Experimental study of NO_x emissions in a 30 kW_{th} pressurized oxy-coal fluidized bed combustor

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Abstract

As one of the most promising carbon capture technologies for coal-fired power plants, oxy-coal combustion has attracted wide interests during the last two decades. In comparison to atmospheric oxy-fuel combustion, pressurized oxy-fuel combustion has the potential to further reduce the energy penalties caused by the carbon capture and storage and improve the net power plant efficiency. Although many researchers have investigated the NO_x emissions of atmospheric oxy-coal combustion, the NO_x emission behaviors under pressurized oxy-coal combustion conditions are much less understood and further comprehensive experimental investigations with continuous fuel-feeding pressurized oxy-coal combustion systems are needed in order to fill this knowledge gap. In the present study, a series of oxy-coal combustion experiments were conducted in a 30 kW_{th} pressurized fluidized bed combustor. The effects of combustion pressure, bed temperature and excess oxygen on the NO_x emissions were investigated systematically. The experimental results have shown that an increase in combustion pressure from 0.1 MPa to 0.4 MPa leads to a significant reduction in NO_x emissions. An increase in bed temperature or excess oxygen results in higher NO_x emissions under the higher combustion pressure conditions, which is consistent with what is observed under the atmospheric pressure combustion condition. Besides, it is found that the promoting effect of temperature increase on NO_x emissions under the higher combustion pressures is weaker than that under the atmospheric pressure.

Keywords: NO_x emission; Oxy-coal combustion; Pressurized fluidized-bed; Temperature; Excess oxygen.

1. Introduction

Oxy-fuel fluidized bed combustion technology which combines the advantages of fluidized bed, e.g., fuel flexibility, in-furnace desulfurization and low NO_x emission, has attracted widespread attention in recent years [1-2]. A large number of oxy-coal combustion studies focusing on the coal combustion performance, heat transfer and emissions of combustion-generated pollutants in atmospheric pressure fluidized beds have been reported [1-5]. Although oxy-coal combustion is one of the most promising technologies to capture carbon dioxide for coal-fired power plants, the extra energy cost of air separation unit and compression purification unit leads to a reduction of about 10% in net plant efficiency [6-7], and this may hinder the commercial application of oxy-coal combustion within the power generation industry. Pressurized oxy-fuel combustion (POFC) can improve the net plant efficiency as the elevated pressure is helpful to recover more thermal energy from the flue gas and reduce the energy cost of CO_2 compression work [8]. In recent years, a number of researchers have carried out economic system analyses on POFC technology and reported results favoring POFC over atmospheric pressure oxy-fuel combustion [6-12]. However, except for those experiments conducted on the pressurized thermogravimetric analyzer (PTGA) [13-14], there are few experimental studies investigating POFC with continuous fuel-feeding pressurized oxy-coal combustion systems [15-16]. In addition, the studies of NO_x emissions under POFC conditions are even less and hence there exists a considerable knowledge gap on the NO_x emission behaviors under pressurized oxy-coal combustion conditions which will ultimately adversely affect the conceptual design of NO_x control strategies for large-scale pressurized oxy-coal combustion systems in the future.

In contrast to the rare investigations of NO_x emissions under POFC conditions, the behavior of NO_x emission under the atmospheric pressure oxy-fuel combustion conditions has been extensively studied in both laboratory-scale and pilot-scale experiments [17-20], and the effects of operation parameters, e.g., temperature, excess air/oxygen, oxygen concentration and staging on the NO_x emission have been comprehensively investigated [2]. Generally, the NO_x emission of oxy-fuel combustion under the atmospheric pressure condition is found to be lower than that of air combustion due to the recycled flue gas and the higher CO concentration around the char particles [1], and an increase in combustion temperature increases the NO_x emission [21-23]. The higher temperature not only accelerates the release of char-N but also promotes the formation of NO precursors by increasing the concentration of free radicals (-O and -OH) [22]. A higher level of excess oxygen leads to a higher NO_x emission in atmospheric oxy-fuel combustion [22-24]. The results from Lupianez et al. [22] showed that the effect of stoichiometric oxygen ratio on the NO_x emission of oxy-fuel combustion was significant within the range of 1.1-1.7. As one of the key operating parameters in atmospheric oxy-fuel combustion, the oxygen concentration in the oxidant also influences the NO_x emissions. Most researchers have shown that an increase in O_2 concentration increased both the NO emission and the conversion ratio of fuel-N to NO_x [23-26]. Nevertheless, there are other experimental studies which have presented the opposite trends, e.g., the work of Diez et al. [27] which reported the findings of an experimental investigation of atmospheric oxy-combustion of anthracite in a 90 kW_{th} bubbling fluidized bed reactor. On one hand, the higher oxygen concentration in oxidant leads to an increase in the reaction rate of fuel-N to NO_x [25]. On the other hand, some previous studies [28] have shown that the high reaction rates with oxygen-rich atmospheres (over 40 vol%) led to the simultaneous combustion of char and volatiles, which limited the transportation of O_2 to the char surface and hence reduced the conversion rate of char-N to NO. In addition, as the NO_x emission is very sensitive to temperature under both air and oxy-fuel combustion conditions and the ratio of O_2/CO_2 in the oxidant can significantly influence the combustion temperature, an increase in NO_x emission with an increase in O_2 concentration was often explained by the higher temperature. Therefore, the contradictory results between different studies are more likely attributed to the different experimental parameters, e.g., the bed temperature.

Because the oxidant used in oxy-fuel combustion is a mixture of pure O_2 and the recycled flue gas, oxygen staging, which provides an opportunity to change the O_2 concentration in the primary and/or secondary oxidant stream, is able to reduce the NO_x emission. The experimental results of oxy-coal combustion in an atmospheric circulating fluidized bed combustor from Duan et al. [23] showed that the NO emission reduced significantly by decreasing the O_2 concentration in the primary oxidant stream while keeping the whole excess oxygen coefficient at the same level. The positive effects of oxygen staging on the reduction of NO_x emission was also observed by many other researchers [29-31]. The recycled flue gas (RFG) can greatly influence the NO_x emissions of real oxy-fuel combustion processes which use the mixture of pure oxygen and the recycled flue gas as the oxidant. Previous studies have shown that RFG could lead to more than 40% reduction in NO_x emissions as the NO in the flue gas was recycled back to the combustion zone where it was reduced to N_2 as a result of the reactions between NO and hydrocarbon radicals through the 'reburning mechanism' [1, 32-33]. It was also noticed that the mass fraction of water vapor in RFG could influence the formation of NO_x [21]. There could be two types of RFG, i.e., wet and dry RFG, and it was shown that the recirculation of wet flue gas was beneficial to reduce NO_x emissions [21, 34-35].

In one of our previous studies [36], we reported the results of oxy-coal combustion experiments conducted with a 15 kW_{th} pressurized fluidized bed combustor. The focus of that study was to investigate the effects of pressure on the combustion efficiency and the chemical composition of fly ash. Recently, we had modified the heat removal system of the 15 kW_{th} combustor [36-37] and managed to double the capacity of the combustor to 30 kW_{th}. In this paper, we present the results of combustion experiments conducted with this 30 kW_{th} pressurized fluidized bed combustor, focusing on the NO_x emission behaviors under pressurized oxy-coal combustion conditions.

2. Experimental

2.1 Experimental setup

A sketch of the combustion system is displayed in Fig. 1(a), which mainly contains a pressurized fluidized-bed combustor, a coal feed sub-system, a gas supply sub-system, a flue gas cooler, a flue gas analyzer, and a distributed control system [36-37]. The combustor's inner diameter is 80 mm and its height is 1.8 m. The designed maximum operation pressure of the combustor is 0.6 MPa, and the water cooling probe located inside the bed zone allows the bed temperature to be controlled within a desired range. Due to the installation of a new water cooling system which can take more heat away from the combustor, the maximum thermal input capacity of the combustor has hence been increased from 15 kW_{th} to 30 kW_{th}. Fig. 1(b) shows the photo of the combustion system.

