An experimental investigation of oxy-coal combustion in a 15 kW$_{th}$ pressurized fluidized bed combustor

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Abstract

Pressurized oxy-coal combustion is considered as a promising carbon capture technology due to its potential of high efficiency and low cost in CO_2 capture. However, experimental investigations of oxy-coal combustion under pressurized conditions are far less common than those under atmospheric pressure conditions and hence further research is needed to elucidate the effects of pressure on oxy-coal combustion in terms of combustion performance and emissions etc. In this study, a series of oxy-coal combustion experiments were carried out under the pressures from 0.1 MPa to 0.4 MPa on a 15 kWth fluidized bed combustion system. The effects of the combustion pressure and oxygen concentration in the oxidant on the temperature profile, unburnt carbon, combustion efficiency, fly ash composition and NO_x emission were investigated. The experimental results have shown that the CO_2 concentration in the oxy-combustion flue gas under different combustion pressures have all exceeded 90%, which is beneficial to the carbon capture process. An increase in pressure is helpful to reduce the unburnt carbon in the fly ash and improve the combustion efficiency under all the tested oxy-combustion atmospheres. The NO_x emission decreases with combustion pressure within the investigated range of 0.1 MPa to 0.4 MPa, while the reduction is more pronounced at lower pressures. Besides, the effect of combustion pressure on the chemical composition of the fly ash is found to be insignificant.

Keywords: Carbon capture; Oxy-coal combustion; Pressurized fluidized-bed.

1. Introduction

Greenhouse gas (GHG) emissions have become an increasing concern as rising GHG emissions are closely related to the climate change observed over past decades, and therefore, the call for the application of CO_2 capture and storage (CCS) technologies has become particularly strong in recent years. As one of the most developed CCS technologies, oxy-fuel combustion is considered as technically feasible and economically competitive for future commercial applications [1-3]. Research and development activities in oxy-combustion have been associated with both pulverized coal combustion and fluidized bed (FB) combustion [4-5]. Compared with pulverized coal oxy-fuel combustion, a critical advantage of fluidized bed combustion is the capability to reduce the recirculated flue gas flow for a given coal input, which can increase the net power generation efficiency significantly [5]. Besides, experimental results have shown that the advantages of fluidized beds under air combustion mode such as fuel flexibility, lower NO_X emissions and better sulfur removal are all inherited by the oxy-fuel combustion mode [6-8].

Oxy-fuel combustion has shown advantages and potentials in both combustion and CO_2 capture processes. However, the biggest obstacle to its application is the net efficiency loss associated with the cost of the air separation unit (ASU) and compression purification unit (CPU). It is estimated that the net efficiency can be reduced by more than 10% when a conventional air-fired coal power plant is converted to oxy-firing [9-11]. In order to improve the efficiency, the pressurized oxy-fuel combustion (POFC) technology has been proposed, and many theoretical and economic system analyses have been carried out on POFC technology [12-16]. Hong et al. [12]

concluded that the elevated pressure raised the dew point and the available latent enthalpy of the flue gas, and hence was helpful to recover more thermal energy. Furthermore, the higher pressure was beneficial to save energy for the downstream CO_2 compression work. Gopan et al. [13] evaluated a staged pressurized oxy-combustion system, and the results showed that the penalty in plant efficiency caused by carbon capture could be reduced by 6 %. Similar positive effects of high pressure on the overall plant efficiency and CO_2 capture have also been demonstrated by the simulation results of many other researchers [14-16]. The optimal pressure has been found to be system dependent as a result of the concurrence of the minimum compression power and the maximum thermal recovery.

Although simulation and theoretical calculation results have showed the advantages of pressurized oxy-fuel combustion technology in increasing the net power generation efficiency, there are few experimental studies on the POFC. Wang et al. [17] and Ying et al. [18] conducted oxy-combustion experiments on the pressurized thermo-gravimetric analyzer (PTGA) and investigated the effects of combustion pressure and oxygen concentration on the ignition and burnout of pulverized coals. Their results indicated that an increase in combustion pressure or oxygen concentration resulted in a decrease in the ignition temperature and an increase in the combustion rate. Lei et al. [19] studied the release behaviors of SO_2, NO and NO_2 of a Chinese bituminous coal by a PTGA. It was found that the conversion of fuel-N to NO_x increased with increasing pressure. Lasek et al. [20-21] carried out pressurized oxy-fuel combustion experiments in a fluidized bed under the pressures from 0.1 MPa to 0.6 MPa. Their studies mainly focused on the emissions of NO_x and N_2O under the elevated pressure conditions, and a reduction in NO_x emissions with an increase in pressure was observed. One possible reason for the contradictory NO_x emission behavior may be the difference between the experimental facilities used by these researchers [19-21]. The whole combustion processes (e.g., pyrolysis, ignition and burnout) within the fluidized bed combustors should be quite different from those within the thermo-gravimetric analyzer.

The pressurized oxy-fuel fluidized bed combustion system used in this study was modified from the pressurized air-combustion system developed by the authors [22]. A series of fluidized bed combustion experiments has been conducted under different combustion pressures and oxy-fuel environments in order to elucidate the effects of pressure and O_2 concentration on the oxy-coal combustion performance.

2. Experimental

2.1 Pressurized oxy-coal fluidized bed combustion system

Fig. 1 shows the schematic of the pressurized oxy-coal combustion system which was modified from the pressurized fluidized bed combustion system used with our previous research on pressurized air combustion [22]. The combustion system was designed as a CFB but it was always operated with the valve in the return leg closed, i.e., as a bubbling fluidized bed combustion system in this study. Only the essential and/or new information of the combustion system is included in this paper as other details can be found from our previous paper [22]. The water cooling probe located inside the bed zone allows the bed temperature to be controlled within a desired range.

For an industrial oxy-fuel combustion system, the oxidant for combustion is a mixture of pure O_2 and recycled flue gas (RFG). As the real flue gas recirculation is not available with the present pressurized fluidized bed combustion system, the oxidant, i.e. the inlet gas to the combustor, was replaced by a premixed flow of CO_2 and O_2 supplied by gas cylinders. The flow rates of CO_2 and O_2 were adjusted by mass flow controllers, to achieve a preselected concentration of O_2 in the oxidant. The fly ash was collected with each test and then analyzed for chemical composition by use of an X-ray fluorescence analyzer (ARL9800XP+) after the tests. Most of the ash was taken from the pipe at the bottom of the cyclone separator, and only a small amount of the ash was found from the bag filter. Because the combustor was operated under pressure, two valves were used to take ash samples during operation. The detailed process is as follow: Before we took ash samples, both valves on the pipe (Fig. 1) were closed. Then, the first valve was opened so that ash entered into the pipe between the two valves. Next, the first valve was closed, and the ash samples were separated from the combustor. Finally, the second valve was opened, and the ash samples were taken out. The above process was repeated several times during a short time until all the ash was taken out, which ensures the next ash sample was produced under the new combustion condition.

