

Article

Study on the emission characteristics of nitrogen oxides with coal combustion in pressurized fluidized bed☆

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ABSTRACT

Nitrogen oxides are one of the most significant pollution sources during coal combustion. This experimental study was conducted in a 15 kW_{th} lab-scale pressurized fluidized bed (inner diameter = 81–100 mm, $H = 2100$ mm) firing with bituminous coals. The effects of operating parameters, including bed temperature (800 °C–900 °C), operating pressure (0.1–0.4 MPa), excess air level (16%–30%) and flow pattern on NO_x and N₂O emissions were systematically studied during the tests. During each test the interaction effects of all the operating parameters were properly controlled. The results show that most operating parameters have an opposite effect on NO_x and N₂O emissions, and the N₂O emissions mainly depend on the bed temperature. Increasing the operating pressure can significantly suppress the fuel-N conversion to NO_x but enhance its conversion to N₂O. With the rise of the excess air level and fluidization number, NO_x emissions grow distinctly while N₂O emissions remain almost unchanged. Total nitrogen oxide emissions increase with the bed temperature while decrease with the operating pressure.

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1. Introduction

Pressurized fluidized bed combustion (PFBC) has been proved as a highly clean and efficient power generation technology [1–4]. Pressurized fluidized bed is the core of the second generation pressurized fluidized bed combustion combined cycle (2R PFBC-CC) [5] and integrated gasification combined cycle (IGCC) [6], which is one of the most promising combustion technologies. Compared with atmospheric fluidized combustion (AFBC), PFBC has higher oxygen partial pressure, so the reaction rates are expected to increase if the reaction takes place under kinetically controlled conditions. Therefore, the combustor vessel has a small plan area per unit output [7]. What's more, due to the higher carbon load in the bed and lower fluidizing velocity, PFBC can achieve lower NO_x reduction in the dense bed compared with that in AFBC [8,9].

Nitrogen oxide (NO_x), which mainly consists of nitric oxide (NO) and nitric dioxide (NO₂), is one of the most significant pollutants produced by thermal power plants. NO is the main component (generally over 90% [10]) of the NO_x in the tail flue gas, and the majority of NO will convert to NO₂ in the air [11,12], which is the main cause of nitric acid rain. Emission of Nitrous oxide (N₂O) has attracted great attention because it enhances the greenhouse effect and the destruction of stratospheric ozone layer. Because of the much lower temperature in fluidized

bed combustion, N₂O emission in fluidized bed is relatively higher compared with conventional pulverized coal boiler, and the N₂O concentration is even higher than the NO_x concentration in some fluidized beds [13,14].

The formation and control of NO_x and N₂O in the pressurized fluidized bed have been a focus of attention. The effects of some operation parameters (bed temperature, operating pressure, excess air level) on the NO_x and N₂O emissions in PFBC have been studied by researchers over the past two decades. The effects of the temperature on the N₂O and NO_x emissions in both AFBC [13–15] and PFBC [16–18] are negatively correlated. The N₂O emissions decrease while the NO_x emissions increase with the increase of temperature. Increasing operating pressure contributes to a reduction of NO_x emissions in the pressurized fluidized bed and further NO_x decrease can be obtained by means of staged combustion and/or ammonia injection to comply with further NO_x emissions. It has been shown that PFBC facility can achieve the NO reduction of 75% to 85% with NH₃ injection and/or air staging [18]. The effect of operating pressure on N₂O emissions was studied in a lab-scale PFBC by [19], and they found that the N₂O emissions in PFBC exerted a maximum when the operating pressures are in the range of 0.2–0.5 MPa. Another study conducted in a 130 kW PFBC test rig showed that N₂O emissions were slightly reduced from 0.6 to 0.9 MPa [17]. However, it has been found that compared with the operating pressure, oxygen partial pressure has opposite influence on the conversion of fuel-N to NO_x, while both operating pressure and oxygen partial pressure cause little effects on the fuel-N conversion to N₂O [20]. In both AFBC and PFBC, the excess air level plays an important role in the NO_x

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emissions, increasing the excess air level in fluidized bed combustor will lead to a significant rise of NO_x emissions [21–23].

At present, according to the author's knowledge, the relationship between nitrogen oxide emissions and fluidization number in PFBC has rarely been reported. The flow pattern and superficial gas velocity change dramatically with the fluidization number, which may have an impact on NO_x and N_2O emissions. An experiment conducted in an atmospheric fluidized bed showed a positive correlation between the N_2O emissions and superficial velocity [14]. It still needs further study on the influence of the fluidization number under pressurized conditions.

