.1 Influence of biomass share

Influence of rice husk mass share on emissions of NO, N₂O, SO₂ and CO during co-firing coal and biomass with air flow rates of 20.8 Nm³/h and 5.1 Nm³/h as primary and secondary air and fuel feeding position R are shown in Fig.3. When mass ratio of rice husk to coal increases from 0, 13 wt%, 22 wt%, 27 wt% and 30 wt%, emissions of NO and N₂O decreases dramatically from 125 to 79 ppm and 122 to 32 ppm, respectively. Emission of SO₂ is found to show a slight increase with the increase of rice husk mass share. The emission of CO is observed to have a higher concentration with large fluctuation at higher rice husk mass share as expected.

Many research results have shown that biomass addition had a positive effect on emissions during co-firing with a stable total mass/energy load by increasing biomass mass/heat fraction as well as decreasing coal mass/heat fraction. Because the nitrogen content in biomass is less than that in coal, the less emission of nitrogenous oxide

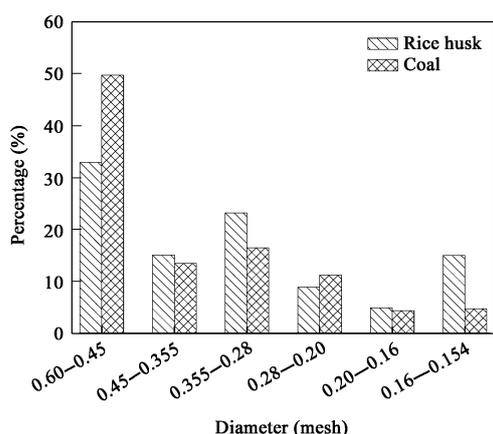


Fig. 2 Diameter distribution of coal and rice husk.

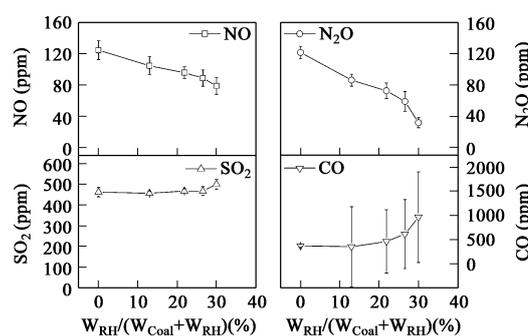


Fig. 3 Effect of rice husk mass share on the NO, N₂O, SO₂ and CO emission during co-firing coal and rice husk. The error bar represents twice the standard deviation associated with each data point.

Table 1 Chemical analysis of coal and biomass samples

Fuel	Proximate analysis ^a (%)			Ultimate analysis ^a (%)				
	VM	A	FC ^b	C	H	N	S	O ^b
Rice husk	68.74	15.93	15.34	44.44	5.68	0.55	0.06	33.34
Coal	27.92	11.41	60.67	72.98	3.69	1.16	0.62	10.14

^aBased on dry basis; ^bby difference; VM: volatile matter; A: ash; FC: fixed carbon.