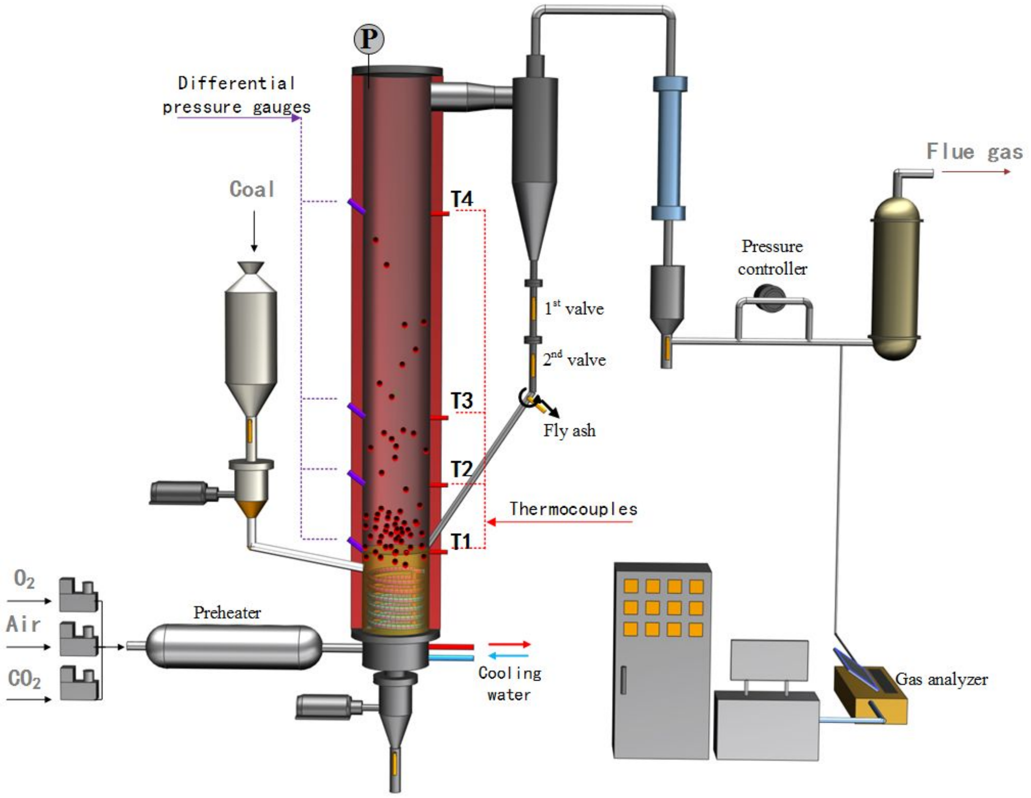

Figure 1. Schematic of the pressurized oxy-coal fluidized bed combustion system

2.2 Fuel and bed material

Silica sand (0.38 - 1.9 mm) and the Inner Mongolia lignite coal (1.18 - 2.40 mm) were selected as the bed material and fuel with their particle size distributions shown in Fig. 2(a) and Fig. 2(b), respectively. The ultimate analysis and proximate analysis of the coal are listed in Table 1.

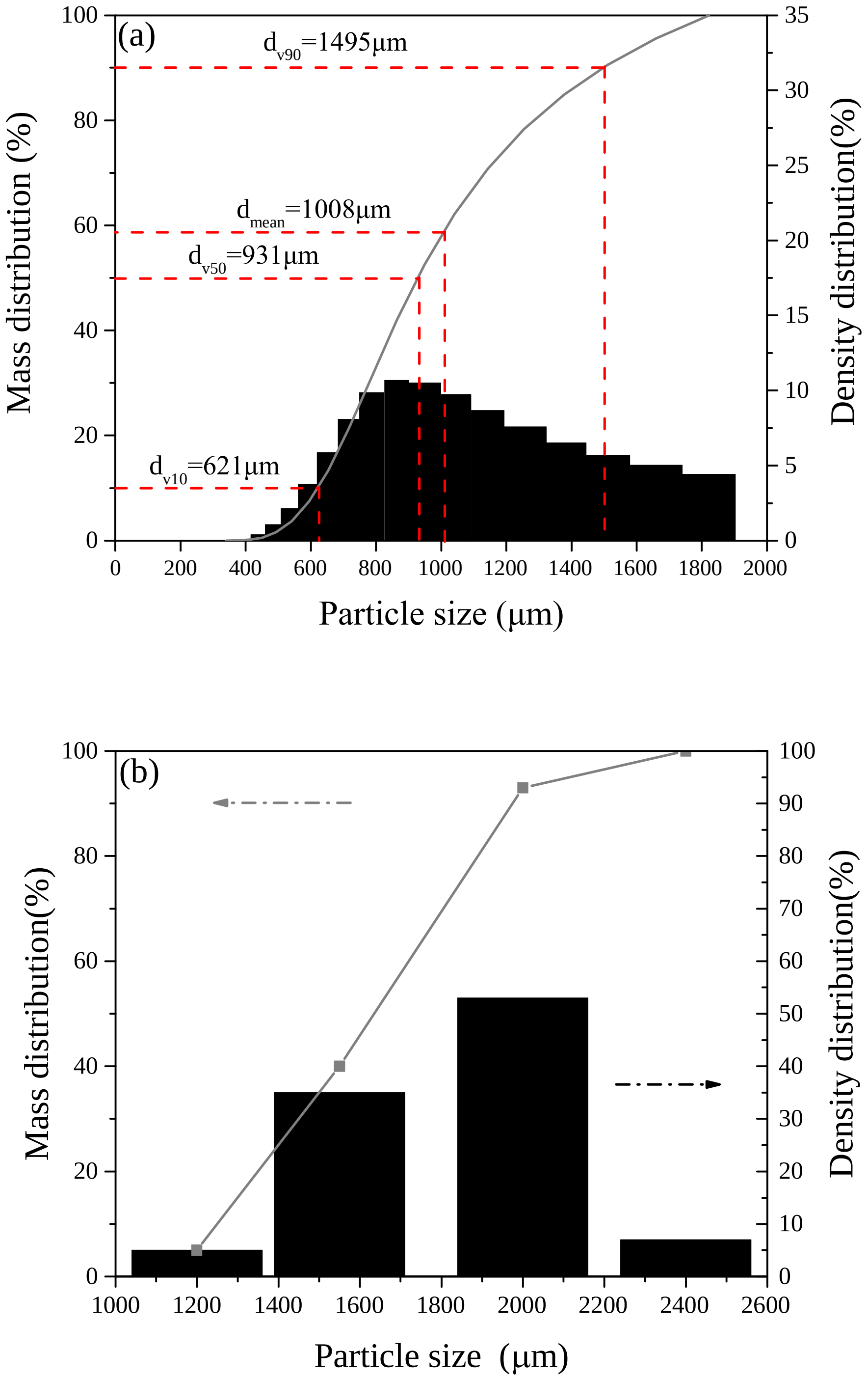

Figure 2. Particle size distribution (a) silica sand (b) coal particles

2.3 Procedure and operating conditions

Before each experiment, the oxidant (inlet gas) was preheated to 600 °C by the electric preheater, and silica sand (2.3 kg) was introduced into the combustor and preheated to about 500 °C. The pressure inside the combustor was adjusted to a desired value by the auto pressure controller. Then, proper amounts of coal and air were fed into the combustion zone continuously and the electric heaters around the combustor (except for the gas preheater) were turned off. Fig. 3 shows the profiles of bed temperatures and flue gas composition in a typical experiment (0.2 MPa). Once the stable air combustion state was reached, the oxidant was changed from air to oxy-fuel oxidant (O_2/CO_2). The major operating parameters are summarized in Table 2. The errors included in Table 2 represent both the differences in the average values of repeated runs and the fluctuations in a single test. It should be noticed that, the combustion conditions inside the combustor were not at steady-state immediately after the change of the feed gas but the steady-state conditions were reached 20-30 minutes after the changeover. The experimental data discussed in 'Results and discussion' were those obtained during the steady-state operation period rather than the whole process. The names for different oxy-fuel conditions, i.e., oxy-21, oxy-25, oxy-30 represent the O_2 concentration (21 vol%, 25 vol%, and 30 vol%) in the oxy-fuel oxidant fed into the combustor. As the excess oxygen coefficient must remain constant, the increase in O_2 concentration was realized by reducing the CO_2 flow rate while keeping the O_2 flow rate and coal feeding rate constant.

It is worth mentioning that, in order to keep the same superficial gas velocity and excess air coefficient, the oxidant flow rate and coal feeding rate should be increased in proportion to the combustion pressure. As more coal is introduced into the combustor, more heat should be removed by the cooling system in order that the combustion temperature can maintain within a desired and safe range. In this study, due to the limited heat exchange capacity of the water cooling system, the coal feeding rates and oxidant flow rates under the pressures of 0.3 MPa and 0.4 MPa were kept the same values as those of 0.2 MPa to avoid excessively high temperatures within the combustor.