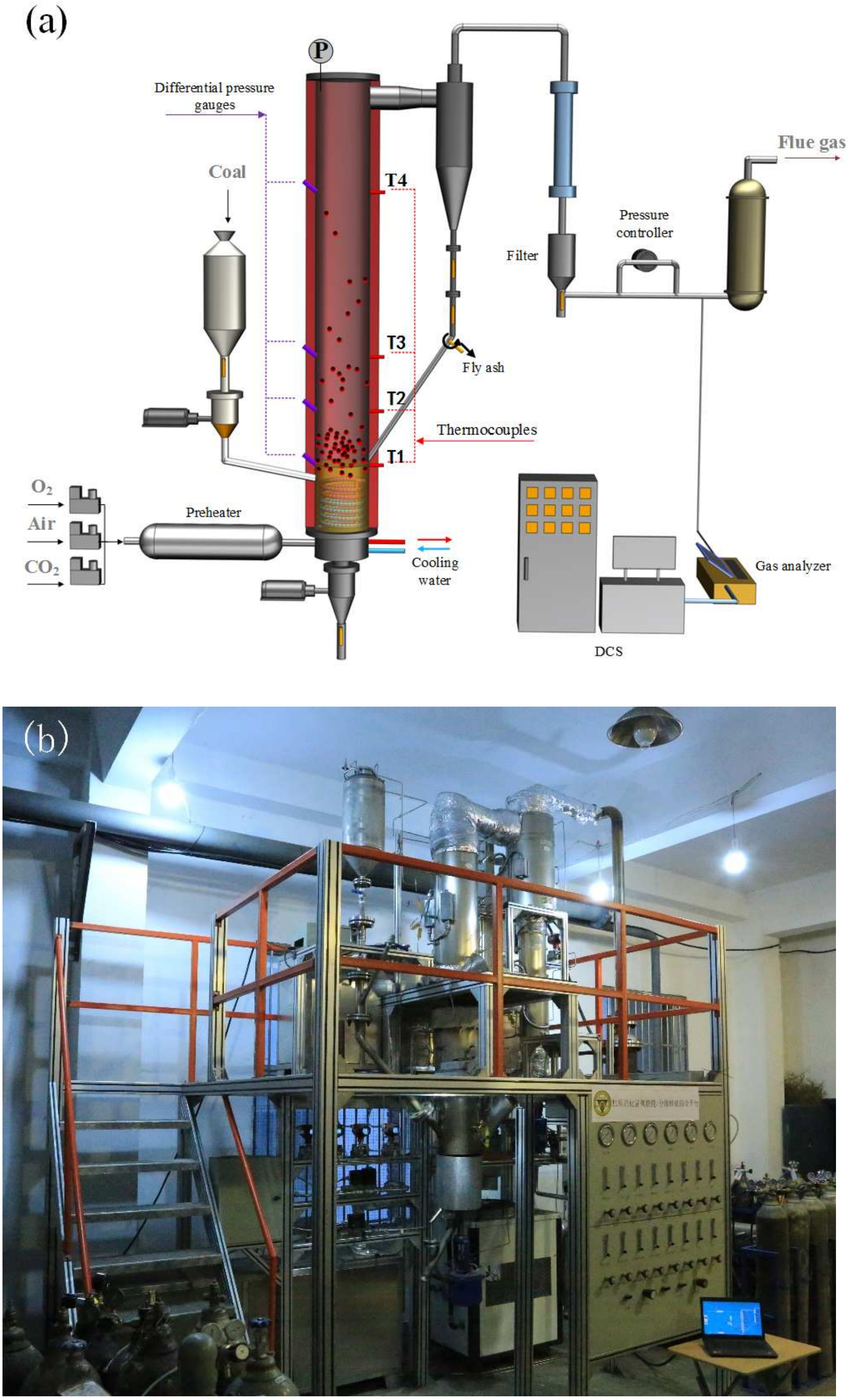
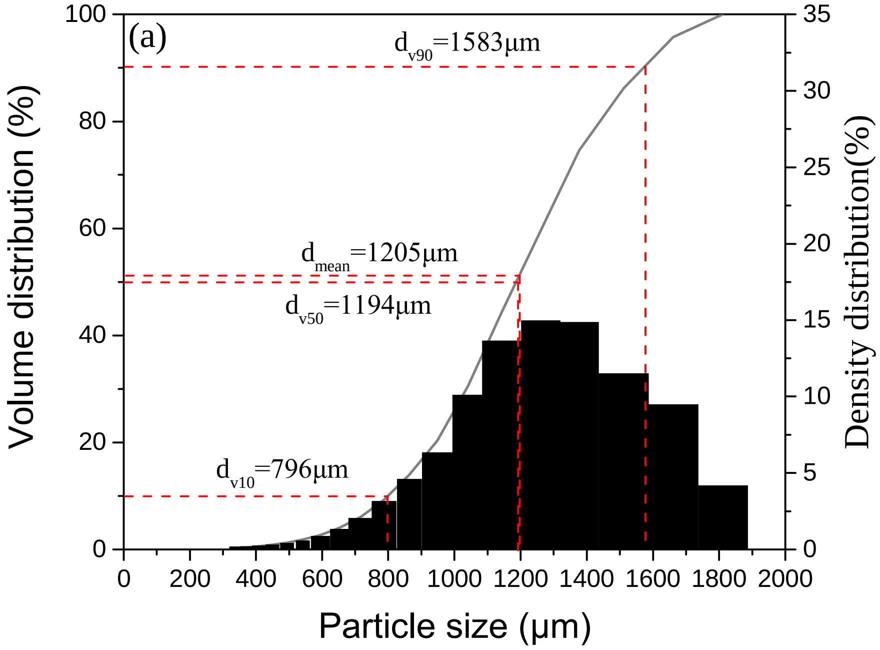


Figure 1. (a) Schematic and (b) Photo of the combustion system

2.2 Fuel and bed material

One anthracite from Shanxi province, China, was used as the fuel in this study. The particle size distribution of the coal is shown in Fig. 2(a), and its average diameter is about 1200 μm while d_{v10} and d_{v90} (the corresponding diameter when the volume distribution is 10% and 90%) is about 800 μm and 1600 μm, respectively. The ultimate analysis and proximate analysis of the coal are listed in Table 1. As shown in Table1, this coal has the representative values of ultimate and proximate analysis of anthracite, i.e., high mass fraction of carbon (over 70%) and low mass fraction of volatiles (10.4%). Silica sand was used as the bed material, and Fig. 2 (b) shows its particle size distribution. The average diameter of the silica sand is 845 μm while d_{v10} and d_{v90} is about 600 μm and 1150 μm, respectively.



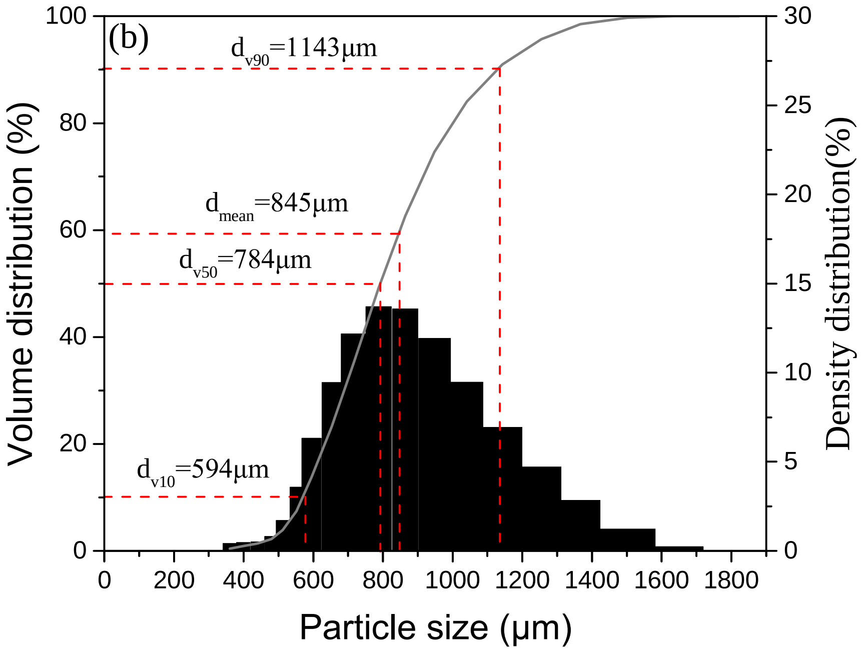


Figure 2. Particle size distribution of (a) coal particle and (b) silica sand

Table 1. Ultimate analysis and proximate analysis of the anthracite coal

	Anthracite
Proximate Analysis (wt%, as received)	
Moisture	2.51
Ash	14.09
Volatile matter	10.44
Fixed carbon (by difference)	72.96
Ultimate Analysis (wt%, as received)	
Carbon	76.83
Hydrogen	2.30
Nitrogen	0.94
Sulfur	1.30
Oxygen (by difference)	2.03
Low Heating Value (MJ/kg, as received)	22.03

2.3 Experimental procedure

Table 2 shows the main operating parameters of the experiments, including the combustion pressure, the O_2 and CO_2 concentrations (vol%) in the oxidant, the coal feeding rate and total oxidant gas flow rate, the bed temperature (T1), the corresponding superficial gas velocity (calculated based on the total oxidant gas flow rate, bed temperature and the diameter of the combustor). Besides, the O_2, CO_2 and NO_x concentration in the flue gas are also listed in Table 2. 1.5 kg silica sand (equivalent to a static bed height of 0.2 m) was introduced into the combustor before each experiment. The bed temperature (T1) was controlled within a range of 830-950 °C by controlling the coal feeding rate and the use of the water cooling system which could take heat away from the combustor. The stoichiometric air/oxygen coefficient (λ) level was kept within a range of 1.1-1.5, i.e., the O_2 concentration in the flue gas was between 2 vol% - 6 vol%. In order to keep the same superficial gas velocity and excess oxygen, the coal feeding rate and oxidant flow rate were increased in proportion to the combustion pressure, e.g., the coal feeding rate and oxidant flow rate were 0.65 kg/h and 7.0 kg/h respectively under 0.1 MPa whereas they were increased to about 2.60 kg/h and 30.5 kg/h when the pressure was increased to 0.4 MPa.