Table 2 Operating conditions of CFB and flue gas analysis

Item	Case											
	1	2	3	4	5	6	7	8	9	10	11	12
Coal feeding rate (kg/h)	2.68	2.68	2.68	2.68	2.68	2.68	2.68	2.68	2.68	2.68	2.68	2.68
Biomass feeding rate (kg/h)	0	0.4	0.75	0.97	1.15	0.75	0.75	0.75	0.75	0.75	0.75	0.75
Biomass share (%)	0	13	22	27	30	22	22	22	22	22	22	22
Fuel feeding position	R	R	R	R	R	R	R	R	R	R	R	R
Total primary air (Nm ³ /h) ^a	20.8	20.8	20.8	20.8	20.8	18.7	22.8	25.9	18.7	22.8	24.9	27.0
Secondary air (Nm ³ /h)	5.1	5.1	5.1	5.1	5.1	7.2	3.1	0.0	5.1	5.1	5.1	5.1
Excess air (%)	26.3	16.5	9.0	4.8	1.6	9.0	9.0	9.0	0.4	17.7	26.3	35.0
T1 (K)	1116	1128	1146	1129	1139	1139	1151	1151	1137	1154	1153	1152
T2 (K)	1147	1161	1175	1159	1171	1173	1181	1180	1172	1177	1166	1155
T6 (K)	984	1004	1039	1011	1030	1050	1026	1024	1093	1032	1035	1033
T7 (K)	1079	1112	1132	1105	1128	1141	1125	1120	1156	1115	1100	1090
T8 (K)	1124	1144	1160	1142	1156	1161	1163	1162	1167	1145	1128	1115
T9 (K)	1148	1161	1176	1160	1171	1174	1180	1181	1171	1181	1176	1172
T3 (K)	1002	1017	1058	1014	1030	1037	1051	1058	1051	1065	1071	1074
T4 (K)	1001	1014	1051	1014	1025	1030	1046	1051	1048	1058	1065	1066
T5 (K)	994	1007	1041	1010	1019	1020	1038	1046	1032	1050	1057	1061
O ₂ (%)	4.52	3.08	2.32	1.90	1.07	1.43	1.66	1.75	0.73	3.00	4.56	8.30
CO ₂ (%)	14.58	15.90	16.65	16.98	17.73	17.36	17.14	17.03	17.78	15.90	14.51	11.21
CO (ppm)	371	348	460	613	964	601	441	451	1477	335	293	346
NO (ppm)	125	105	96	89	79	81	111	121	82	140	177	204
N ₂ O (ppm)	122	86	73	59	32	46	50	52	31	69	84	88
SO ₂ (ppm)	462	456	467	467	500	520	486	483	500	494	503	483
Item	13	14	15	16	17	18	19	20	21	22	23	
Coal feeding rate (kg/h)	2.68	2.68	2.68	2.68	2.68	2.68	2.68	2.68	2.68	2.68	2.68	
Biomass feeding rate (kg/h)	0	0.4	0.75	0.97	1.15	0.75	0.75	0.75	0.75	0.75	0.75	
Biomass share (%)	0	13	22	27	30	22	22	22	22	22	22	
Fuel feeding position	D	D	D	D	D	D	D	D	D	D	D	
Total primary air (Nm ³ /h) ^a	20.8	20.8	20.8	20.8	20.8	18.7	22.8	25.9	22.8	24.9	27.0	
Secondary air (Nm ³ /h)	5.0	5.1	5.1	5.1	5.1	7.2	3.1	0.0	5.1	5.1	5.1	
Excess air (%)	26.3	16.5	9.0	4.8	1.6	9.0	9.0	9.0	17.7	26.3	35.0	
T1 (K)	1125	1138	1144	1139	1142	1141	1145	1146	1147	1139	1147	
T2 (K)	1153	1167	1173	1167	1171	1171	1173	1174	1168	1154	1155	
T6 (K)	1064	1074	1085	1079	1088	1111	1076	1059	1067	1038	1035	
T7 (K)	1123	1142	1155	1148	1157	1152	1153	1147	1141	1115	1110	
T8 (K)	1139	1153	1162	1157	1163	1162	1164	1165	1151	1133	1129	
T9 (K)	1155	1168	1174	1168	1172	1172	1174	1175	1173	1166	1170	
T3 (K)	1051	1063	1075	1069	1075	1074	1076	1075	1077	1056	1066	
T4 (K)	1049	1066	1068	1065	1063	1068	1073	1075	1078	1058	1063	
T5 (K)	1046	1047	1052	1047	1048	1050	1056	1056	1057	1041	1044	
O ₂ (%)	3.55	2.17	1.46	1.33	0.93	1.30	1.78	1.97	3.04	4.17	5.38	
CO ₂ (%)	15.34	16.56	17.23	17.34	17.68	17.34	16.92	16.74	15.82	14.86	13.77	
CO (ppm)	257	363	609	887	1334	793	594	418	295	235	236	
NO (ppm)	101	94	87	85	86	80	102	111	117	142	181	
N ₂ O (ppm)	122	65	49	47	34	43	57	62	72	83	86	
SO ₂ (ppm)	474	490	500	513	551	503	480	460	493	480	472	