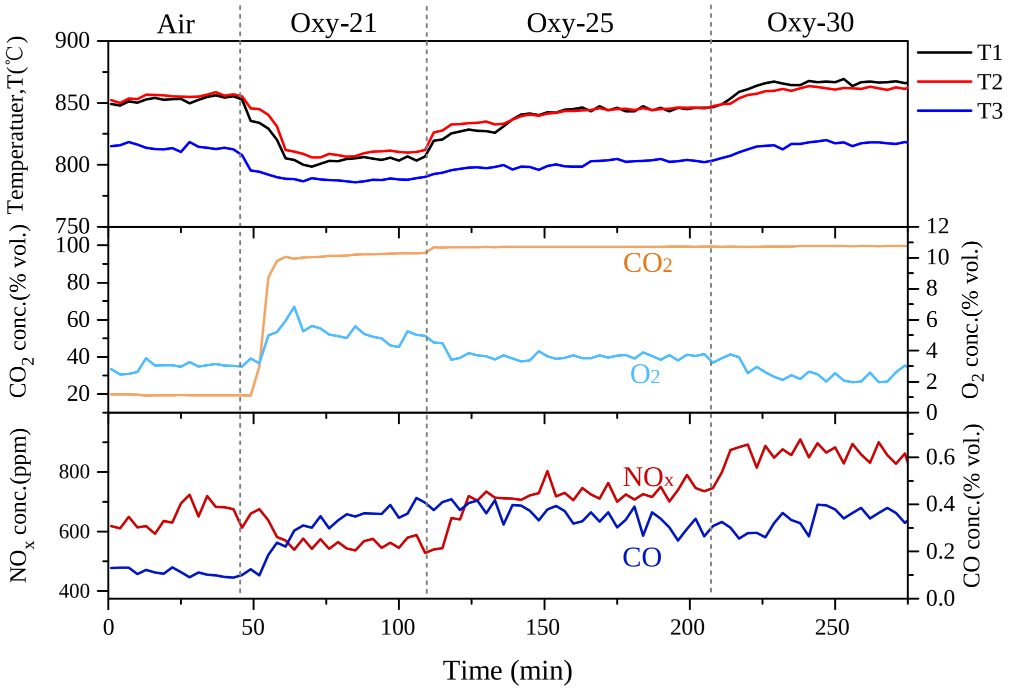

Figure 3. The temperature profiles, and gas concentrations at the outlet of the combustor under air and oxy-fuel conditions (0.2 MPa)

3. Results and discussion

One important target for oxy-fuel combustion is to obtain high CO_2 concentration in the flue gas and hence improve the CO_2 capture efficiency. In this study, the oxy-coal fluidized bed combustion experiments were conducted under the pressures from 0.1 to

0.4 MPa. It can be seen from Fig. 3 and Table. 2, after the steady oxy-coal combustion conditions were achieved, the CO_2 concentrations in the dry flue gases exceeded 90 % under all the tested pressures. The effects of combustion pressure and oxygen concentration in the oxidant on the fluidized bed combustion performance were systematically investigated while the CO_2 concentration in the dry flue gas remained higher than 90 %.

3.1 Temperature profile

The temperatures of the bed zone (T1) under different combustion pressures and atmospheres are shown in Fig. 4. Under all the tested combustion pressures, T1 decreases sharply as the oxidant is switched from air to oxy-21 atmosphere. Then, a significant temperature increase is observed by increasing the O_2 concentration in the oxidant from 21 vol% to 25 vol% and to 30 vol%. The temperature decrease from air to oxy-21 atmosphere is mainly resulted from the higher specific heat of CO_2 compared with that of nitrogen. The higher temperature under oxy-25 or oxy-30 atmosphere than that of oxy-21 atmosphere is a consequence of both the increase in O_2 concentration in the oxidant and the reduction of the CO_2 flow rate in the oxidant. Under all the tested combustion pressures from 0.1 MPa to 0.4 MPa, the temperature of air combustion is between that of oxy-25 and oxy-30 atmosphere, which agrees with the findings of previous studies [23-24]. With an increase in combustion pressure, the temperature of the bed zone under the same combustion atmosphere increases, e.g., T1 with oxy-21 atmosphere increases from 790 °C to 810 °C when the pressure increases from 0.1 MPa to 0.2 MPa. Previous experiments [25] had showed that the higher combustion pressure was beneficial to accelerate the combustion rate of coal particles, and the higher oxygen partial pressure increased not only the reaction rates but also the particle temperature. The temperature increase with pressure changing from 0.1 MPa to 0.2 MPa is mainly owing to the effect of the elevated pressure on the coal combustion, whereas the temperature increase from 0.2 MPa to 0.4 MPa is a combined result of the higher pressure and lower gas velocity. The lower gas velocity leads to a longer residence time of the coal particle, which is beneficial to the burnout of the coal and release more heat.

Fig. 5 shows the temperature distributions along with the height of combustor (0.2 MPa). The maximum temperature is seen to appear at the dense-phase zone of the combustor where most of the fuel particles are burned and the heat released. Above the dense-phase zone, temperature decreases along with the combustor height due as the heat loss is bigger than the heat release from combustion. At the top of the combustor, the main heat source is the flue gas as there is little combustion happening in this part of the combustor, and the temperature differences between different combustion atmospheres become smaller. Differing from the observation of the combustion experiments with biomass [26], the temperature of the dilute-phase zone is lower than that of the dense-phase zone due to the lower volatile in the coal and hence smaller heat release in the dilute-phase zone resulted from volatile combustion.

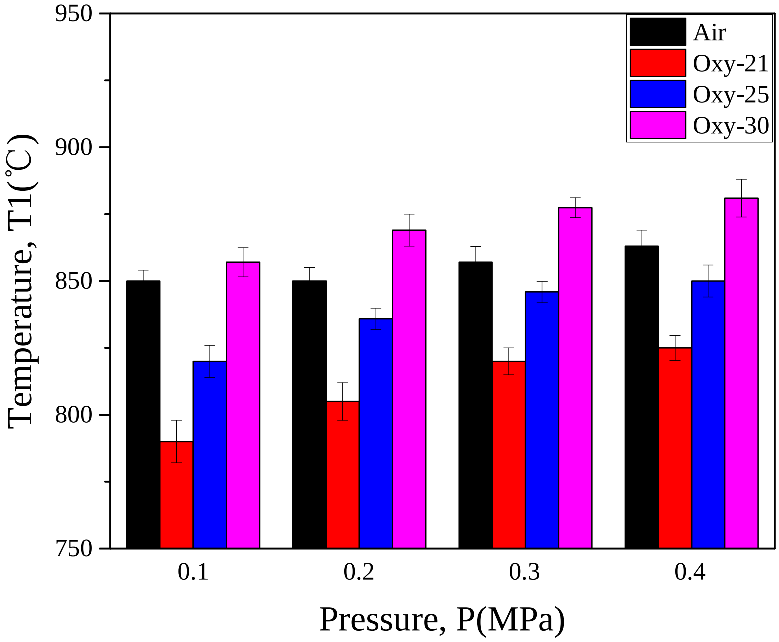

Figure 4. The bed zone temperatures (T1) under different combustion pressures and atmospheres

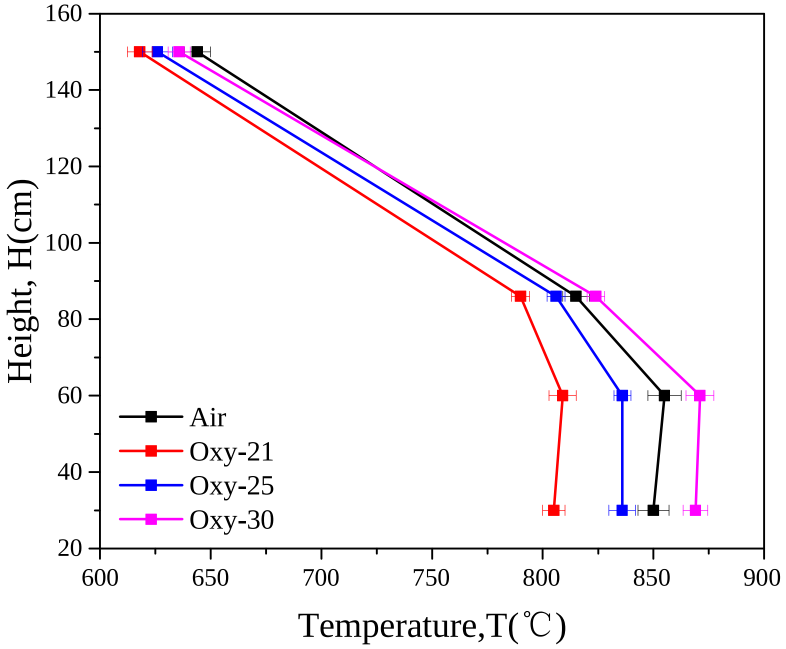

Figure 5. Temperature distributions along the combustor height (0.2MPa)