In this study, a kind of typical Chinese bituminous coal was used to study the effects of operating conditions on the emissions of NO_x and N_2O systematically. Operating parameters, including bed temperature, operating pressure, excess air level and fluidization number, are taken into consideration with a 15 kW_{th} lab-scale pressurized fluidized bed combustor. The goal of the study is to find out the rule about the emission characteristics of NO_x and N_2O during the combustion process in a pressurized fluidized bed.

2. Experimental

2.1. Experimental setup

The investigation was performed on a 15 kW_{th} lab-scale fluidized bed combustor, as is shown in Fig. 1. The system consists of a gas distribution system, a coal feeding system, a bubbling fluidized bed reactor, a dust removal system, a water-cooled refrigeration system and an automatic control system. The combustor is made of a stainless-steel tube with high temperature and pressure resistance. The combustor is 2600 mm in height with three sections: dense zone of 81 mm i.d. and 1000 mm height, transition zone of 600 mm height and dilute zone of 100 mm i.d. and 1000 mm height. A water-cooled

heat extraction pipe in the dense zone of combustor is used to control the bed temperature. What's more, the flow rate of the cooling water inside the pipe can be adjusted to control the heat transfer and hence the bed temperature.

The air flow rate is adjusted by a mass flow meter. During all the tests, little flows of compressed air were fed into the coal hopper and the feeding pipe to avoid backfire and prevented the sand particles from entering the feeding pipe. An electric air preheater and four external electric half-cylindrical heating elements are installed to pre-heat the combustion air as well as the combustor during the start-up of each test. A star feeder is set up with an inverter to control the feeder motor frequency for controllable and stable coal feed rate under elevated pressures. After de-dusted by an efficient cyclone and cooled by the condenser tube, the flue gas is exhausted to the vent-pipe and some of which is extracted to be analyzed by the online gas analyzer continuously. O_2 , CO_2 , CO , NO , NO_2 and N_2O concentrations are measured by a Madur online continuous gas analyzer (Madur, GA-21plus). Pressure differentials and temperatures across the combustor are measured by pressure gauges and K-type thermocouples respectively. The combustor is equipped with a computer system to display and record all the measured process data, including pressure differentials, temperatures and gas composition.

2.2. Experimental conditions

Before the experiment, silica sand was introduced into the combustor and then heated to 600–700 °C by an air preheater and electrical heating elements. After that, a certain amount of coal and air (as shown in Table 1) was fed into the combustion zone continuously and then the electrical elements were turned off. After the introduction of coal, the fluidized bed temperature was controlled in the ranges of 800–900 °C. The total pressure inside the combustor was maintained