^aTotal primary air is composed of primary air, carrier gas and fluidized gas of U-valve.

and sulfur dioxide during co-firing can be easily explained as the dilution of N and S content in the mixed fuel (Dayton *et al.*, 1999; Gayan *et al.*, 2004; Leckner and Karlsson, 1993; Spliethoff and Hein, 1998). However, in this study, the co-firing experiments were performed with rice husk mass share as 0, 13 wt%, 22 wt%, 27 wt% and 30 wt%, whereas coal feeding rate kept at 2.68 kg/h. Hence, the energy load in this study was increasing. This is why results from this study do not agree with reported results which explained by the “diluting effect”. The reason for that could be explained as follows: (1) O₂ concentration in the CFB combustor decreases with the increase of amount of fuel, therefore, rapid conversion of carbon in fuels to CO reduces oxygen reaction competition ability with N to form NO and N₂O (Jenkins *et al.*, 1998); (2) the formation of NO from fuel nitrogen takes place via combustion of

nitrogen species as volatiles and oxidation of nitrogen in char (Glarborg *et al.*, 2003; Johnsson, 1994). Due to the density difference between coal and rice husk particles, rice husk particle has a smaller terminal velocity than that of coal or silica sand particles (Fang *et al.*, 2004). Therefore the rice husk particles will be devolatilized and combusted at higher region than coal in the riser, the released volatile gases, such as CH₄, HCN and NH₃ from rice husk, can reduce generated NO from oxidation of coal char at higher region of the riser to form N₂, just like the “reburning” mechanism reported elsewhere (Smoot *et al.*, 1998; Spliethoff *et al.*, 1996).

Compared with coal combustion, the slight increase of SO₂ emission during co-firing can be considered as a result of fuel S increase with the increasing rice husk mass share as shown in Fig.3. In those experiments about 88%–

94% fuel S is converted to SO₂, the increase tendency and the non-linear relationship between SO₂ emission and rice husk mass share can be considered as variation of sulfur conversion rate (Spliethoff and Hein, 1998) or the increase of biomass share. It is known that there are some alkaline metal in rice husk, such as calcium and potassium (Armesto *et al.*, 2002; Natarajan *et al.*, 1998; Werther *et al.*, 2000), and those alkali metal elements have strong ability to capture SO₂ at CFB combustor via the formation of calcium and potassium sulfates under oxidizing conditions (Cheng *et al.*, 2003; Knudsen *et al.*, 2004; Wolf *et al.*, 2005). However, the results in this paper showed the sulfur retention of alkaline metal is of neglectable.

General speaking, emission of CO is closely related with temperature, oxygen concentration, mixing of fuel particles with air, and residence time of gaseous products (Armesto *et al.*, 2002; Permchart and Kouprianov, 2004; Spliethoff and Hein, 1998; Svoboda *et al.*, 2003; Werther *et al.*, 2000). Armesto *et al.* (2002) measured that 200–2000 mg/Nm³ of CO can be emitted during combustion of rice husks in a bubbling fluidized bed. The decreased O₂ concentration and high content of volatile gases of rice husk in the riser should be the important reasons for high CO emission observed in this study.