Table 2. Operating parameters and dry flue gas compositions

Pressure (MPa)	O_2 in (vol%)	CO_2 in (vol%)	Coal feeding rate (kg/h)	Total gas flow (kg/h)	Superficial gas velocity (m/s)*[1]	T1 (°C)	O_2 out (vol%)	CO_2 out (vol%)	NO_x (ppm)
0.1	Air	Air	0.55-0.80	5.8-8.4	1.01-1.61	830-950	2.0-6.3	14-19	560-680
0.1	21	79	0.65	10.2	1.20*[2]	800*[2]	3.5-4.5*[2]	92-93*[2]	400-500*[2]
0.1	25	75	0.65	8.5	1.05	850-860	3.5-4.5	92-93	520-550
0.1	30	70	0.5-0.7	6.0-7.3	0.74-1.00	830-950	2.0-6.1	90-94	610-790
0.4	Air	Air	2.50-2.90	28.4-34.8	1.23-1.67	830-950	1.9-5.9	14-19	220-300
0.4	30	70	2.50-2.80	28.4-33.0	0.88-1.13	830-950	1.6-6.9	90-94	280-390

*[1] Superficial gas velocities were calculated on the basis of the measured bed zone temperature T1
*[2] unstable condition

3. Results and discussion

3.1 Oxygen concentration

Many researchers have investigated the effect of oxygen concentration on the oxy-coal combustion [39-41]. As expected, the switch from air combustion to 21 vol% O_2/79 vol% CO_2 (denoted as oxy-21) combustion caused a reduction in temperature due to the higher specific heat of CO_2 than that of N_2. In some previous studies [25], the oxygen concentration in the oxidant varied from 21 vol% to over 50 vol%. However, the steady combustion condition under oxy-21 in a fluidized bed could only be achieved with a very high oxidant preheating temperature [15, 36, 41], i.e., over 500 °C, which greatly exceeds the oxidant preheating temperature in real large-scale oxy-fuel combustion processes. In this study, the oxidant preheating temperature was kept at 250 °C. Fig. 3 shows the real-time experimental data under the combustion pressure of 0.1 MPa. The temperature decreased continuously after the oxidant was switched from air to oxy-21, and it was unable to achieve a steady combustion state. The lower combustion temperature (lower than 800 ^{o}C) led to a lower combustion rate of the coal particles, and hence the total mass of unburnt char in the bed zone increased with time, which resulted in the higher CO concentration and a reduction in NO_x emissions. The CO concentration increased continuously from 200 ppm to over 3000 ppm, which indicated the bad combustion condition prevailed under the condition of oxy-21. The switch of oxidant from oxy-21 to oxy-25 (i.e. 25 vol% O_2/75 vol% CO_2) led to an increase in temperature while it was still lower than that under air. Only when the oxygen concentration in the oxidant reached 30 vol%, the combustion temperature was close to that of air. The results agreed with most of the previous studies [38-40] which suggested that the required oxygen concentration in the oxy-fuel oxidant needed to be in the range between 25-30 vol%. In this study, the NO_x emissions under oxy-30 (i.e.

30 vol% O_2/70 vol% CO_2) were compared with those under air. It is worth mentioning that, the water cooling system was designed to operate only after the pressure was increased to 0.4 MPa, and it was not in use with the combustion tests under atmospheric pressures. Therefore, in order to keep the same combustion temperature with air combustion at atmospheric pressure, the coal feeding rate under oxy-30 (0.1 MPa) was decreased slightly, and the flow rate of oxidant was also decreased to keep the excess oxygen at the same level.

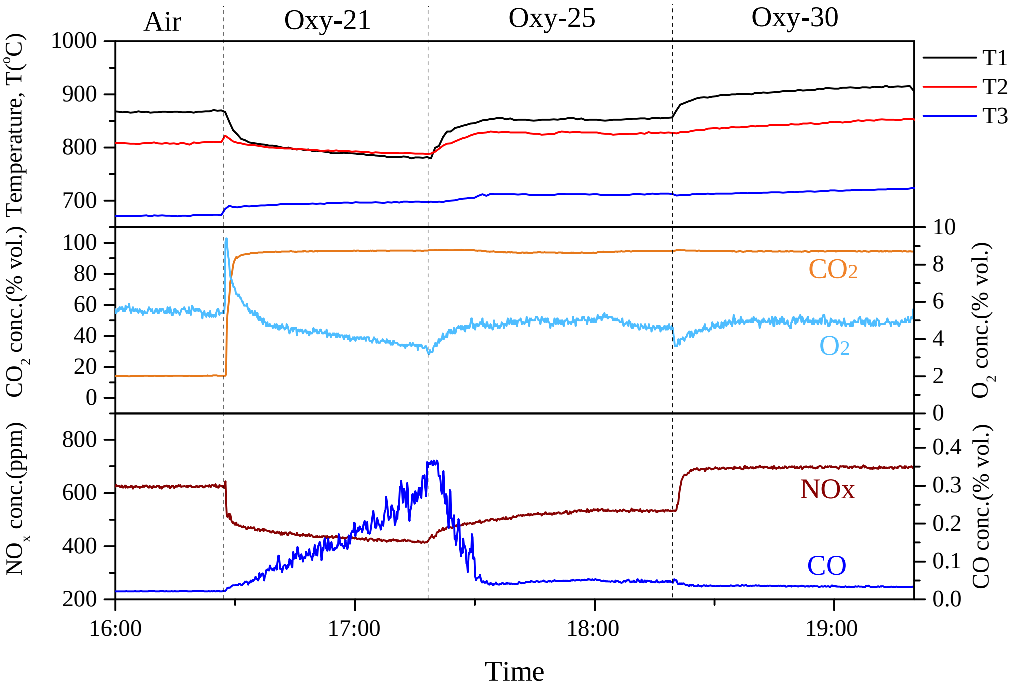
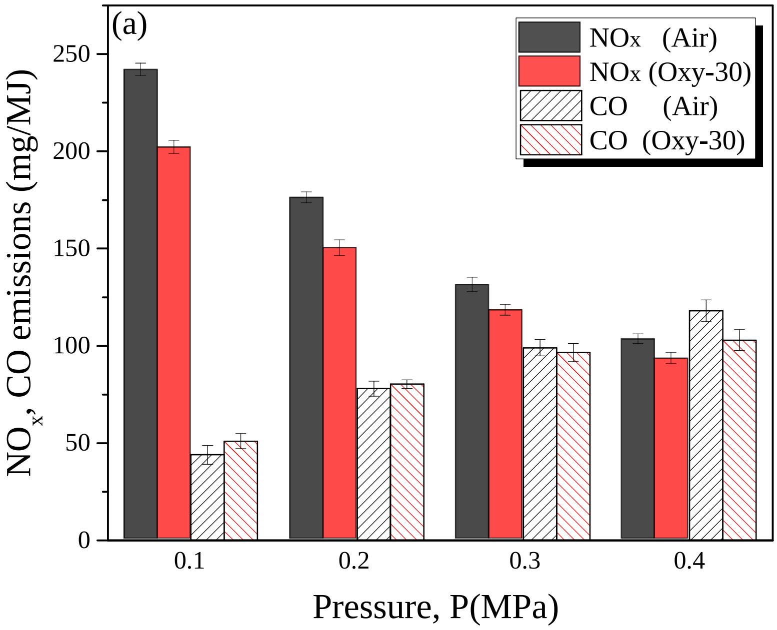


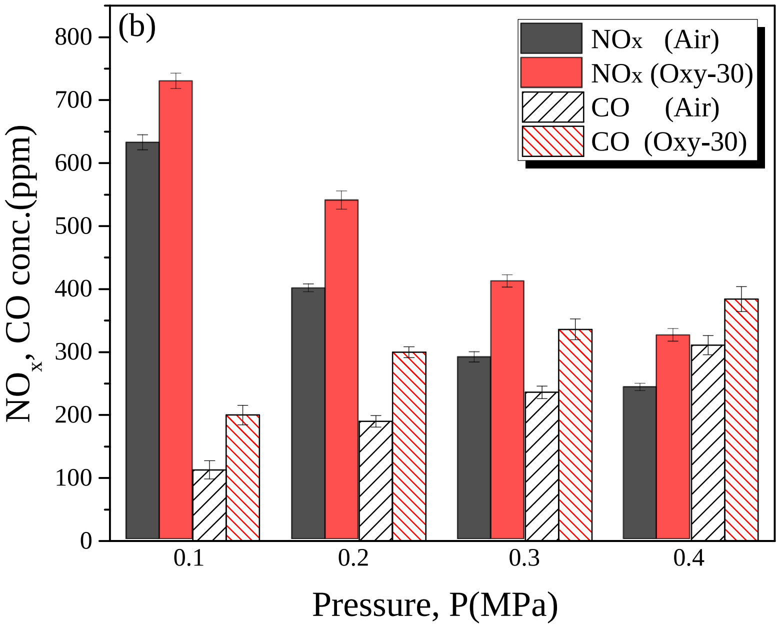
Figure 3. Real-time data of temperatures and flue gas (0.1 MPa)