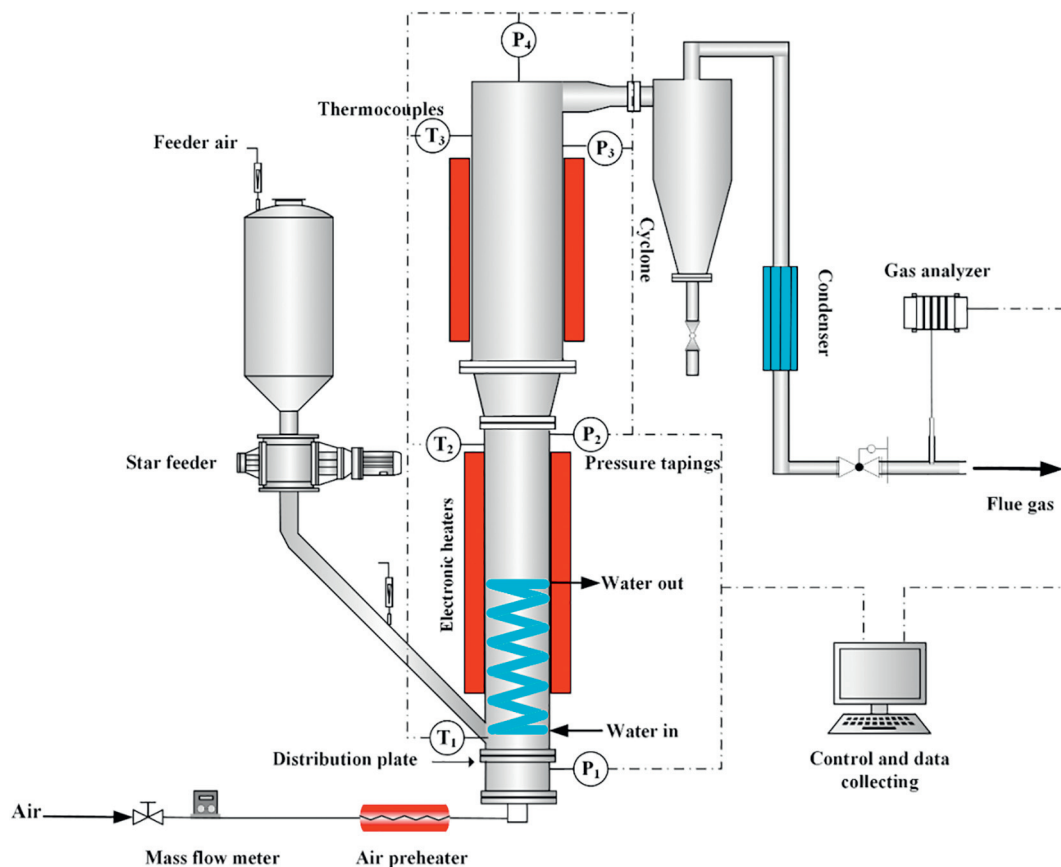


Fig. 1. Schematic representation of the experimental unit for PFBC.

Table 1

List of the main experimental conditions

	Total air flow ^① /m ³ ·h ⁻¹	Coal feed rate/kg·h ⁻¹	Temperature inside bed/°C	O ₂ outlet concentration/vol%	Superficial gas velocity (<i>u_g</i>) ^② /m·s ⁻¹	Excess air level/%	Density of bed materials/kg·m ⁻³	Static height of bed materials/mm	Average diameter of bed materials/mm	Cooling water flow rate/L·min ⁻¹
0.1 MPa	6.5 ± 1	0.9 ± 0.1	850 ± 10	4 ± 1	1.28–1.92	16–32	2400	200	1.1	0
0.2 MPa	14 ± 3	2 ± 0.2	850 ± 10	4 ± 1	1.28–1.92	16–32	2400	200	1.1	2 ± 1
0.3 MPa	14 ± 3	2 ± 0.2	850 ± 10	4 ± 1	0.85–1.28	16–32	2400	200	1.1	2 ± 1
0.4 MPa	14 ± 3	2 ± 0.2	850 ± 10	4 ± 1	0.64–0.96	16–32	2400	200	1.1	2 ± 1

^① Measured at room temperature (around 20 °C) and 1 MPa.^② Calculated at 850 °C.

from 0.1 MPa to 0.4 MPa. The exhaust gas from the combustion process was cooled, depressed and then introduced into the gas analyzer. In this study, parameters including temperature, pressure, excess air level and fluidization number were adjusted to different values for investigating their effects on NO_x and N₂O emissions. All of the data, including pressure, temperature and gaseous emissions were collected online and used in this paper.

Fig. 2 presents the temperature profiles and the gas product (O₂, NO_x and N₂O) distribution at the outlet of the combustor from a typical experiment. All the tests were started with the atmospheric air combustion. After stabilization, the combustion environment was converted from atmospheric to pressurized combustions with continuous coal feeding.

2.3. Fuel and bed material

Table 2 shows the ultimate and proximate analysis of the typical Chinese bituminous coal used in the experiment. The particle size of bituminous coal ranges from 0.55 to 1.4 mm (true density: 1200 kg·m⁻³). Silica sand (particle size range: 0.38–1.7 mm, mean particle size: 1.1 mm, true density: 2400 kg·m⁻³) was used as the bed material. Table 3 shows the chemical composition from the bituminous coal ash.

3. Results and Discussion

3.1. Effect of temperature on NO_x and N₂O emissions

Fig. 3 illustrates the impact of bed temperature on NO_x and N₂O emissions under 0.2 MPa and 0.4 MPa respectively. The bed

temperature is controlled by adjusting the star feeder and the water-cooling device. The overall oxygen concentration at the outlet remained 3.5%–4% in this test. The results are expressed by the amount of emissions per energy unit (mg·MJ⁻¹). This kind of emission unit is used for better comparing the conditions of different volumetric flow rates and fuel input. The NO_x emissions increase steadily with increasing bed temperature. As the bed temperature increases, firstly, the combustion efficiency increases, more char-N is released from the N site in the coal matrix to form NO_x precursors. Secondly, more active O and OH radicals are produced from molecular O₂, and the precursors are easier to be oxidized to NO_x. Thirdly, CO and char concentrations in the combustor decrease with the increment of bed temperature, and both the homogeneous and heterogeneous reduction reactions of NO are suppressed [25]:



The N₂O emissions are strongly affected by the bed temperature in PFBC. N₂O emissions decrease fast as the bed temperature rises up. Similar results were also observed by [26]. Because of the relatively low combustion temperature (800 °C–900 °C) in PFBC, the oxidation of N₂ in the air can be neglected, so the nitrogen in N₂O is mainly from the fuel-N. HCN and NH₃ are the precursors of both volatile-N and char-N conversion into the nitrogen oxide. The homogeneous oxidation of HCN plays the most important role in the mechanism of homogeneous formation of N₂O [27],