As many researchers [2, 4] have pointed out, the higher specific heat of CO_2 than that of N_2 led to a sharp decrease in combustion temperature when the combustion environment was changed from air to oxy-21 atmosphere. In many previous atmospheric oxy-fuel combustion studies [24, 26], it was impossible to stabilize the temperature once the combustion environment was changed to oxy-21 atmosphere (21 vol% O_2/79 vol% CO_2) from air. However, some other studies [20-21, 27] showed that this switch only decreased the combustion temperature by less than 100 °C, and it was possible to achieve a steady combustion state. The main reason that leads to the difference in the combustion temperature achieved with oxy-21 with different studies lies with the temperature of the oxidant or the inlet gas. It is obvious that the temperature of the oxidant affects the combustion temperature significantly. In this study, the oxidant was heated to about 600 °C by the electric preheater, and all the experimental results were based on this experimental setting. Although the high oxidant temperature is helpful to achieve the steady combustion state and maintain the combustion temperature within a suitable range, it is worth mentioning that the energy input of the electric preheater under oxy-21 atmosphere is higher than that under air (even though the oxidant was heated from 30 to 600 °C under both conditions), and the negative effect of higher specific heat of CO_2 than nitrogen on the combustion temperature is offset by the preheater to some extent. It should also be pointed out that it was not necessary to heat the oxidant (air or the mixture of oxygen and CO_2) to 600 °C, and we plan to decrease the oxidant temperature from 600 °C to 200 °C which is more likely to be the case for actual industrial processes in our future experiments.

3.2 Unburnt carbon

This section focuses on the discussion of the unburnt carbon in fly ash as the mass fraction of unburnt carbon in bottom ash was lower than 2% under all the tested conditions. The mass fractions of unburnt carbon in fly ash under different combustion pressures and atmospheres are shown in Fig. 6. Under the same combustion pressure, the unburnt carbon in fly ash under the oxy-21 atmosphere is higher than that under air, and it decreases slightly as the O_2 concentration in the oxidant increases from 21 vol% to 30 vol%. The higher mass fraction of unburnt carbon under oxy-21 atmosphere is mainly caused by the lower combustion temperature. It can be seen from Fig. 4 that the temperatures under the oxy-21 atmosphere are lower than those under air. As mentioned in section 3.1, the switch from oxy-21 to oxy-25 or oxy-30 atmosphere not only increases the O_2 concentration but also reduces the CO_2 flow rate. The higher oxygen partial pressure accelerates the combustion rate, while the lower flow rate increases the residence time of coal particles, and hence the unburnt carbon in fly ash is reduced.

Increasing the combustion pressure from 0.1 MPa to 0.4 MPa leads to a lower unburnt carbon in fly ash under the same combustion atmosphere. Take the oxy-30 atmosphere as an example, the mass fraction of unburnt carbon in fly ash decreases from 29.17 % to 23.74 % when the pressure is increased from 0.1 MPa to 0.2 MPa, and a further decrease from 23.74 % to 10.64 % is observed when the pressure is increased from 0.2 MPa to 0.4 MPa. The reduction of unburnt carbon in fly ash from 0.1 MPa to 0.2 MPa is mainly caused by the increase in combustion pressure as most of the operating parameters (e.g., temperature, superficial gas velocity) are kept at the same values. However, the decrease in unburnt carbon from 0.2 MPa to 0.4 MPa is a combined result of the higher combustion pressure and the lower gas velocity. As explained in section 2.3, the superficial gas velocities under 0.3 MPa and 0.4 MPa are lower than that of 0.1 MPa or 0.2 MPa, and the lower gas velocity results in a longer residence time of coal particles, which is beneficial to the burnout of coal. It can be estimated that the unburnt carbon under 0.3 MPa will be higher than the measured one if the gas velocity under 0.3 MPa is kept at the same value as that of 0.2 MPa. Besides, it is noticed that the reduction in unburnt carbon becomes smaller when the pressure increases from 0.3 MPa to 0.4 MPa than that from 0.1 MPa to 0.2 MPa. This phenomenon agrees with the previous experiment results [25] that the effect of pressure increase on the combustion rate was the greatest at near 0.1 MPa and getting smaller at higher pressures.

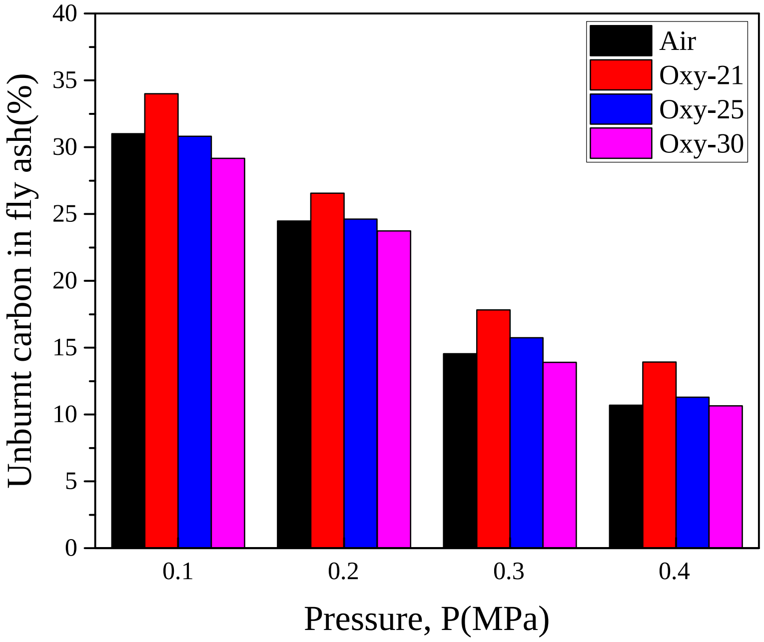

Figure 6. Unburnt carbon in fly ash

3.3 CO emissions

Normalized mass emissions of CO under different pressures and atmospheres are shown in Fig. 7 which reveals that the CO emissions under the oxy-combustion atmospheres are higher than those under air. This is mainly due to the higher concentration of CO_2 with oxy-coal combustion. The reactions involving char during the combustion process can be written as:

$$C+O_2 \rightleftarrows CO_2 \tag{R1}$$

$$C+0.5O_2 \rightleftarrows CO \tag{R2}$$

$$CO+0.5O_2 \rightleftarrows CO_2 \tag{R3}$$

$$C+CO_2 \rightleftarrows 2CO \tag{R4}$$

When the oxidant is changed from air to the oxy-atmosphere, the high concentration of CO_2 is beneficial to its reduction reaction with carbon (R4), and hence the CO emission increases significantly. As the previous studies [26-28] which were conducted under atmospheric pressure had showed, the CO emission decreased as the O_2 concentration in the oxidant increased. In this study, the significant reductions in CO emission with an increase in O_2 concentration from 21 vol % to 30 vol % can be observed under the pressures of 0.1 MPa and 0.2 MPa, i.e., a 32% decrease (from 2185 to 1483 mg/MJ) and a 40 % decrease (from 1495 to 891 mg/MJ), respectively. The reductions of CO emissions under higher O_2 concentration atmospheres are mainly caused by the higher combustion temperatures and the longer gas residence time. As it can be seen from Fig. 5, the temperatures of the combustor increase with O_2 concentration, which is helpful to decrease the CO emissions. Besides, as mentioned in section 2.3, the higher O_2