3.2 Effect of pressure

Fig. 4 (a) and (b) shows the NO_x emissions and concentrations under different combustion pressures with both air and oxy-30 atmospheres, respectively. In order to eliminate the influence caused by the flow rate (the oxidant gas flow rate under oxy-30 is lower than that under air if the total flow rate of oxygen is kept at the same value), the normalized emission per energy unit is more commonly used in oxy-fuel combustion studies. Fig. 4 (a) shows that an increase in combustion pressure led to a significant reduction of NO_x emissions under both air and oxy-30 atmospheres. The NO_x emission under air reduced from 242 mg/MJ to 103 mg/MJ as the pressure increased from 0.1 MPa to 0.4 MPa, meanwhile, the NO_x emission under oxy-30 reduced from 202 mg/MJ to 91 mg/MJ. The same phenomenon was reported by several researchers [16, 42]. Svoboda and Pohorely [42] investigated the effect of pressure on NO_x emissions of coal-air combustion and found that the NO_x emissions were substantially reduced when the pressure was increased from 0.1 MPa to 0.5 MPa. Lasek et al. [16] indicated that the NO_x emissions of "Sobieski" lignite under oxy-30 were reduced from 300 ppm to 150 ppm when the pressure was increased from 0.1 MPa to 0.47 MPa. However, the oxidant was excessive in their study as the O_2 concentration in the flue gas was over 10 vol%. The NO_x emissions data shown in Fig. 4 were obtained from the tests of this study with almost the same operating parameters except for the combustion pressure, i.e., bed temperature (890 - 910 ^oC), excess oxygen (the O_2 concentration in the flue gas was kept at 3.5 - 4.5 vol%) and superficial gas velocity (1.3 - 1.4 m/s for air atmosphere and 0.9 – 1.0 m/s for oxy-30 atmosphere). Although the coal feeding rate under the pressure of 0.4 MPa was four times of the coal feeding rate under the pressure of 0.1 MPa, however, with the use of the water cooling system, the bed temperature under the pressure of 0.4 MPa was controlled to the level similar to that achieved under the pressure of 0.1 MPa. Therefore, the reduction of NO_x emission observed in Fig. 4 was mainly caused by the pressure increase. On one hand, as the diffusion coefficients of O_2 in both N_2 and CO_2 are smaller under higher pressures, the transport of O_2 to the surface of coal particles is slower, and the rate of oxidation of fuel-N is reduced. Fig. 5 shows the diffusion coefficient of O_2 in both N_2 and CO_2 under different pressures [16], and it is clear that both of them decrease with an increase in pressure. Specifically, the diffusion coefficient of O_2 in N_2 decreases from 1.66 cm^2/s to 0.42 cm^2/s as the pressure increases from 0.1 MPa to 0.4 MPa, and the coefficient in CO_2 decreases from 2.09 cm^2/s to 0.52 cm^2/s. On the other hand, the higher pressure prolongs the time for the diffusion of NO_x throughout the char particles, which is beneficial to the reduction reaction of NO_x with char and CO (R1).

It is widely accepted that the prompt NO_x and thermal-NO_x are insignificant in the fluidized bed combustor due to its relatively low combustion temperature (lower than 1000 ^oC), and the NO_x is mainly coming from the conversion of fuel-N. As shown in literature [16, 25, 32, 40-41, 49-50], the mass fraction of nitrogen in coal varied in a wide range (as low as ca. 0.2 % to as high as ca. 2.0 %), and it is clear that the NO_x emissions' level depends directly on the nitrogen content of the coal. In order to compare the formation of NO_x with different coals, the conversion ratio of fuel-N to NO_x is calculated and compared with the values reported by a number of previous studies [40-41, 49-50] (Fig. 4 (c)). It can be seen that the conversion ratio under atmospheric oxy-coal combustion determined by this study is within the range of the values reported by the previous studies.


(a)
NOx (Air)
NOx (Oxy-30)
CO (Air)
CO (Oxy-30)
NO_x, CO emissions (mg/MJ)
0
50
100
150
200
250
0.1
0.2
0.3
0.4
Pressure, P(MPa)


(b)
NOx (Air)
NOx (Oxy-30)
CO (Air)
CO (Oxy-30)
NO_x, CO conc.(ppm)
0
100
200
300
400
500
600
700
800
0.1
0.2
0.3
0.4
Pressure, P(MPa)

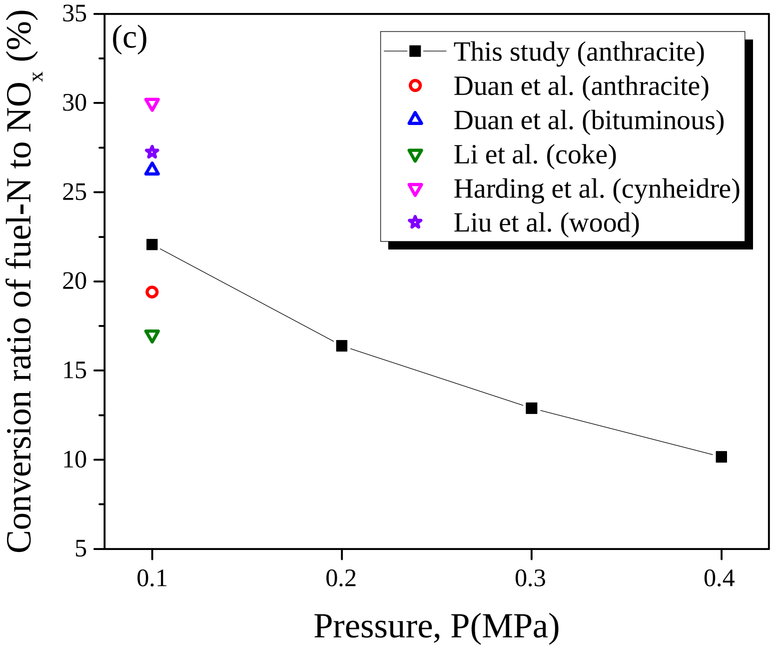


Figure 4. NO_x and CO emissions: (a) with normalized emission per energy unit (b) concentration with a unit of ppm (c) conversion ratio of fuel-N to NO_x (800-900°C)

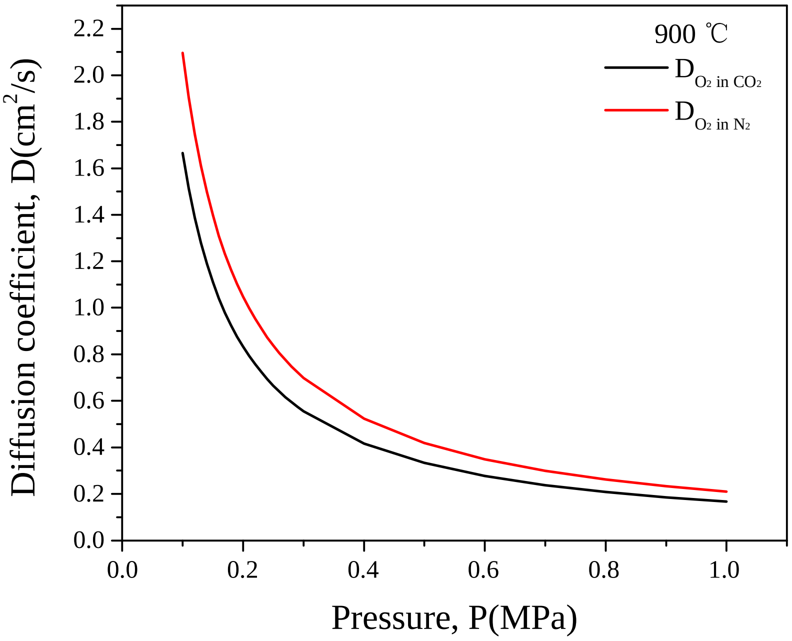
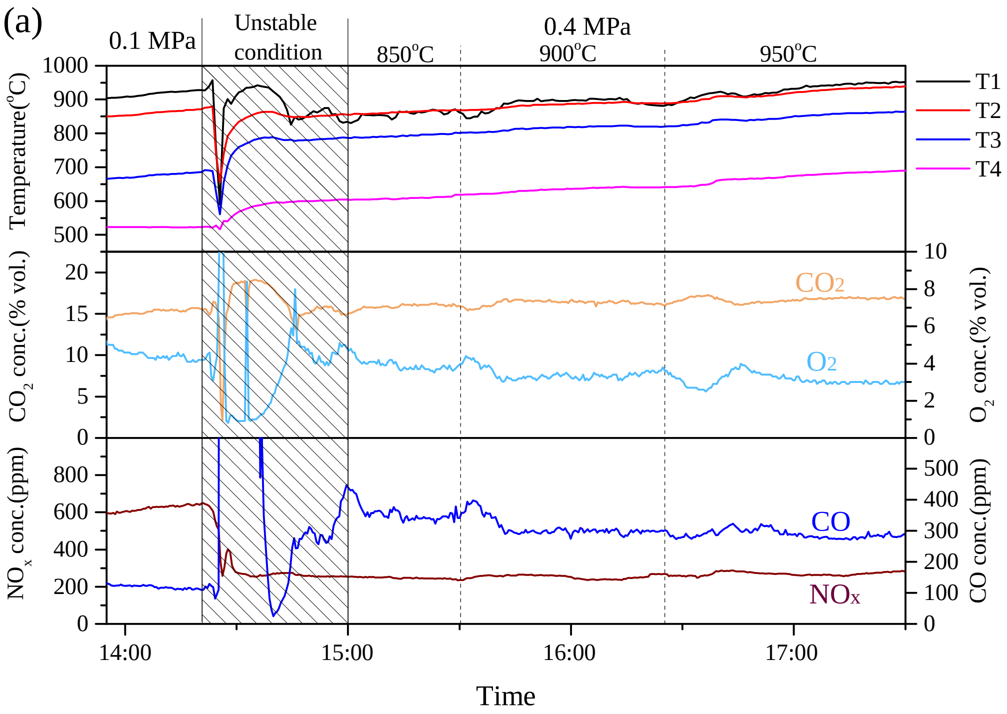


Figure 5. Diffusion coefficients of O_2 in N_2 and CO_2 under different pressures

$$NO+CO \xrightarrow{char} \frac{1}{2} N_2+CO_2 \qquad (R1)$$

Fig. 6 (a) and Fig. 6 (b) show the real-time data in some typical combustion tests which included the processes of pressure increase and atmosphere switch. After the steady-state conditions were reached, the NO_x emissions were seen to stay at much lower values under the higher pressure conditions. However, even though the bed temperature (T1), excess oxygen and superficial gas velocity were kept at the same levels, it was noticed that the CO emissions (concentrations) were much higher for the pressurized conditions. Fig. 4 shows that the CO emissions (concentration) increased with an increase in combustion pressure from 0.1 MPa to 0.4 MPa. It is worth mentioning that the higher CO emission (concentration) is not a direct consequence of the pressure increase. It is expected that the increase in coal feeding rate with pressure leads to the higher CO concentration in this study. As mentioned above in Section 2.3, in order to keep the superficial gas velocity at the same value, both the coal feeding rate and oxidant flow rate increased proportionally with an increase in pressure. The higher coal feeding rate means more coal particles are introduced into the combustor within a given time, and hence the thermal load of the combustor increases with the combustion pressure. In theory, the higher thermal input of a fluidized bed combustor can be realized by increasing combustion pressure while keeping the same fluidization velocity at the same value. However, one practical problem is that the combustibles of the coal particles fed in the combustor may not be burned out completely. In this study, the maximum value of CO concentration was still quite low, i.e., less than 1000 ppm, and hence the combustion under 0.4 MPa could still be considered as normal.