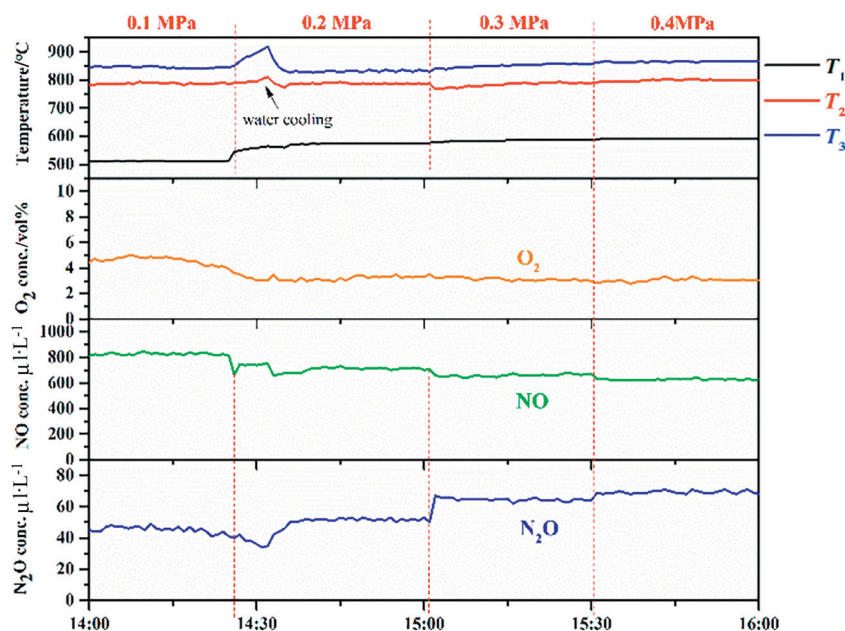
**Fig. 2.** Emissions of NO_x and N₂O at flexible change of the operating pressures.

Table 2
Proximate and ultimate analysis of the bituminous coal samples

Proximate analysis (dry basis)/wt%	
Fixed carbon	61.80
Ash	19.10
Volatile matter	15.82
Moisture	3.30
Calorific value/MJ·kg ⁻¹ [24]	25.04
Ultimate analysis (dry basis)/wt%	
Carbon	65.83
Hydrogen	3.01
Nitrogen	1.07
Sulfur	2.01
Oxygen	5.68

the main elementary reactions of the conversion are as follows [28]:



As the temperature increases, more O and OH radicals were produced, the key intermediate product NCO is easier to react with these radicals, which reduces the effect of homogeneous formation of N₂O [29]. Meanwhile, the concentration of H radical increases as the temperature increases, the N₂O is reduced by the following reaction, which has been proved to be the fastest homogeneous N₂O reduction reaction [28,30,31]:



Despite the decline of N₂O emissions, total nitrogen oxide emissions increase with bed temperature under pressurized conditions.

3.2. Effect of pressure on NO_x and N₂O emissions

Because of the relatively low combustion temperature in the fluidized bed, both prompt-NO_x and thermal-NO_x can be neglected, the NO_x emissions are mainly originated from the fuel-N conversion [32]. In order to better investigate the source of nitrogen of NO_x and N₂O,

Table 3
Chemical composition of ash^①

Ash content/wt%	
SiO ₂	41.66
Al ₂ O ₃	35.35
Fe ₂ O ₃	16.22
MnO	0.01
CaO	1.78
MgO	0.58
K ₂ O	0.13
Na ₂ O	0.11
P ₂ O ₅	0.20
TiO ₂	1.37
SO ₃	1.74
ZrO ₂	0.20
SrO	0.13

^① The test was in accordance with Chinese standard DL/T 1073-2016 "Standard test method for major and minor elements in coal ash".