2.2 Influence of excess air

The effect of excess air on emissions of NO, N₂O, SO₂ and CO during coal combustion and co-firing coal and biomass introduced at position R is shown in Fig.4. The rice husk mass share was kept at 22 wt%; excess air was changed from 11% to 53% for coal combustion and 0.4% to 35% for co-firing by keeping the secondary air at 5.1 Nm³/h and changing the primary air from 18.7 to 27.0 Nm³/h. It can be seen from Fig.4a that the emission of NO increase with increasing excess air during both fuel combustion processes; however, the increase tendency during co-firing is slightly lower than that during coal combustion. Hence, NO emission during co-firing is lower than that during coal combustion at higher excess air.

No obvious influence of excess air on emission of N₂O can be found not only for coal combustion, but also for co-firing. Although the emission of N₂O during coal combustion is kept almost constant with different

excess air, a lower N₂O emission can be observed with the same excess air during co-firing (Fig.4b). Emission of SO₂ during co-firing (Fig.4c) is about 40 ppm higher than that for coal combustion, and no great fluctuation with the increasing excess air can be obtained during both firing and co-firing. Higher SO₂ emission during co-firing is due to extra sulfur charged from biomass (Leckner and Karlsson, 1993). Emission of CO decreases with the increase of excess air from 0 to 9% during co-firing (Fig.4d). However, CO emission during co-firing is higher and more fluctuated than that during coal combustion. The high CO emission with large fluctuation is leveled off with the increasing excess air; hence excess air above 35% is of benefit to improve combustion efficiency during co-firing.

There are two oxygen consumption regions in the riser during coal combustion charactering a shorter phase for volatile combustion and a longer phase for char combustion (Werther *et al.*, 2000). However, this will be changed during co-firing because volatile matters in rice husk is significantly higher than that in coal (Table 1), considerable amount of volatile matters can be burned at suspension region in the riser during co-firing (Natarajan *et al.*, 1998). Most fuel nitrogen in rice husk can be volatilized during pyrolysis or gasification and released as NH₃ and so on, but coal retains more nitrogen in char (Glarborg *et al.*, 2003; Leppalahti and Koljonen, 1995). NO formed partly from coal nitrogen can be easily reduced by NH₃ from pyrolysis of rice husk, or by CH_i, whose quantity is proportional to the amount of local CO (Nussbaumer, 2003; Salzmann and Nussbaumer, 2001; Smoot *et al.*, 1998). However, the reduction of NO by this route is not remarkable under low oxygen concentration condition during co-firing, because a large amount of NO can be generated at higher region in the riser, where the formed NH₃ is not available any longer by oxidizing of O or OH radical to NO. Furthermore, the higher CO concentration during co-firing also indicates that a larger amount of char exists in the riser and the char can reduce NO to form molecular nitrogen (Johnsson, 1994; Leckner and Karlsson, 1993).

Compared with coal combustion, 22 wt% of rice husk share during co-firing can lead to a 30 K temperature increase in the riser. Hence, the formed N₂O can be effectively decomposed over char at higher temperature

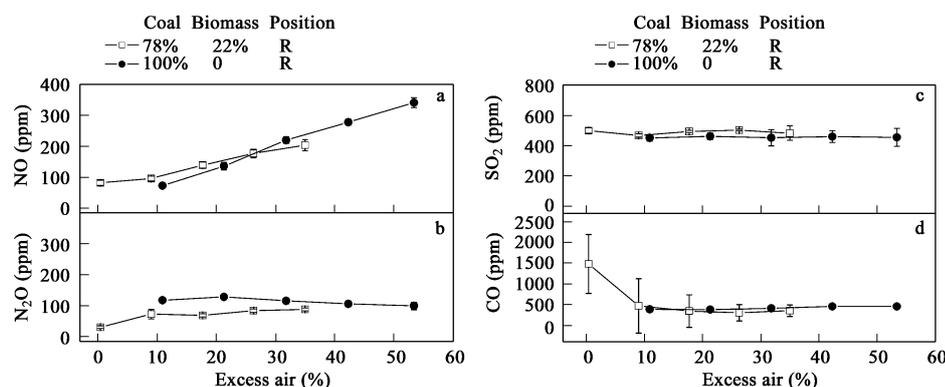
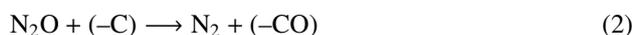
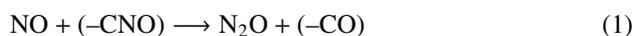