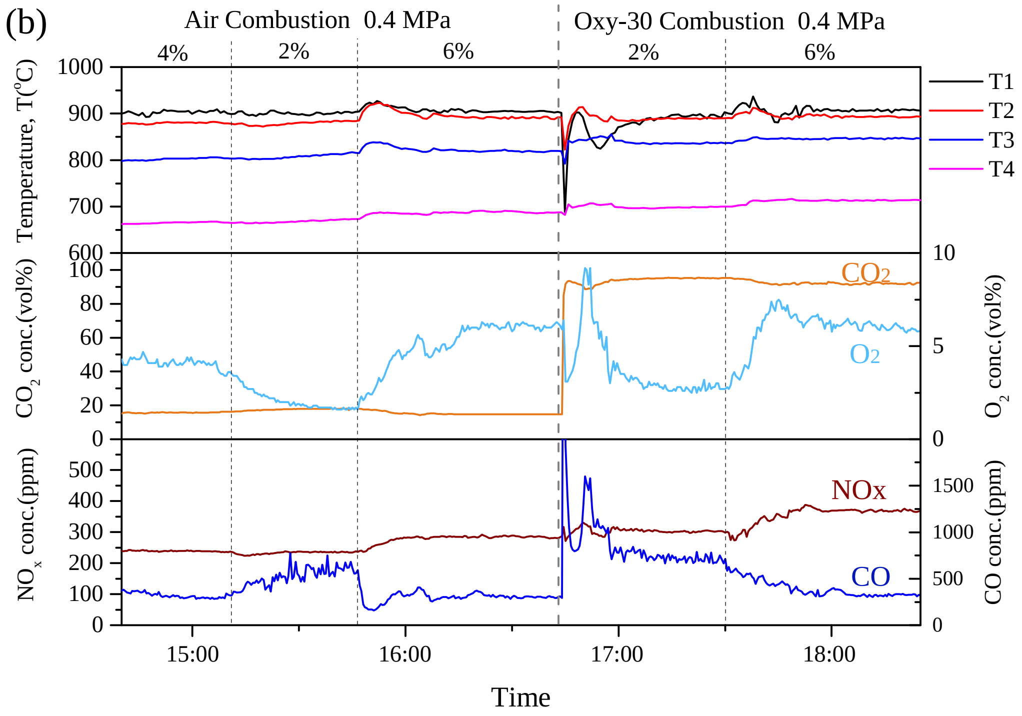
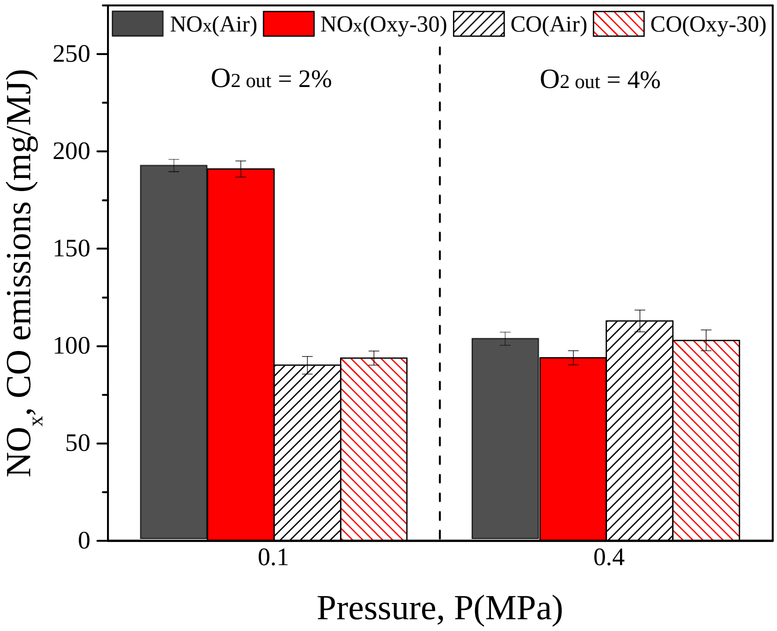


Figure 6. Real-time data of temperatures and flue gas (a) pressure increase with air (b) atmosphere switch under 0.4 MPa

The higher CO emission (concentration) should lead to a reduction in NO_x emission [1-2]. Fig. 4 shows that the CO emission in the flue gas increased from 44 mg/MJ to 113 mg/MJ as the pressure increased from 0.1 MPa to 0.4 MPa under air, whereas it increased from 51 mg/MJ to 103 mg/MJ under oxy-30. As the reduction of NO_x emissions may be caused by an increase in CO emissions rather than the pressure increase, it is necessary to further analyze the effect of CO emissions on NO_x emissions. Fig. 7 compares the NO_x emissions under 0.1 MPa and 0.4 MPa while the CO emissions' values were very similar. The NO_x emissions under both air and oxy-30 decreased significantly as the pressure increased from 0.1 MPa to 0.4 MPa while the difference of CO concentrations were much smaller, and this indicates that the reduction of NO_x emissions is mainly attribute to the increase in pressure rather than the higher CO emissions. Although the NO_x emissions and CO emissions data in Fig. 7 were obtained from the tests with different excess oxygen, the results are useful to separate the effect of CO emissions on NO_x emissions from that of combustion pressure.

(a)



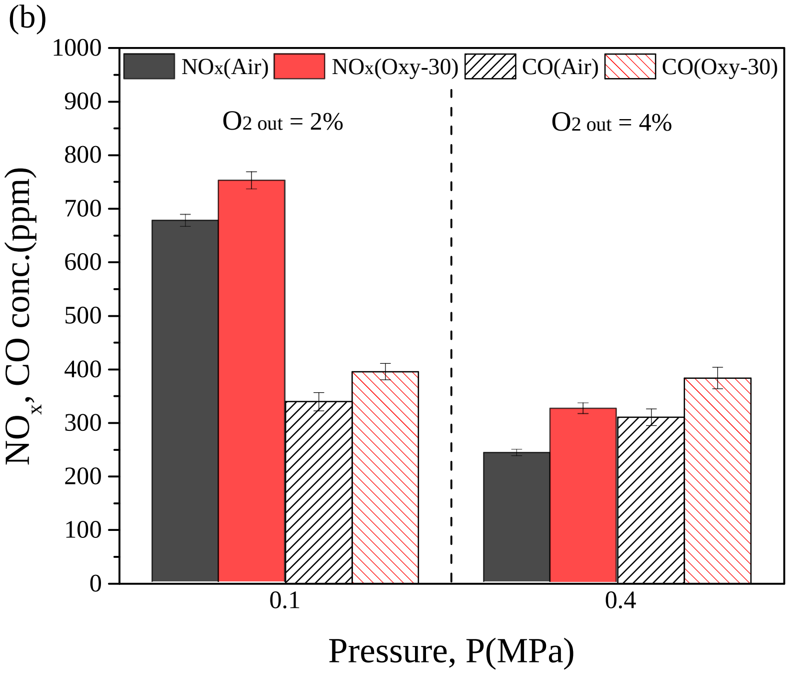


Figure 7. Comparison of NO_x emissions with CO emissions under different pressures (a) with normalized emission per energy unit (b) concentration with a unit of ppm

As shown in Fig. 4, the pressure increase led to a reduction of 57.4% and 54.9% in NO_x emissions with air and oxy-30 combustion, respectively. The reduction of NO_x emission resulted from the pressure increase was quite significant, and hence it is necessary to find out if there was a significant portion of the Coal-N left in the fly ash under the higher pressure conditions. Table 3 shows the results of the elemental analysis of the fly ash under different pressures and atmospheres. A more detailed discussion about the effects of pressure on unburnt carbon/combustibles in fly ash can be found in some previous studies [36-37], and the main focus of this study was the residual coal-N in the fly ash. The values of TML and NML (Equation 1-2 [43]) are listed in Table 3, and the higher value of NML than that of TML with each test indicated that most of the coal-N had been released rather than being left in the fly ash. Table 3 also shows the combustion efficiencies (η, Equation 3-7 [8-9]) under different combustion conditions, and it is clear that the combustion efficiency increased with the combustion pressure (from 90.22 % to 92.17 % to 91.26 % to 93.34 % under air combustion and oxy-coal combustion, respectively), having the same trend as TML.