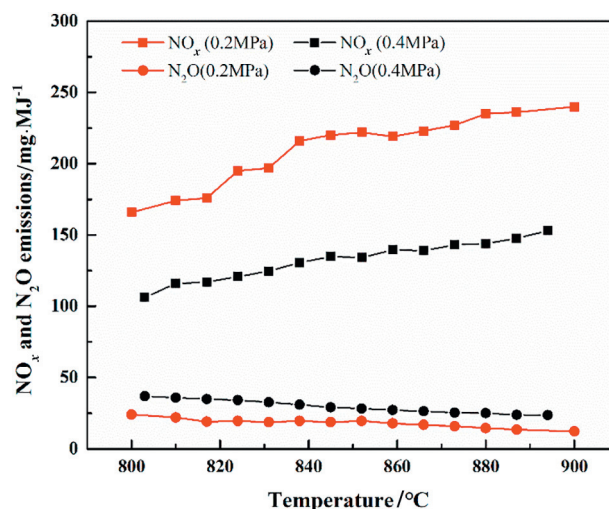


Fig. 3. Effect of temperature on NO_x and N₂O emissions under 0.2 MPa and 0.4 MPa.

two paths of conversion from fuel-N to NO_x and N₂O are calculated as follows:

$$\text{Fuel-N} \rightarrow \text{NO}_x \text{ conversion} = \frac{M_N \int_0^t Q[\text{NO}_x] dt}{V_m m_c x_N}$$

$$\text{Fuel-N} \rightarrow \text{N}_2\text{O} \text{ conversion} = \frac{2M_N \int_0^t Q[\text{N}_2\text{O}] dt}{V_m m_c x_N}$$

where M_N is the atomic mass of nitrogen in g·mol⁻¹, and Q is the gas flow rate. $[\text{NO}_x]$ and $[\text{N}_2\text{O}]$ are the NO_x and N₂O concentrations in μL·L⁻¹. V_m is the mole volume under normal conditions (22.4 L·mol⁻¹), m_c is the mass of fuel input in g, and x_N is the mass fraction of nitrogen in the fuel in wt%.

The effect of operating pressure on NO_x and N₂O emissions in PFBC is shown in Fig. 4 where the bed temperature is in the range of 840 °C–860 °C. For further investigations, we compared the conversion rate of fuel-N to NO_x and N₂O of our experimental results with the calculated values modeled by AHO [33] of pressurized pulverized coal combustion in an entrained flow reactor, which is shown in Figs. 5 and 6.

As is mentioned in the Introduction, an increase in pressure can significantly reduce the NO emission. Fig. 5 shows that the reduction is more remarkable when the pressure increases from 0.1 MPa to

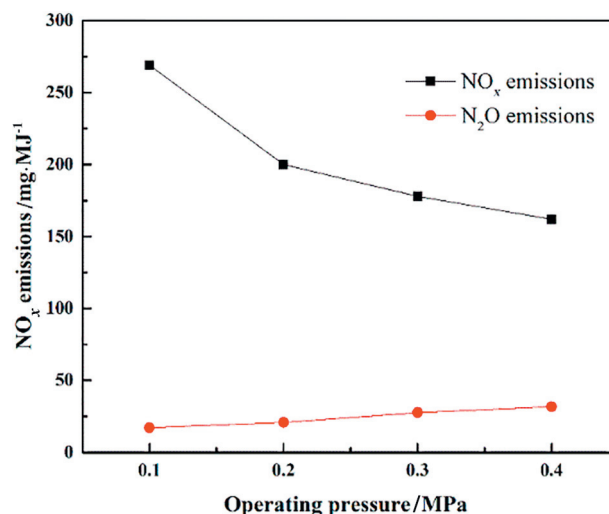


Fig. 4. Effect of pressure on NO_x emissions, $T \approx 850$ °C.

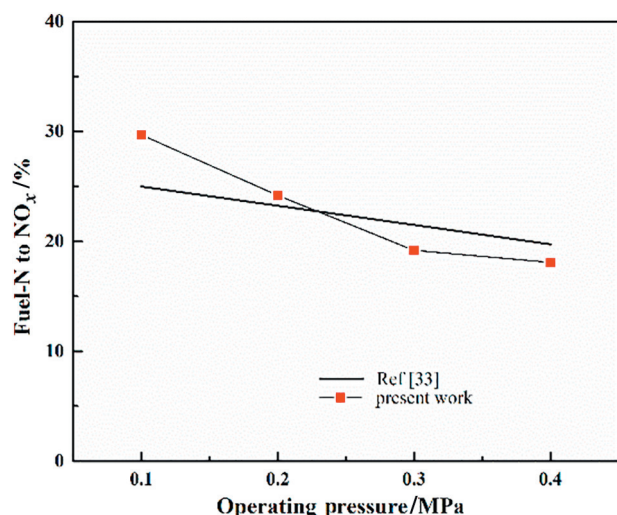


Fig. 5. Comparison of calculated values (by AHO) with experimental results for fuel-N to NO_x of different pressures.