Fig. 4 Effect of excess air on the NO(a), N₂O(b), SO₂(c) and CO(d) emission during coal combustion without and with rice husk addition (the mass share of rice husk is stable at 22 wt%). The error bar represents twice the standard deviation associated with each data point.

during co-firing (Amand *et al.*, 1991; Johnsson, 1994; Leckner and Karlsson, 1993). Analysis (De Soete *et al.*, 1999) of the triple trade-off between N_2O , NO and N_2 shows that the major N_2 produced from NO in the range of 900–1050 K is via Reaction (1) and (2), rather than Reaction (3) described as follows:



The observed slight increase of N_2O with the increasing excess air (Fig.4b) may be related with char decrease in the suspension region in the riser during co-firing.

2.3 Influence of first stage stoichiometry

Effect of first stage stoichiometry on emissions of NO, N_2O , SO_2 and CO during coal combustion and co-firing coal and biomass introduced at position R is shown in Fig.5. The biomass mass share is kept at 22 wt% and total introduced air is kept at 25.9 Nm^3/h . The influence of the first stage stoichiometry on emissions of NO, N_2O , SO_2 and CO shows almost the same tendency as the influence of excess air shown in Fig.4.

Emission of NO during co-firing shows a smaller increase with the increase of first stage stoichiometry than that during coal combustion. The NO emission was kept at a very low value when the first stage stoichiometry is greater than 0.95 during co-firing. These indicate that NO can be effectively reduced in oxygen-rich atmosphere. Air staging does not lead to an appreciable change in N_2O emission during co-firing as shown in Fig.5b. A little higher SO_2 emission and fluctuated CO emission are found in Fig.5c and Fig.5d, respectively during co-firing, and both of them seem to be not sensitive to the first stage stoichiometry.

2.4 Influence of feeding positions

To investigate influence of fuel feeding positions on emissions, two groups of co-firing experiments were performed in this study by changing feeding fuel from traditional position R to position D. The relative concentration is applied to present emission variation from

changing feeding positions. The relative concentration of each pollutant gas can be expressed as a percentage with respect to the basis of coal combustion feeding at position R, and negative relative concentration means a decrease of pollutant emission resulting from changing fuel feeding position.

The relationship between first stage stoichiometry and relative emissions of NO, N_2O , SO_2 and CO during co-firing coal and biomass introduced at R and D are shown in Fig.6. The relative emissions of NO, N_2O , SO_2 and CO during coal combustion introduced at position D are also presented in Fig.6. An obvious decrease of relative NO emission can be found with the increase of the first stage stoichiometry in three studied cases. Changing fuel feeding position from R to D will result in an obvious decrease of emission of NO during firing in all the four test runs, however, a smaller emission of NO can be obtained when the first stage stoichiometry is greater than 0.95 during co-firing in spite of feeding position at R or D. Emission of NO can be reduced about 40% at the first stage stoichiometry of 1.08 during co-firing with fuel feeding position D.

Emission of N_2O increases when the first stage stoichiometry is greater than 0.97 during coal combustion with fuel feeding position D. No difference of N_2O emissions is observed during co-firing with different fuel feeding positions or different first stage stoichiometry.

The relative SO_2 emissions during coal combustion with coal feeding at D or co-firing with fuel feeding at D and R are illustrated in Fig.6c. The relative concentrations show an increase with the increase of the first stage stoichiometry from 0.87 to 1.24.

The relative emission of CO will reduce during coal combustion by changing the feeding position from R to D, but relative emission of CO is observed to increase during co-firing at two feeding positions as showed in Fig.6d.