$$\text{Total Mass Loss（TML）} = (1.0 - \frac{\text{Ash}_{\text{coal}}}{\text{Ash}_{\text{fly ash}}}) \times \frac{100}{100 - \text{Ash}_{\text{coal}}} \tag{1}$$

$$\text{Nitrogen Mass Loss（NML）} = 1.0 - \frac{\text{Nitrogen}_{\text{fly ash}}}{\text{Nitrogen}_{\text{coal}}} \times \frac{\text{Ash}_{\text{coal}}}{\text{Ash}_{\text{fly ash}}} \tag{2}$$

$$\eta = 1 - q_3 - q_4 \tag{3}$$

where q_3 and q_4 are the efficiency losses associated with the combustible gases and the unburnt carbon, respectively, and can be calculated based on the GB10184-88 and ASME PTC4-1998.

$$q_3 = \frac{Q_{CO} + Q_{H_2} + Q_{CH_4}}{Q_{\text{net, ar}}} \tag{4}$$

where Q_{CO}, Q_{H2} and Q_{CH4} are the heating values of CO, H_2 and CH_4 in the flue gas, respectively. $Q_{net,ar}$ is the thermal input of the coal.

$$q_4 = q_4^{ba} + q_4^{fa} \tag{5}$$

$$q_4^{ba} = \frac{Q_c * C_{ba} * G_{ba}}{Q_{\text{net, ar}}} \tag{6}$$

$$q_4^{fa} = \frac{Q_c * C_{fa} * G_{fa}}{Q_{\text{net, ar}}} \tag{7}$$

where q_4^{ba} and q_4^{fa} are the efficiency losses associated with the unburnt carbon in bottom ash and fly ash, respectively. C_{ba} and C_{fa} are the mass ratio of the unburnt carbon in the bottom ash and fly ash, respectively. G_{ba} and G_{fa} are the mass of bottom ash and fly ash. Q_C is the heating value of the carbon (Q_C=32.7 MJ/kg).

Table 3. Analysis of the fly ash and the calculated combustion efficiency[*1]

Pressure (MPa)	Atmosphere	Unburnt combustibles (%)	C (%)	H (%)	N (%)	TML (%)	NML (%)	η[*2] (%)
0.1	**Air**	**45.28±0.6**	**44.33**	**0.47**	**0.24**	**86.43**	**93.42**	**90.22**
0.1	**Oxy-30**	**40.41±0.4**	**39.65**	**0.44**	**0.22**	**88.87**	**94.46**	**91.26**
0.4	**Air**	**36.55±0.6**	**36.49**	**0.22**	**0.15**	**90.55**	**96.45**	**92.17**
0.4	**Oxy-30**	**31.73±0.3**	**31.41**	**0.19**	**0.13**	**92.38**	**97.14**	**93.14**

[*1] Bed temperature ≈ 900 °C, O_2 concentration in the flue gas ≈ 3.5-4.5 vol%

[*2] Combustion efficiency

3.3 Effect of temperature

Fig. 8 shows the effect of bed temperature on NO_x emissions within a range of 830 to 950 °C under different pressures and atmospheres. In order to separate the effect of excess oxygen on NO_x emissions from that of bed temperature, the O_2 concentrations in the flue gas were kept at the same level, i.e., 3.5-4.5 vol%. With an increase in bed temperature from 830 °C to 950 °C, the NO_x emissions increased under both air and oxy-30 with the atmospheric pressure (0.1 MPa). The increasing tendency of NO_x emissions with temperature is in agreement with most of the previous studies, e.g., Lupianez et al. [44] showed that the NO_x emissions under oxy-combustion atmosphere (40 vol% O_2/60 vol% CO_2) increased from 100 mg/MJ to 140 mg/MJ when the temperature increased from 820 °C to 880 °C. Besides, an increase in NO_x emissions was also observed by Svoboda and Pohorely [42] as the temperature increased from 800 °C to 900 °C. As some researchers [22] pointed out, coal devolatilization is strongly influenced by the temperature, and the releases of volatile-N and char-N also depend on the temperature. The higher temperature not only improves the char combustion and char-N release, but also increases the concentration of free radicals (-O and -OH) which promotes the oxidation of NO_x precursors (R2-R12). Besides, the higher bed temperature can also reduce the char and CO concentrations in the combustor, which decreases the heterogeneous reduction of NO_x on the char surface [21]. Fig. 9(a) summaries the CO concentration and NO_x emissions under atmospheric pressure with different bed temperature, and it shows that the CO concentration decreases with an increase in bed temperature while the reduction of CO is more obvious under oxy-30.

$$\mathrm{HCN+0.5O_2 \rightarrow CNO+H} \quad \text{(R2)}$$

$$\mathrm{CNO+H \rightarrow NH+CO} \quad \text{(R3)}$$

$$\mathrm{NH+OH \rightarrow NO+H_2} \quad \text{(R4)}$$

$$\mathrm{CNO+0.5O_2 \rightarrow NO+CO} \quad \text{(R5)}$$

$$\mathrm{NH_3+OH \rightarrow NH_2+H_2O} \quad \text{(R6)}$$

$$\mathrm{NH_3+O \rightarrow NH_2+OH} \quad \text{(R7)}$$

$$\mathrm{NH_3+H \rightarrow NH_2+H_2} \quad \text{(R8)}$$

$$\mathrm{NH_2+O \rightarrow NHO+H} \quad \text{(R9)}$$

$$\mathrm{HNO+M \rightarrow NO+H+M} \quad \text{(R10)}$$

$$\mathrm{HNO+OH \rightarrow NO+H_2O} \quad \text{(R11)}$$

$$\mathrm{HNO+NH_2 \rightarrow NO+NH_3} \quad \text{(R12)}$$

As shown in Fig. 8, the NO emissions' increase under 0.4 MPa is smaller than that under 0.1 MPa when the bed temperature increased from 830 °C to 950 °C. Specifically, it increased from 94 mg/MJ to 109 mg/MJ and from 82 mg/MJ to 96 mg/MJ under air and oxy-30, respectively. As some previous studies indicated [36, 45], the higher combustion pressure accelerated the combustion rate of coal particles and decreased the mass fraction of unburnt carbon in fly ash. Because the combustion of the coal has been effectively improved by an increase in pressure, it is expected that the effect of temperature increase on the combustion performance gets weaker under higher pressures, and hence the increase in NO_x emissions with an increase in temperature becomes smaller. Fig. 9(b) summaries the CO concentration in the flue gas and NO_x emissions under the pressure of 0.4 MPa with different bed temperatures, and it shows the similar tendency with Fig. 9(a) that the higher bed temperature leads to the reduction of CO concentration in the flue gas and an increase, albeit at a lower rate, in NO_x emissions.