0.2 MPa, then it declines steadily as the pressure continues to increase. Similar tendency is shown about the conversion rate of fuel-N to NO from 0.1 MPa to 0.4 MPa in Fig. 6, and the experimental results match well with the calculated values. The NO partial pressure and CO partial pressure grow with the increase of total pressure, which strengthens CO reducing action for NO. Moreover, the rise of pressure increases the residence time for the diffusion of NO throughout the char particles and further reduces the amount of NO in the char particles consequently. In summary, the lower NO_x emission can be explained by the creation of preferential conditions for the homogeneous and heterogeneous reduction reactions shown in Eqs. (1) and (2).

As it can be observed from Fig. 5, the increase of bed pressure causes more N₂O emission (from 17 mg·MJ⁻¹ to 32 mg·MJ⁻¹). The similar dependence of conversion rate of fuel-N to N₂O on operating pressure is shown in Fig. 7. However, the calculated conversion rate from fuel-N to N₂O (from 4% to 13%) grows significantly than that of our experimental results (from 3.5% to 6%). It can be explained by the different conditions between the pressurized entrained flow reactor and the fluidized bed when considering the particle size and particle temperature, which have been proved to play a significant role in the combustion kinetics and nitrogen chemistry [34,35]. The resistance of volatiles diffusing in the coal particles accelerates with the increase of bed

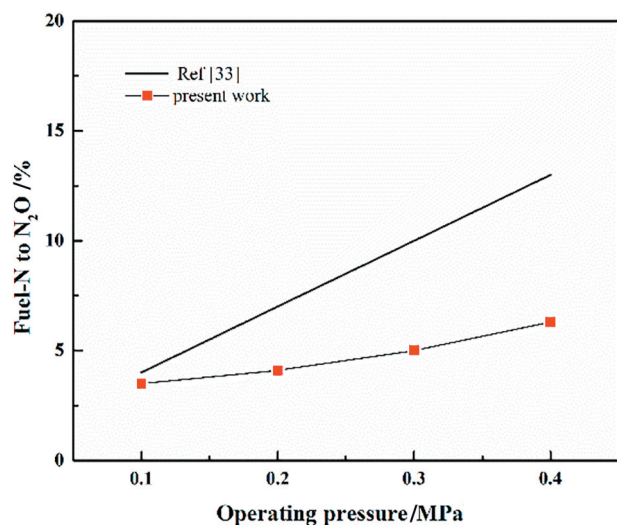


Fig. 6. Comparison of calculated values (by AHO) with experimental results for fuel-N to N₂O of different pressures.

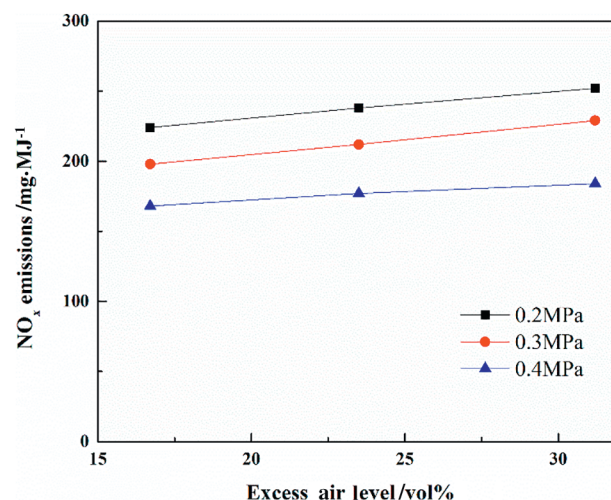


Fig. 7. Effect of excess air level on NO_x emission, $T \approx 850^\circ\text{C}$.

pressure, which results in a decrease in the volatile release [36]. Therefore, more fuel-N are converted to char-N, promoting the heterogeneous generation of N₂O [37,38]:



All of these mentioned above lead to higher values for total N₂O emissions.

Due to the dominant role of NO_x emissions, total nitrogen oxide emissions show a decline with the operating pressure.

3.3. Effect of excess air level on NO_x and N₂O emissions

In this work, the excess air level can be changed by adjusting the total air flow, which is shown in Table 1. The effect of excess air level on the NO_x emissions is shown in Fig. 7. The following expression is used for more detailed and direct display of the excess air level:

$$\text{Excess air level} = \left(\frac{21\%}{21\% - [\text{O}_2]} - 1 \right) \times 100\%$$

where [O₂] is the value of the outlet oxygen concentration in vol%. As the excess air level increases from 16% to 32%, the NO_x emissions for all the pressures have an obvious increase, while the dependence of NO_x emissions is weaker under higher operating pressure. The reason is that as the excess air level increases, the NO formation also increases due to the oxidation of nitrogen species, such as HCN and NH₃. What's more, the surface temperature of the burning coal particles is relatively lower in less O₂ concentration atmosphere [35,39]. At the same time, both the volume and the surface area of char available for NO reduction reactions decrease, and we observed a lower CO concentration in the flue gas with the increase of O₂ concentration. Consequently, both the homogeneous and heterogeneous reductions of NO are suppressed, which leads to an increase of NO_x emissions.