concentration in the oxy-atmosphere is realized by reducing the total gas flow rate, which results in a lower superficial gas velocity and a longer gas residence time, and CO has more chances to react with O_2 (R3). However, the CO emissions under the pressures of 0.3 MPa and 0.4 MPa with different oxy-atmospheres are different from those under the pressures of 0.1 MPa and 0.2 MPa. As shown in Fig. 7, under the pressure of 0.3 MPa, the CO emission with oxy-30 atmosphere is 1296 mg/MJ which is much higher than that with oxy-25 atmosphere (583 mg/MJ). Besides, under the pressure of 0.4 MPa, the CO emissions with oxy-25 and oxy-30 atmospheres are higher than that with oxy-21 atmosphere. The unusual high emission of CO is mainly due to the low O_2 concentration in the flue gas. As it can be seen from Table 2, the O_2 concentration in the flue gas (0.3 MPa) decreases from 2.59 % to 1.56 % when the oxidant is converted from oxy-25 to oxy-30 atmosphere, and another decrease in O_2 concentration in the flue gas is noticed under the pressure of 0.4 MPa. The lower O_2 concentration slows down the oxidizing reaction of CO (R3) in the freeboard region of the bed, which leads to higher CO emissions. The same relation between the lower O_2 concentration in the flue gas and higher CO emission was also observed by other researchers [20-21]. In this study, CO emission started to increase when the O_2 concentration in the flue gas was lower than about 2 % under the pressures of 0.3 MPa and 0.4 MPa.

As shown in Fig. 7, the CO emissions under different combustion atmospheres reduce sharply as the combustion pressure increases from 0.1 MPa to 0.2 MPa. The higher pressure results in higher combustion rate [25], lower unburnt carbon in fly ash

(Fig. 6) and higher combustion temperature (Fig. 4), which is beneficial to reduce CO emissions. Besides, according to the Le Chatelier's principle, the elevated pressure accelerates the forward reaction rate of R3. The reduction of CO emission is more pronounced when the pressure increases from 0.2 MPa to 0.3 MPa (except for the oxy-30 atmosphere), and this is the result of the increased pressure and the longer gas residence time (as mentioned in section 2.3, the coal feeding rate and gas flow rate under 0.3 MPa were kept at the same values as those under 0.4 MPa and hence the superficial gas velocity was reduced). It is worth mentioning that, compared with some other studies [27-28], the higher CO emission in this study is mainly caused by the lower height of the combustor. In addition, previous studies [4, 29-30] showed that the O_2 staging and recycled flue gas were beneficial to reduce CO emissions. In practice, about 70-75 % flue gas will be circulated back to the combustor and CO emissions will be reduced proportionally [30].

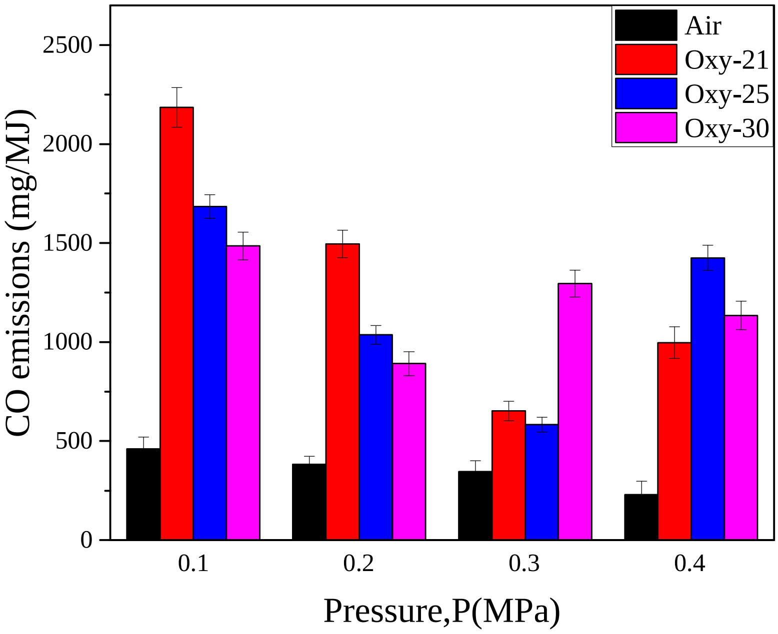

Figure 7. CO emissions under different combustion pressures and atmospheres

3.4 Combustion efficiency

The combustion efficiency (η) can be calculated by Eqn. (1-5), and more detailed information can be found elsewhere [22, 27, 31]:

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

$$q_3 = \frac{Q_{CO} + Q_{H_2} + Q_{CH_4}}{Q_{\mathrm{net,\ ar}}} \tag{2}$$

$$q_4 = q_4^{ba} + q_4^{fa} \tag{3}$$

$$q_4^{ba} = \frac{Q_c * C_{ba} * G_{ba}}{Q_{\mathrm{net,\ ar}}} \tag{4}$$

$$q_4^{fa} = \frac{Q_c * C_{fa} * G_{fa}}{Q_{\mathrm{net,\ ar}}} \tag{5}$$

Because both the quantity of the bottom ash and the unburnt carbon in bottom ash are quite small in this study, the heat loss associated with unburnt carbon is mainly results from the unburnt carbon in fly ash.

The combustion efficiencies under different combustion pressures and atmospheres are shown in Fig. 8. Fig. 8 reveals that the combustion efficiency decreases as the oxidant is changed from air to the oxy-21 atmosphere, and then it increases with an increase in O_2 concentration in the oxidant. The decrease in combustion efficiency from air to the oxy-21 atmosphere is mainly caused by the higher values of q_3 and q_4, as it can be seen from Fig. 6 and Fig. 7 that both the unburnt carbon in fly ash and the CO emission increase. The switch from oxy-21 to oxy-25 or oxy-30 leads to the higher oxygen partial pressure and lower gas velocity as well as the faster combustion rate and higher combustion temperature, which decreases the heat losses and improves the combustion efficiency.

It is noticed that the combustion efficiencies under different atmospheres increase significantly as the combustion pressure increases from 0.1 MPa to 0.2 MPa, i.e., 3.22 % (from 88.26% to 91.48 % under air), 4.51 % (from 84.98% to 89.49 % under oxy-21), 3.81 % (from 87.21% to 91.02 % under oxy-25) and 3.09 % (from 88.23% to 91.32 % under oxy-30), respectively. As the superficial gas velocities were kept at the same value, the increase in combustion efficiency is caused by the increased devolatilization and combustion rates under the high pressure conditions. A further increase in combustion efficiency is observed when the pressure increases from 0.2 MPa to 0.3 MPa, i.e., 3.91 % (from 91.48 % to 95.39 % under air), 4.44% (from 89.49 % to 93.93 % under oxy-21), 3.73 % (from 91.02 % to 94.75 % under oxy-25) and 3.40 % (from 91.32 % to 94.72 % under oxy-30), respectively, but these increases in combustion efficiency are attributed to both the elevated pressure and the longer gas residence time with the 0.3 MPa tests. However, when the pressure increases from 0.3 MPa to 0.4 MPa, the increase in combustion efficiency is much smaller compared with that from 0.1 MPa to 0.2 MPa or that from 0.2 MPa to 0.3 MPa, and this indicates the positive effect of a further increase in pressure or a further decrease in gas velocity on the combustion efficiency becomes smaller.