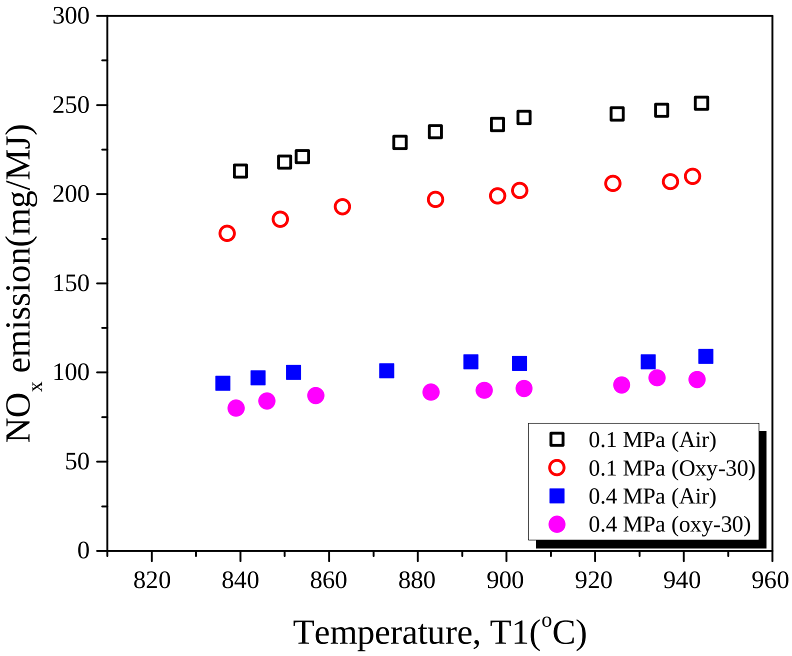


Figure 8. Effect of bed temperature on the NO_x emissions

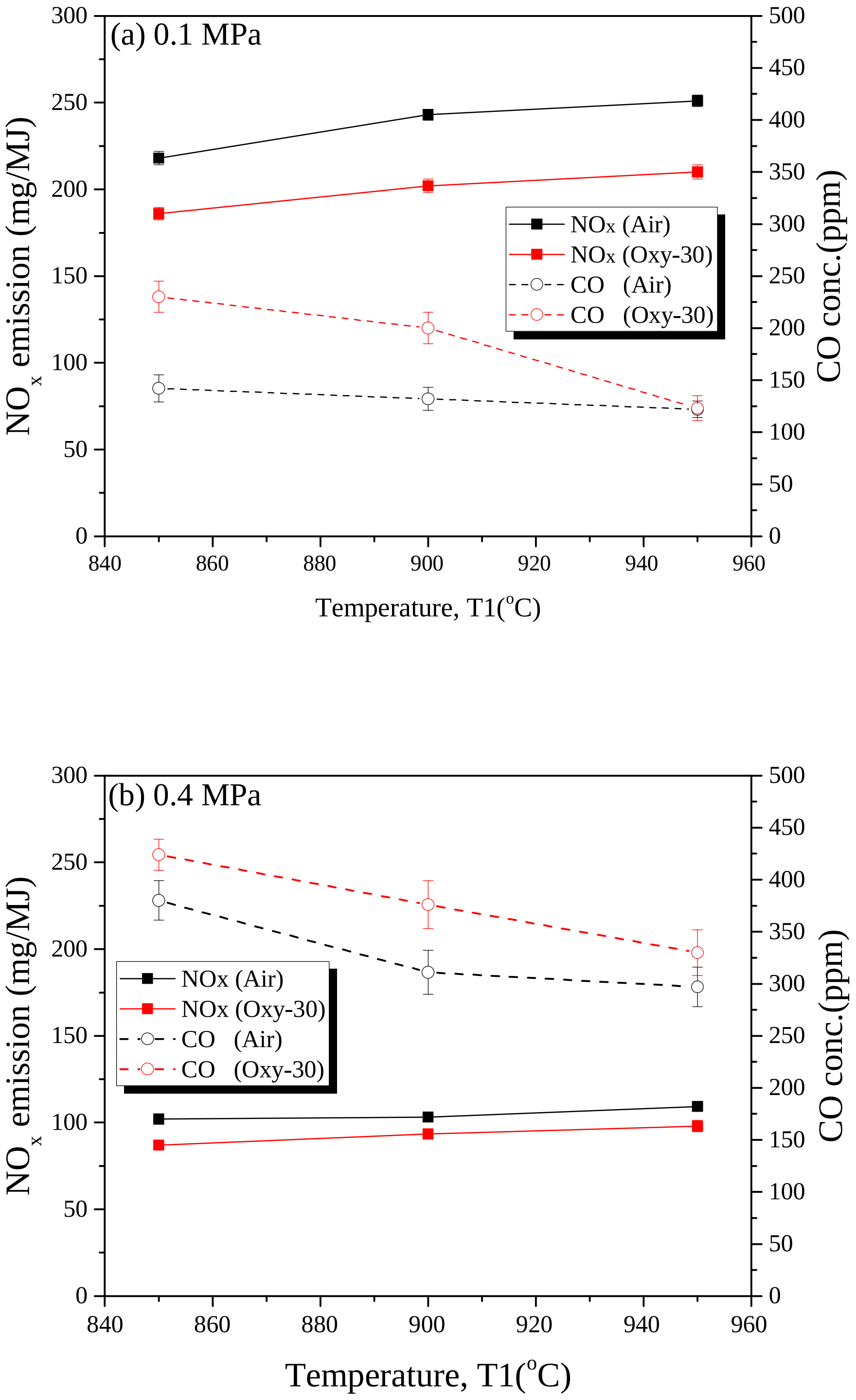


Figure 9. NO_x emissions and CO concentrations (a) 0.1 MPa (b) 0.4 MPa

It is worth mentioning that, although the bed temperature (T1) can be kept at the same value under different pressures by the water cooling system, the temperatures within the freeboard were always higher in the pressurized combustion tests than those in the atmospheric combustion tests. As shown in Fig. 6, the temperatures above the bed zone (T2, T3 and T4) increased significantly after the pressure was increased to 0.4 MPa, whereas the temperature of the bed zone (T1) was maintained at the same level. As mentioned above in section 2.3**,** the coal feeding rate and oxidant flow rate were increased proportionally with an increase in combustion pressure, and hence the flow rate of flue gas also increased with pressure. Because more heat was taken from the bed zone to the upper zone of the combustor by the flue gas, all the temperatures along the combustor were higher under pressurized combustion conditions (as shown in Fig. 10, the temperatures of the upper zone were higher under 0.4 MPa, which was mainly caused by the larger flow rate of flue gas under pressurized combustion). In theory, all the temperatures along the combustor can be controlled to maintain the desired values if the water cooling system was installed along the whole combustor rather than only in the bed zone, but it is difficult to realize it with a laboratory-scale FB combustor. Fig. 10 illustrates the temperature distribution profiles of the combustor with different combustion pressures. The temperature differences within the dilute zones (T3 and T4) between 0.1 MPa and 0.4 MPa were about 150 -180 ^{o}C even though the bed temperatures (T1) were kept at the same value, i.e., 900 ^{o}C. As some previous studies [46-47] indicated that the kinetics of NO_x formation was of relevance for a temperature over 600 ^{o}C, the temperature differences in the dilute zones between different pressures may influence the NO_x emissions. However, it should be noticed that the higher temperature in the dilute zones is more likely to increase the NO_x emissions, and hence the NO_x emissions under 0.4 MPa is expected to be higher than that under 0.1 MPa, which is contradictory to the experimental results shown in section 3.2, i.e., the NO_x emissions decreased with an increase in pressure. In other words, if the temperature distribution profiles under different pressures were kept the same, the reduction in NO_x emissions with an increase in pressure may be even more significant. In this study, as most of the conversion happened in the dense zone due to the quite low volatile content of the coal, the effect of freeboard temperature on the NO_x emissions is expected to be limited.

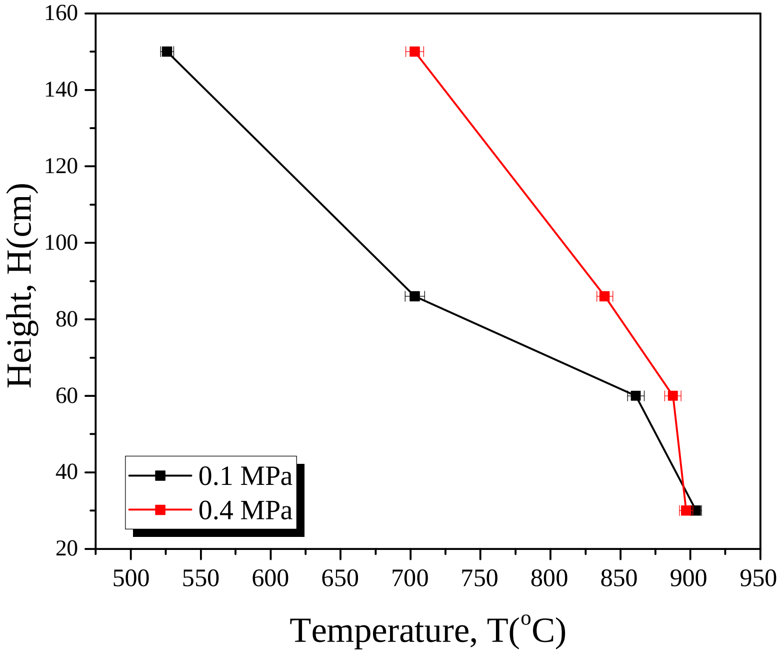


Figure 10. Temperature distribution profiles with different combustion pressures (oxy-30)

3.4 Effect of excess oxygen

Fig. 11 shows the impact of excess oxygen on the NO_x emissions behavior under different pressures and atmospheres with a bed temperature of about 900 °C. Under atmospheric pressure, the NO_x emissions under air increased from 192 mg/MJ to 242 mg/MJ when the O_2 concentration in the flue gas increased from 2 vol% to 4 vol% and no obvious increase was observed with a further increase from 4 vol% to 6 vol%, whereas the NO_x emissions under oxy-30 increased gradually from 191 mg/MJ to 223 mg/MJ as the O_2 concentration increased from 2 vol% to 6 vol%. The promoting effect of excess oxygen on NO_x emissions has been observed by many other researchers. Duan et al. [23] showed that both the NO_x emissions with bituminous coal and anthracite increased as the stoichiometric ratio increased from 1.1 to 1.3 under oxy-30. The results obtained by Czakiert et al. [24] indicated that the conversion ratio of fuel-N to NO_x under oxy-combustion atmosphere (28 vol% O_2/72 vol% CO_2) increased by 50%, i.e., from 8.5% to 13%, when the stoichiometric ratio was changed from 1.2 to 1.3. De diego et al. [48] concluded that both the increases of combustion temperature and excess air increased the NO_x emissions. The higher NO_x emissions were attributed to the enhanced combustion of the volatile matter and char in the oxygen-rich atmosphere. In addition, the higher excess oxygen led to the lower char and CO concentrations in the combustor, which weakened the heterogeneous reduction of NO on the char surfaces. Fig. 12(a) summaries the CO concentration and NO_x emissions under atmospheric pressure with different excess oxygen. An increase in NO_x emissions is closely related to the reduction of CO concentration. It can be seen that the CO concentration decreased dramatically as the O_2 concentration increased from 2 vol% to 4 vol%, meanwhile the NO_x emissions increased significantly. When the O_2 concentration increased from 4 vol% to 6 vol%, the CO concentration under oxy-30 decreased continuously while NO_x emissions increased, whereas the NO_x emissions and CO concentration under air maintained at almost the same value. The effect of excess oxygen on the combustion is more significant when the excess oxygen is relatively low, and getting smaller with an increase in excess oxygen. In this study, increasing the O_2 concentration from 2 vol% to 4 vol% can decrease the CO concentration effectively under both air and oxy-30, but the reduction with a further increase in O_2 concentration from 4 vol% to 6 vol% is limited under air. It is expected that the minimum concentration of CO is about 100 ppm in this study because no further reduction was observed when the O_2 concentration in the flue gas was increased from 4 vol% to 6 vol% under air. Therefore, although the CO concentration under oxy-30 decreased from 200 ppm to 125 ppm as the O_2 concentration increased from 4 vol% to 6 vol%, the reduction of CO concentration is expected to be insignificant with a further increase in excess oxygen because the CO concentration has almost reached its minimum value.