The relationships between the relative emissions of NO, N_2O and the first stage stoichiometry during co-firing at two feeding positions suggest that changing fuel feeding position may lead to a variation of fuel nitrogen transformation. In this study, air at flow rate of 4 Nm^3/h is applied not only as carrier gas for fuel feeding system but also as gasification agent in the downer when fuel

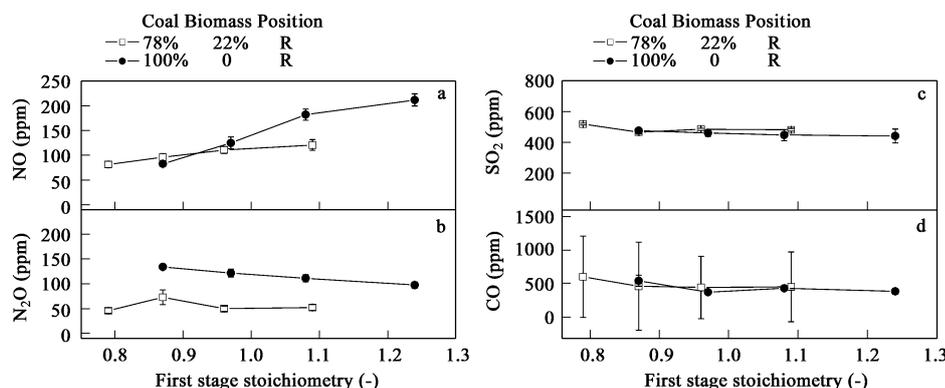


Fig. 5 Effect of first stage stoichiometry on the NO (a), N_2O (b), SO_2 (c) and CO (d) emission during coal combustion without and with rice husk addition (the mass share of rice husk is stable at 22 wt%). The error bar represents twice the standard deviation associated with each data point.

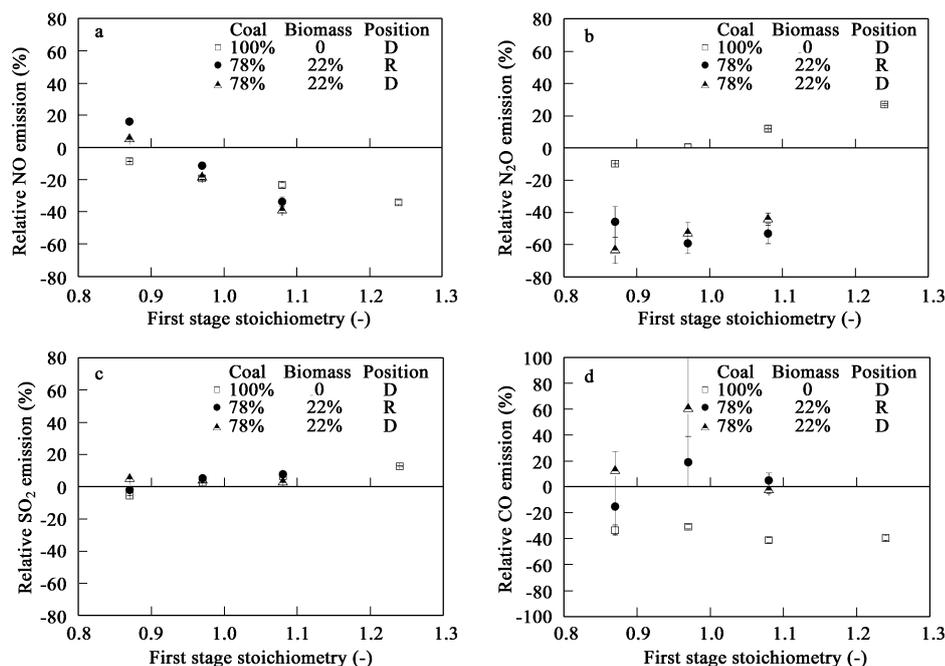


Fig. 6 Relative NO (a), N₂O (b), SO₂ (c), CO (d) emission vs. first stage stoichiometry when changing fuel added position (expressed as a percentage with respect to the situation only coal added at riser). The error bar represents twice the standard deviation associated with each data point.