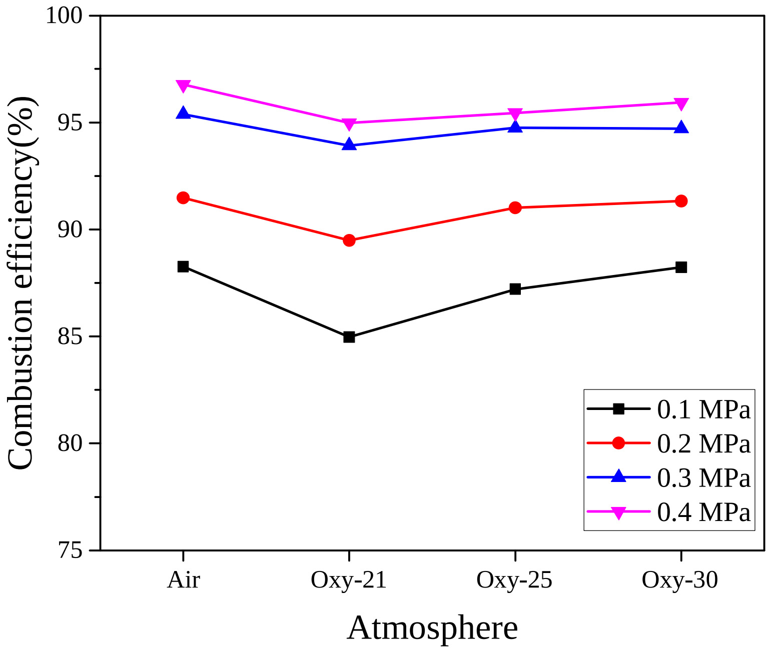

Figure 8. Combustion efficiency under different combustion pressures and atmospheres

3.5 NO_x emissions

Both NO and NO_2, collectively termed as NO_x, have been measured in each test. NO has always been the dominant part of NO_x (> 95%) for all the tests of this study. The results of NO_x emissions under different combustion pressures and atmospheres are plotted in Fig. 9. Fig. 9 shows that the NO_x emission decreases when the combustion atmosphere is switched from air to oxy-21 and increases with an increase in O_2 concentration in the oxidant. This agrees with most of the previous studies [21, 27-28] where NO_x emissions were found to decrease in the order of air > oxy-30 > oxy-21 under the same pressure. Reactions (5)-(7) show the main fuel-NO_x formation mechanism during the combustion process. The fuel nitrogen is released with the volatiles and converted to the NO_x precursors, i.e., cyanide (HCN) and ammonia (NH_3) etc. Then, depending on the reaction conditions, NH_3 could be oxidized to NO (R6) or reduce NO to N_2 (R7). More detailed discussion on the fuel-NO_x formation mechanism can be found in other literature [26, 32].

$$\mathrm{HCN+2[H]} \rightarrow \mathrm{NH_3+[C]} \tag{R5}$$

$$\mathrm{NH_3}+\frac{5}{4}\mathrm{O_2} \rightarrow \mathrm{NO}+\frac{3}{2}\mathrm{H_2O} \tag{R6}$$

$$\frac{2}{3}\mathrm{NH_3+NO} \rightarrow \frac{5}{6}\mathrm{N_2+H_2O} \tag{R7}$$

$$\mathrm{NO+CO} \xrightarrow{char} \frac{1}{2}\mathrm{N_2+CO_2} \tag{R8}$$

The NO_x emissions are mainly affected by O_2 concentration, temperature and CO concentration under the same combustion pressure. Generally, the higher O_2 concentration and higher temperature often lead to higher NO_x emissions while the higher CO concentration is helpful to reduce NO_x emissions. The reduction of NO_x emissions resulted from the change of combustion environment from air to oxy-21 is the combined effects of lower combustion temperature and higher CO concentration [32]. As shown in Fig. 4 and Fig. 7, changing the environment from air to oxy-21 leads to a sharp decrease in the bed zone temperature at 0.1 MPa (from 850 to 790 °C), while the CO emission increases significantly from 460 to 2185 mg/MJ, which is beneficial to the reduction of NO emission (R8). An increase in NO_x emission is observed when the combustion environment is switched from oxy-21 to oxy-25 or oxy-30 as the higher partial pressure of O_2 and the higher combustion temperature result in more NH_3 or other fuel-N intermediates being oxidized to NO_x [33]. Besides, the lower CO emissions also caused the higher NO_x emission as less NO was reduced by CO (R8). The lower gas velocity under oxy-25 or oxy-30 than that under oxy-21 atmosphere should be beneficial to the reduction of NO_x emissions (R8). However, the higher NO_x emissions under oxy-25 or oxy-30 atmosphere indicates that the effect of lower gas velocity on NO_x emissions is inferior to the effect of higher O_2 concentration and higher combustion temperature in this study.

As shown in Fig. 4, the combustion temperature increased with an increase in pressure from 0.1 MPa to 0.2 MPa whereas the CO concentration reduced, and hence the NO_x emission was expected to increase if only the effects of temperature and CO concentration are taken into account. However, Fig. 9 reveals that the NO_x emission decreases with an increase in combustion pressure under the same combustion atmosphere (except for the lowest NO_x emission under the pressure of 0.1 MPa and oxy-21 atmosphere, which is caused by the quite low combustion temperature). The lower NO_x emission is mainly resulted from the reduction reaction with CO (R8) as an increase in pressure increases the time for the diffusion of NO_x throughout the char particles. Besides, an increase in pressure from 0.1 MPa to 0.2 MPa decreases the diffusion coefficient of O_2 in CO_2 from 1.55 cm^2/s to 0.77 cm^2/s, which limits the oxidation of fuel-N by the transport of O_2 to the boundary layer of coal particles [21]. When the combustion pressure was further increased from 0.2 MPa to 0.4 MPa, the NO_x emission decreased further as a result of the combined effects of the pressure increase and lower O_2 concentration in the free board/outlet gas which itself was resulted from the enhanced combustion at higher pressures.

As shown in Fig. 9, the decrease rate of NO_x emission becomes smaller as the pressure increases from 0.1 MPa to 0.4 MPa. Take the NO_x emission under oxy-30 atmosphere as an example, it decreases by 17.3 % (0.1-0.2 MPa, from 283 to 234 mg/MJ), 9.4% (0.2-0.3 MPa, from 234 to 212 mg/MJ) and 6.6% (0.3-0.4 MPa, from 212 to 198 mg/MJ), respectively. The weaker effect of pressure increase on NO_x emissions can also be explained by the diffusion coefficient of O_2 in CO_2 as the decrease rate of the diffusion coefficient of O_2 in CO_2 becomes smaller with the higher pressure [36]. Meanwhile, As mentioned in section 3.1 and 3.3, the combustion temperature increases with an increase in pressure, which is beneficial to produce more NO_x and then to restrain the positive effect of high pressure on the reduction of NO_x emission. The same NO_x emission behavior was observed by the previous pressurized air combustion experiments [35] where the authors indicated that the NO_x emissions reduced substantially with the pressure increasing from 0.1 MPa to 0.5 MPa, and further increases in pressure led to much smaller reductions in NO_x emissions.

It is worth mentioning that for all of the NO_x reduction mechanisms in oxy-fuel combustion, the recycled flue gas plays an important role. Many researchers [4] have found a more pronounced reduction in NO_x emissions with flue gas recycles as part of the recycled NO_x can be reduced to N_2. In addition, as 70-75% flue gas is circulated back to the combustor and only about 25-30% of the flue gas is exhausted [30], the NO_x emissions (mg/MJ) will be only about a quarter of the measured values without flue gas recycling.