As is shown in Fig. 8, the N₂O emissions remain almost constant or increase slightly with the excess air level at different pressures. Redick [40] investigated the pollutant formation during coal combustion in a fluidized bed test rig and found that the formation of the H radicals of the H₂/O₂ mechanism is significantly suppressed by the absence of oxygen. Therefore, the concentration of H radicals declines with the excess air level, which weakens the homogeneous destruction of N₂O. The relatively low excess air level leads to low concentrations of O and OH radicals, which decreases the NCO formation reactions (3), (4) and (5). As a result, the drop of NCO concentrations moderates the

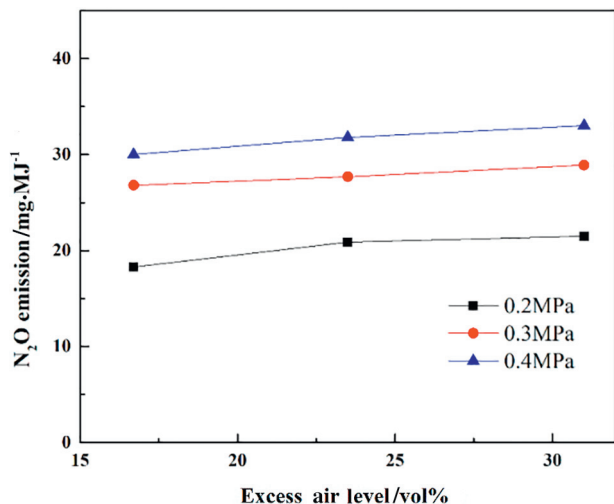


Fig. 8. Effect of excess air level on N₂O emission, $T \approx 850^\circ\text{C}$.

formation reactions of N₂O. This explains a slight increase of N₂O emissions with the excess air level.

3.4. Effect of flow pattern on NO_x and N₂O emissions

In this work, the flow pattern was mainly changed by controlling the fluidization number. Excess air level was kept constant during all the tests. The critical fluidization velocity is calculated by simultaneous equations of Ergun [41], and Wen and Yu [42]:

$$d_p u_{mf} \rho_g / \mu = \left[(33.7)^2 + 0.0408 d_p^3 \rho_g (\rho_s - \rho_g) g / \mu^2 \right]^{1/2} - 33.7$$

Fig. 9 shows that both NO_x and N₂O emissions increase with the increasing fluidization number in PFBC, and the growth of NO emissions (from 216 mg·MJ⁻¹ to 264 mg·MJ⁻¹) far exceeds that of N₂O emissions (from 33.4 mg·MJ⁻¹ to 38.9 mg·MJ⁻¹). The result of N₂O emissions is similar with the experiment conducted in the atmospheric fluidized bed combustion by [14]. Adding the fluidization number equals to an increase in the superficial gas velocity in the bed. As is shown in Table 4, the gas residence time is corresponding to the superficial gas velocity. When the gas residence time decreases, there is less time for the NO

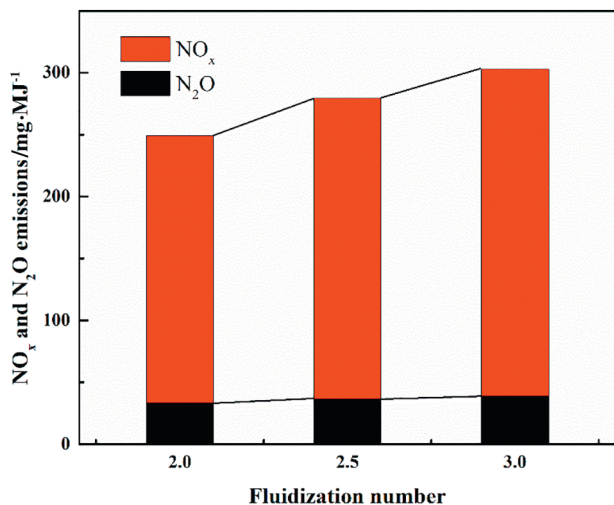


Fig. 9. Effect of fluidization number on N₂O emission, $T \approx 850^\circ\text{C}$, $P = 0.4\text{ MPa}$.