is introduced at position D. Chang *et al.* (2003) believe that oxidation of coal with 4% O₂ in a temperature from 672 to 873 K leads to formation of HCN and NH₃ due to the enhancement of H radical production. When those reducing gases including CH_i are introduced into the riser through U-valve, they can combine easily with NO or O and OH radical depending on the local atmosphere (Nussbaumer, 2003; Smoot *et al.*, 1998). There is not enough oxygen available in the primary zone at the lower first stage stoichiometry, NH₃ and HCN introduced from the downer will be oxidized to NO. This is the main reason why higher relative emission of NO is observed during co-firing when the first stage stoichiometry is less than 0.95. However, NO reduction will take place in the primary air zone under excess-oxygen conditions, similar with the thermal De-NO_x process (Leckner *et al.*, 1991; Miller and Bowman, 1989). It is well known that NH₃ can effectively reduce NO at temperature window roughly between 1100 and 1400 K when molecular oxygen is present in sufficient quantities. Furthermore, high concentration of hydrocarbon in the case of rice husk added during co-firing may lead to temperature window shift effectively to a lower level. On the other hand, the obtained higher concentration of CO during co-firing than that of during coal combustion corresponds higher CH_i in the riser, CH_i may react with fuel N to form HCN which would be oxidized to molecular nitrogen by O or OH radicals (Smoot *et al.*, 1998).

Compared with co-firing, coal combustion introduced at position D emits higher relative N₂O emission, as HCN released during coal gasification in the downer can be oxidized in the riser. N₂O formation from Reaction (1) is also the possible route for higher relative N₂O emission (De Soete *et al.*, 1999). In the case of co-firing, changing the fuels feeding position seems to have no appreciable

variation to relative N₂O emission.

No obvious change of relative SO₂ emission is shown when fuel feeding position is changed to D during coal combustion or co-firing.

When only coal is burned, the relative CO emission is likely to decrease because a pre-oxidation occurs in the downer. No such a similar tendency is found during co-firing. However, the violence oscillate of CO emission during co-firing indicates that a higher excess air is favourable for complete combustion.

3 Conclusions

Different CFB operation parameters such as the first stage stoichiometry, excess air, biomass mass share and fuel adding position on the emissions of NO, N₂O, SO₂ and CO during coal combustion and co-firing coal and biomass in a CFB combustor were investigated in this study. Increasing the biomass mass share during coal-biomass co-firing can significantly decrease emissions of NO and N₂O, however, non-linear increase relationship between SO₂ emission and fuel sulfur content is observed. Taking the coal feeding position R as a reference, it is observed that the effect of fuel feeding position on the NO and N₂O emission depends on the first stage stoichiometry. When the first stage stoichiometry keeps greater than 0.95, the relative NO emission can significantly decrease during coal-biomass co-firing fed fuel samples at position D. The reduce of NO and N₂O during coal-biomass co-firing fed fuel samples at position D can be explained with the same mechanism as the De-NO_x process and reburning process.

However, the gasification combined with combustion occurred in the downer is not the most important reason to reduce NO and N₂O because some of gasification products such as H₂, CH₄, and CO can be partly burned in the

downer. The decoupling combustion (Lin, 1994), pyrolysis combined with combustion, may be an *in-situ* measure to reduce the NO, N₂O and SO₂ simultaneously during CFB combustion. Using pyrolysis gas as reducing gas to reduce NO emission had been carried out in pulverized coal combustion boilers (Rudiger *et al.*, 1997; Rudiger *et al.*, 1996; Spliethoff *et al.*, 1996). However, applying this technology to CFB coupled with Ca-based absorbent addition to simultaneously reduce NO, N₂O and SO₂ by means of *in-situ* is still open to discussion.

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