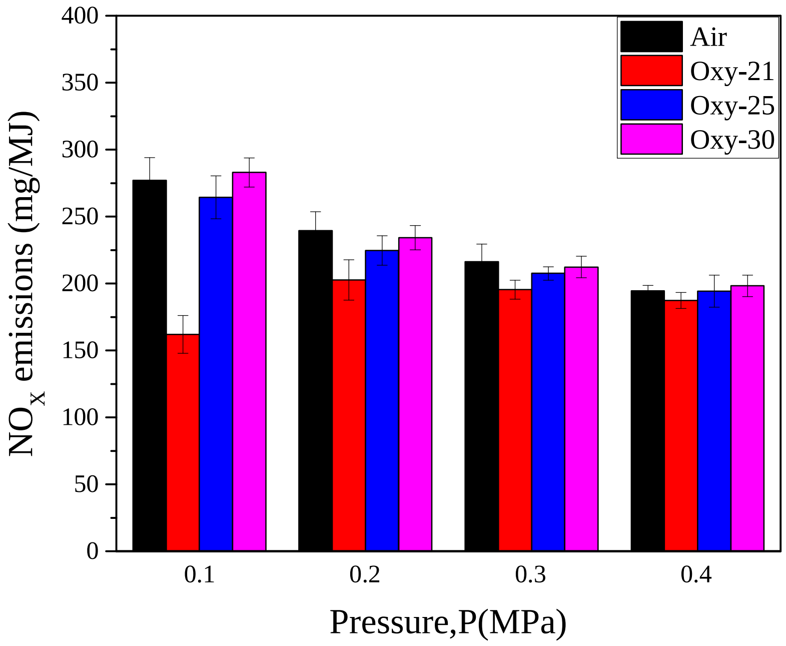

Figure 9. NO_x emissions

3.6 Elemental analysis and chemical composition of fly ash

The results of the elemental analysis of the fly ash samples are shown in Table 3. The Total Mass Loss (TML), and the elemental losses (Carbon Mass Loss (CML), Hydrogen Mass Loss (HML) and Nitrogen Mass Loss (NML)) of the coal after undergoing combustion in the fluidized bed can be estimated by using ‘ash as a tracer’ method [34] (Equation 6-9) and the elemental analyses of the coal and fly ash. The TML, CML, HML and NML values are included in Table 3. From Table 3, it can be see that the values of TML and CML are about 88% when the unburned combustibles in fly ash is about 30%; when the unburn combustibles in fly ash is about 11%, the TML and CML values are about 97%. These TML and CML values are similar to the combustion efficiencies shown in Fig. 8. Table 3 also shows that the values of NML are slightly higher than the values of TML and this indicates the fly ash is not ‘fuel-N enriched', i.e. most of the fuel-N has been released proportionally with the combustion of coal particles rather than staying in the fly ash. This indicates that an improvement in unburned carbon in fly ash will not likely overturn the conclusion of Section 3.5 that 'the NOx emission decreases with an increase in combustion pressure'.

$$\text{Total Mass Loss} = \left(1.0 - \frac{\text{Ash}_{\text{coal}}}{\text{Ash}_{\text{fly ash}}}\right) \times \frac{100}{100 - \text{Ash}_{\text{coal}}} \tag{6}$$

$$\text{Carbon Mass Loss} = 1.0 - \frac{\text{Carbon}_{\text{fly ash}}}{\text{Carbon}_{\text{coal}}} \times \frac{\text{Ash}_{\text{coal}}}{\text{Ash}_{\text{fly ash}}} \tag{7}$$

$$\text{Hydrogen Mass Loss} = 1.0 - \frac{\text{Hydrogen}_{\text{fly ash}}}{\text{Hydrogen}_{\text{coal}}} \times \frac{\text{Ash}_{\text{coal}}}{\text{Ash}_{\text{fly ash}}} \tag{8}$$

$$\text{Nitrogen Mass Loss} = 1.0 - \frac{\text{Nitrogen}_{\text{fly ash}}}{\text{Nitrogen}_{\text{coal}}} \times \frac{\text{Ash}_{\text{coal}}}{\text{Ash}_{\text{fly ash}}} \tag{9}$$

Where Ash_{coal} and $\text{Ash}_{\text{fly ash}}$ are the mass fractions of ash in the raw coal and the collected fly ash, respectively. $\text{Carbon}_{\text{coal}}$, $\text{Hydrogen}_{\text{coal}}$ and $\text{Nitrogen}_{\text{coal}}$ are the carbon, hydrogen and nitrogen contents of coal, respectively, whereas $\text{Carbon}_{\text{fly ash}}$, $\text{Hydrogen}_{\text{fly ash}}$ and $\text{Nitrogen}_{\text{fly ash}}$ are the carbon, hydrogen and nitrogen contents of the fly ash, respectively.

The chemical compositions of fly ash (excluding the unburnt carbon/combustibles) under different combustion pressures and atmospheres are presented in Fig. 10 and Fig. 11. As many researchers had indicated that oxy-fuel combustion didn't have a significant effect on the chemical composition of the fly ash [4, 37], the compositions of the fly ash under the same pressure are almost identical. It can be seen from Fig. 10 that the fly ash mainly consists of SiO_2, Al_2O_3 and Fe_2O_3 while the other species only make up small fractions. Agreeing with most of the previous studies [28, 38-39], the mass fraction of the solid-state SO_3 in the fly ash decreases in the order air > oxy-21 > oxy-25 > oxy-30. The reduction is mainly the result of the higher combustion temperature, which increases the release of coal-S to gaseous SO_2 and SO_3, and hence results in lower S retention in the fly ash. Besides, it is observed that the mass fraction of Fe_2O_3 increases as the oxidant is changed from air to oxy-21 atmosphere, and then it decreases with an increase in O_2 concentration in the oxidant. The higher mass fraction of Fe_2O_3 under oxy-21 atmosphere than that under air contradicts with the experimental results from Sheng et al. [4, 40], which showed that more iron melted into the glass silicates and less was oxidized. It is believed that the differences in reactors (drop tube furnace and fluidized bed) result in the opposite trend, however, further research is needed to confirm this.

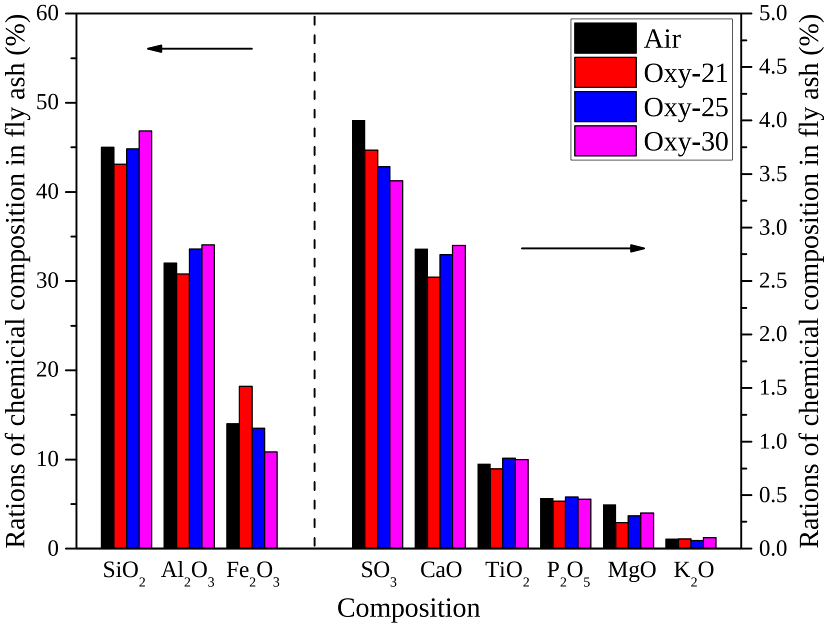

Figure 10. Chemical composition of the fly ash under different combustion atmospheres (0.4 MPa)

Fig. 11 shows the effect of pressure on the chemical compositions of the fly ash. The results indicate that an increase in pressure from 0.1 to 0.4 MPa has no significant impact on the ash composition, except for the slight reductions in SO_3 (solid-state) and CaO, which is the result of higher CO_2 concentration and higher combustion temperature. Specifically, the high CO_2 partial pressure inhibits the sulfate formation of alkaline earth metals, and the higher combustion temperature increases the release of coal-S to gaseous SO_2 and SO_3. Till now, there are only a few reports about pressurized oxy-coal combustion, and none of them presents the result of ash composition. Previous experiments [17-18] conducted in pressurized thermo-gravimetric analyzer showed that the reaction pressure affected the transformations of minerals in the fly ash due to the variations of the ignition mechanism under different pressures. However, the critical pressure for the ignition changed from heterogeneous mode to homogeneous mode was over 1 MPa which is higher than that the highest pressure investigated in this study.