As shown in Fig. 11, the promoting effect of excess oxygen on NO_x emissions under 0.4 MPa was consistent with that under atmospheric pressure. Both the NO_x emissions under air and oxy-30 increased with an increase in excess oxygen. Fig. 12(b) summarizes the CO concentration in the flue gas and NO_x emissions under 0.4 MPa with different O_2 concentration in the flue gas. Similar to the results obtained at atmospheric pressure shown in Fig. 12(a), an increase in NO_x emissions was always accompanied by the reduction of CO concentration. The CO concentration under 0.4 MPa with both air and oxy-30 decreased obviously when the O_2 concentration increased from 2 vol% to 6 vol%. As mentioned in section 3.2, the CO concentrations under 0.4 MPa were higher than those under 0.1 MPa in this study, and the CO concentration was about 200-300 ppm which still has a potential to decrease when the O_2 concentration was increased to 6 vol%. However, it is noticed that the reduction rate of CO concentration has become smaller as the O_2 concentration in the flue gas increased from 4 vol% to 6 vol%, and the reduction rate with a further increase in excess oxygen should be even smaller. In an actual commercial combustion system, the oxygen excess has to be controlled as low as possible to avoid extra operational costs and heat loss through the exhaust flue gas, whereas the excessively low oxygen cannot meet the requirement of complete combustion. Based on the pressurized oxy-coal combustion results obtained in this study, it is suggested that a reasonable value of O_2 concentration in the flue gas should be around 4 vol% which can not only meet the requirements of oxygen consumption but also avoid the further increase in NO_x emissions.

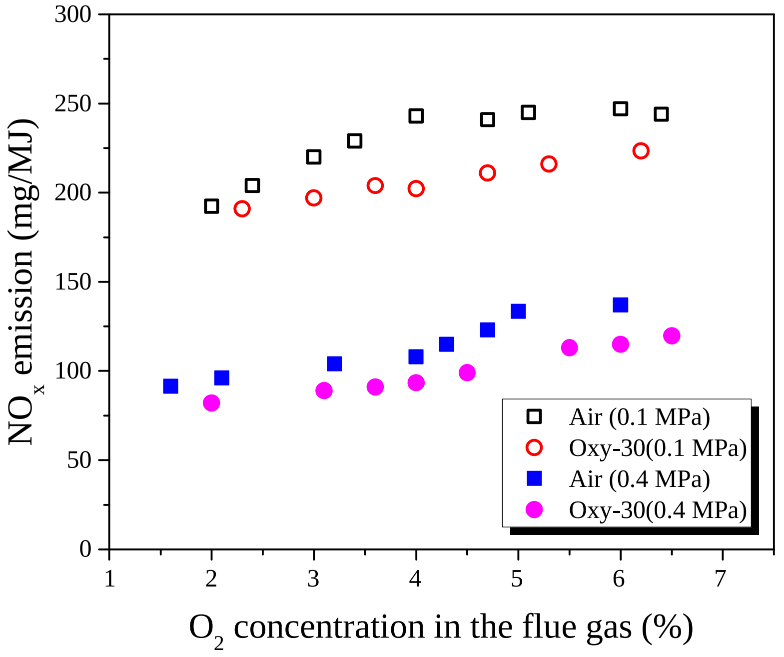
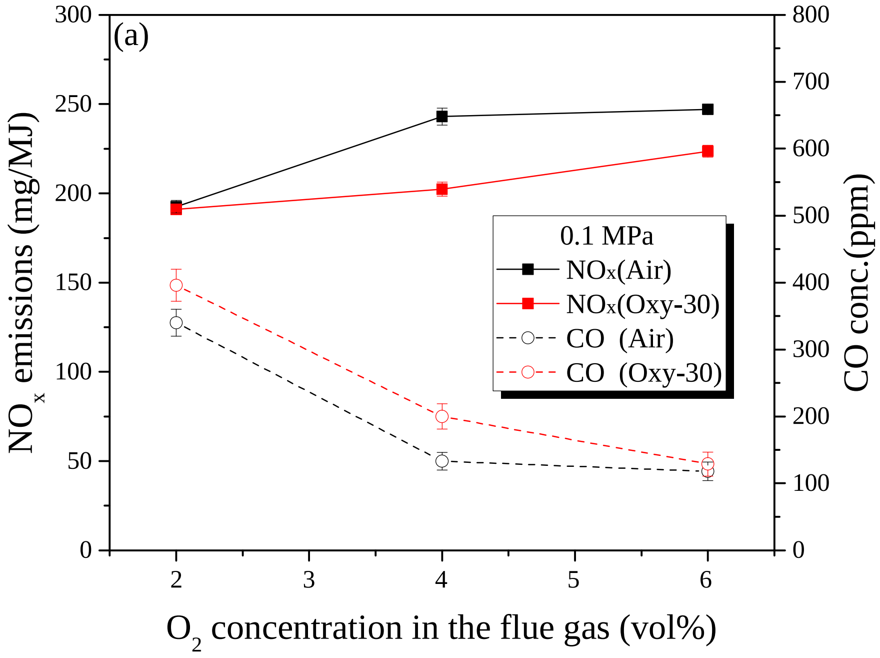


Figure 11. Effect of excess oxygen on the NO_x emissions (T1≈900 °C)



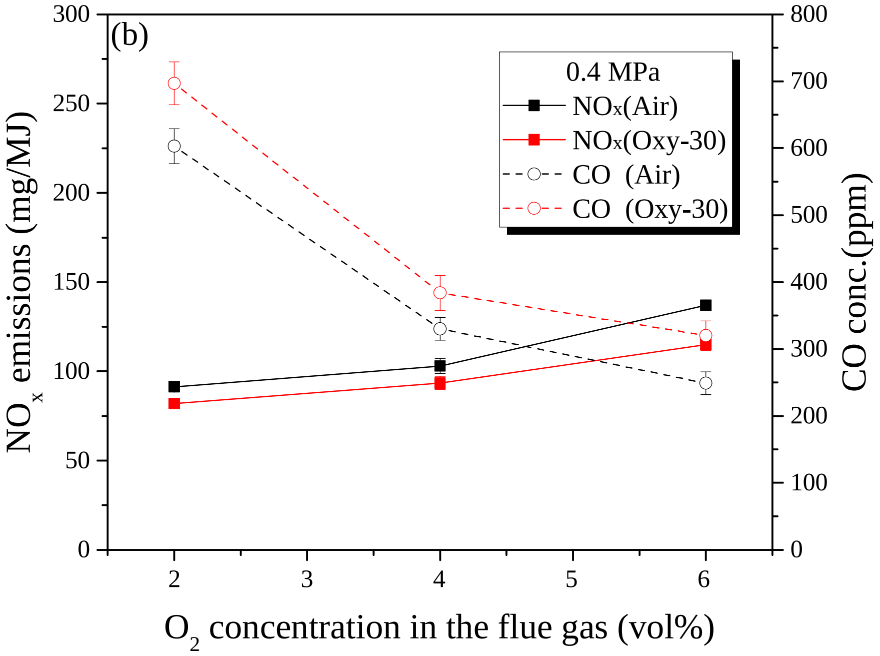


Figure 12. NO_x emissions and CO concentrations with different excess oxygen

(a) 0.1 MPa (b) 0.4 MPa

4. Conclusions

Oxy-coal combustion experiments focusing on the NO_x emission behavior under high pressures were conducted in a 30 kW_{th} pressurized fluidized bed combustor. The effects of combustion pressure, temperature and excess air/oxygen on NO_x emissions under both air combustion and oxy-combustion conditions were systematically investigated with a series of carefully designed experiments. Based on the analysis and interpretation of the experimental results, the following conclusions can be drawn:

(1) The NO_x emission of oxy-coal combustion decreased significantly with an increase in combustion pressure from 0.1 MPa to 0.4 MPa, and the reduction was mainly caused by the pressure increase as the bed temperature, excess oxygen and fluidization velocity were kept at the same levels during the experiments with different combustion pressures.

(2) An increase in bed temperature led to an increase in NO_x emissions under both atmospheric and pressurized oxy-fuel combustion, whereas the promoting effect of bed temperature on NO_x emissions was weaker under higher pressures.

(3) The excess oxygen had a significant effect on NO_x emissions under pressurized oxy-coal combustion, which was consistent with the trend found under atmospheric pressure. The O_2 concentration in the flue gas should be controlled at about 4 vol%, which can not only meet the requirement of coal combustion but also avoid high NO_x emissions.

(4) The NO_x emissions of oxy-coal combustion were closely related to the CO concentration in the flue gas under both pressurized and atmospheric conditions. An increase in NO_x emissions caused by the increase of combustion temperature or excess oxygen was accompanied by a reduction in CO emissions.

From the point of view of reducing NO_x emissions, a pressurized oxy-coal fluidized bed combustion system should have a higher combustion pressure, a lower bed temperature and a lower excess oxygen coefficient. However, it should be noticed that these three parameters also have remarkable influences on the net power plant efficiency, other pollution emissions (such as SO_2 emissions) and desulfurization efficiency etc. Therefore, to determine the most suitable operating condition for pressurized oxy-coal fluidized bed combustion, further research is still needed and this may include both economic analysis such as those of [refs 6-8] and experimental investigations with a more advanced facility than the one used in this study, e.g., a pilot-scale pressurized oxy-coal fluidized bed combustion system.

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