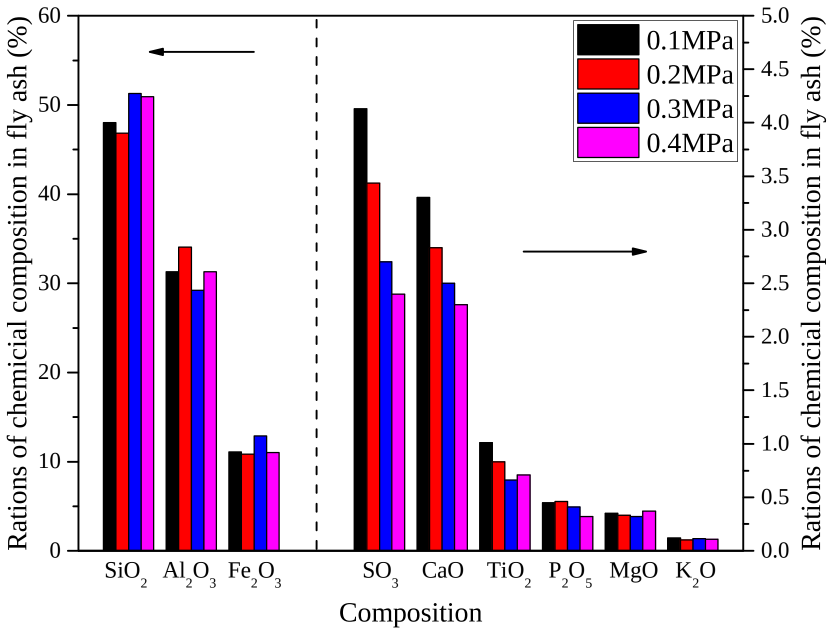

Figure 11. Chemical composition of the fly ash (oxy-30 atmosphere)

4. Conclusions

A series of oxy-coal combustion experiments were carried out under the pressures of 0.1 MPa to 0.4 MPa. The effects of the combustion pressure, combustion atmosphere (air and oxy-fuel) and oxygen concentration on the temperature profile, unburnt carbon in fly ash, combustion efficiency, ash composition and NO_x emissions were systematically investigated. The following conclusions can be drawn from the experimental results:

(1) After the steady oxy-combustion condition is achieved, the CO_2 concentrations in the dry flue gases have exceeded 90% under all the tested pressures, which is beneficial to the CO_2 capture and utilization processes.

(2) The combustion efficiencies under different combustion atmospheres increase

significantly with an increase in pressure from 0.1 MPa to 0.4 MPa due to a lower efficiency loss resulted from unburnt carbon/combustibles in fly ash.

(3) The switch from air to oxy-fuel combustion environment results in a pronounced increase in CO emissions, and an increase in combustion pressure or O_2 concentration in the oxidant can reduce CO emissions effectively.

(4) The NO_x emission decreases with combustion pressure within the investigated range of 0.1 MPa to 0.2 MPa, and the decrease is mainly caused by an increase in pressure. A further decrease of NO_x emission is observed when the pressure increases from 0.2 MPa to 0.4 MPa, however, the decrease is believed to be due to the combined effects of an increase in pressure and a reduction in excess oxygen resulted from better carbon burnout at higher pressures.

(5) The combustion pressure and atmosphere has no significant impact on the chemical composition of fly ash.

The experimental results have shown that the oxy-fuel combustion in a fluidized bed can be operated under high pressures and can achieve a high CO_2 concentration (> 90 vol%) in the dry flue gas at the same time. Besides, the results have shown the advantages of pressurized oxy-fuel combustion on combustion efficiency and NO_x emissions. In agreement with the positive analysis results of previous studies, POFC is experimentally proved by this study to be a practical and effective CO_2 capture technology.

Acknowledgement

Funding: This work was supported by National Key R&D Program of China (2016YFB0600802), National Natural Science Foundation of China (Key Program, 51736002) and Scientific Research Foundation of Graduate School of Southeast University (YJBB1810).

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Table 1. Ultimate analysis and proximate analysis of coal sample

Sample	Ultimate analysis (%)					Proximate analysis (%)			
	C_{ad}*	H_{ad}	O_{ad}	N_{ad}	S_{ad}	FC_{ad}	V_{ad}	A_{ad}	M_{ad}
lignite	**65.83**	**3.01**	**5.68**	**1.07**	**2.01**	**61.8**	**15.8**	**19.1**	**3.3**

*ad—air dried

Table 2. Operating parameters and average dry flue gas compositions at steady state for different conditions

No	Pressure (MPa)	O_2 in (vol %)	CO_2 in (vol %)	Fuel input (kg/h)	Total gas flow (NM^3/h)*	Superficial gas velocity (m/s)**	β	T1 (°C)	O_2 out (vol %)	CO_2 out (vol %)	CO (vol %)	NO_x (ppm)
1	0.1	Air	Air	0.99	7.1	1.61	1.10	850±4	4.10±0.4	15.7±0.5	0.12±0.02	751±45
2	0.1	21	79	0.99	7.1	1.53	1.10	793±8	4.94±0.6	93.2±0.7	0.57±0.04	390±34
3	0.1	25	75	0.99	6.0	1.33	1.10	820±6	3.72±0.4	94.1±0.6	0.52±0.03	736±43
4	0.1	30	70	0.99	5.0	1.14	1.10	857±5	4.08±0.3	94.5±0.5	0.55±0.03	937±37
5	0.2	Air	Air	2.00	14.2	1.61	1.09	852±4	3.20±0.4	16.4±0.5	0.10±0.03	648±38
6	0.2	21	79	2.00	14.2	1.55	1.09	806±5	4.31±0.5	93.8±0.6	0.39±0.04	543±41
7	0.2	25	75	2.00	12.0	1.35	1.09	836±4	3.76±0.4	94.5±0.4	0.32±0.03	703±34
8	0.2	30	70	2.00	10.0	1.16	1.09	869±6	2.13±0.5	96.9±0.4	0.33±0.04	878±36
9	0.3	Air	Air	2.00	14.2	1.08	1.09	857±6	2.78±0.3	16.7±0.5	0.09±0.02	593±31
10	0.3	21	79	2.00	14.2	1.05	1.09	820±5	3.84±0.5	94.2±0.6	0.17±0.03	521±19
11	0.3	25	75	2.00	12.0	0.90	1.09	845±4	2.59±0.4	95.8±0.7	0.18±0.02	641±23
12	0.3	30	70	2.00	10.0	0.78	1.09	877±4	1.56±0.6	97.1±0.5	0.48±0.04	799±34
13	0.4	Air	Air	2.00	14.2	0.81	1.09	863±6	3.15±0.4	16.4±0.6	0.04±0.01	518±29
14	0.4	21	79	2.00	14.2	0.79	1.09	825±5	1.41±0.5	96.7±0.5	0.26±0.03	502±17
15	0.4	25	75	2.00	12.0	0.68	1.09	850±4	0.82±0.4	97.6±0.4	0.44±0.02	602±37
16	0.4	30	70	2.00	10.0	0.58	1.09	881±5	0.95±0.3	97.3±0.5	0.42±0.03	744±30

*Standard condition (0 °C, 1 atm)

** Superficial gas velocities were calculated based on the measured bed zone temperature T1

Table 3: Analysis of fly ash and the estimated total mass loss and elemental loss

Pressure (MPa)	Atmosphere	Unburnt combustibles (%)	C (%)	H (%)	N (%)	TML (%)	CML (%)	HML (%)	NML (%)
0.1	Air	31.23±0.3	29.01	0.83	0.17	89.28	87.76	92.34	95.59
0.1	Oxy-30	29.49±0.5	28.77	0.68	0.19	90.13	88.16	93.88	95.19
0.4	Air	11.12±0.6	11.47	0.39	0.14	97.05	96.25	97.21	97.19
0.4	Oxy-30	10.93±0.4	10.42	0.27	0.10	97.10	96.28	98.08	98.00