Table 4

Superficial gas velocity corresponding to the residence time in different fluidization numbers

Fluidization number	Superficial velocity/m·s ⁻¹	Gas residence time/s
2.00	0.64	3.91
2.50	0.80	3.25
3.00	0.96	2.60

and N₂O to react with the char particles, which weakens the heterogeneous reaction of NO_x (as shown in Eq. (2)) and N₂O on the char surfaces [37]:



Furthermore, due to the same oxygen concentration in the air, more oxygen is introduced to the bed at higher superficial gas velocity. As a result, the char combustion is enhanced, accelerating the heterogeneous formation of NO_x and N₂O from char-N. As is mentioned above, more fuel-N will be converted to char-N under elevated pressure, and NO_x is mostly formed by heterogeneous oxidation of char-N during char combustion, while the N₂O is mainly formed by the homogeneous reaction of HCN [43,44]. This explains why NO_x emissions have a larger increment with higher fluidization number.

4. Conclusions

This paper presents the results of a typical Chinese bituminous coal tested in a 15 kW·h⁻¹ lab-scale pressurized fluidized bed combustor. The effects of bed temperature, operating pressure, excess air level and fluidization number on NO_x and N₂O emissions were investigated systematically. Based on the cited literature and obtained experimental results, the following conclusions can be drawn:

- (1) The bed temperature is quite an important operating variable in NO_x emissions and the N₂O emissions mainly depend on the bed temperature. An increase of NO_x emissions was observed when the bed temperature rises from 800 °C to 900 °C, while N₂O emissions decrease rapidly when the bed temperature is over 800 °C and reaches a relatively low level around 900 °C.
- (2) A drastic decrease of NO_x emissions can be achieved for bituminous coal under pressurized conditions when the operating pressure increases from 0.1 MPa to 0.4 MPa. On the contrary, elevating operating pressure from 0.1 MPa to 0.4 MPa enhances the fuel-N conversion to N₂O.
- (3) Excess air level is a dominant operating variable on NO_x emissions because of its influence on CO concentration and surface temperature of coal particles. However, excess air level has little effect on the N₂O emissions, only a slight increase of N₂O yield was observed with the outlet O₂ concentration.
- (4) Influence of fluidization number on NO_x emissions under elevated pressures cannot be neglected. The increase of fluidization number reduces the gas residence time, which weakens the heterogeneous reduction of NO and hence enhances the NO_x emissions, while the N₂O emissions only increase slightly with the rise of fluidization number.

Nomenclature

d_p	particle diameter, m
H	height, m
i.d.	inner diameter, m
t	time, s
u_g	superficial gas velocity, m·s ⁻¹
u_{mf}	critical fluidization velocity, m·s ⁻¹
μ	gas viscosity, Pa·s
ρ_p	particle density, kg·m ⁻³
ρ_g	gas density, kg·m ⁻³

References

- [1] A.J. Minchener, Fluidized bed combustion systems for power generation and other industrial applications, *Proc. Inst. Mech. Eng. A J. Power Energy* 217 (2003) 9–18.
- [2] A.S. Kudjoi, Combustion of gasification residues in a pressurized fluidized-bed, *Fuel Energy Abstr.* 38 (1997) 107.
- [3] H. Sasatsu, N. Misawa, M. Shimizu, R. Abe, Predicting the pressure drop across hot gas filter (CFT) installed in a commercial size PFBC system, *Powder Technol.* 118 (2001) 58–67.
- [4] S. Sakuno, T. Shimizu, N. Misawa, H. Ueda, H. Sasatsu, H. Gotou, NO_x emission from a 71 MWe pressurized fluidized bed combustor, *Fuel* 81 (2002) 373–379.
- [5] R. Xiao, B.S. Jin, Y.Q. Xiong, Z.P. Zhong, Y.F. Duan, X.P. Chen, H.C. Zhou, M.Y. Zhang, Research and development of the pilot-scale second generation pressurized fluidized bed combustion combined cycle technology, *J. Eng. Thermophys.* 27 (2006) 537–539.
- [6] T. Wang, 1 — An overview of IGCC systems, Integrated Gasification Combined Cycle (IGCC) Technologies, Woodhead Publishing, Sawton, United Kingdom 2017, pp. 1–80.
- [7] T. Shimizu, 15 — Pressurized fluidized bed combustion (PFBC) A2, in: Fabrizio Scala (Ed.), Fluidized Bed Technologies for Near-Zero Emission Combustion and Gasification, Woodhead Publishing, Sawton, United Kingdom 2013, pp. 669–700.
- [8] A. Jensen, J.E. Johnsson, Modelling of NO_x emissions from pressurized fluidized bed combustion — A parameter study, *Chem. Eng. Sci.* 52 (1997) 1715–1731.
- [9] J. Li, J.A.M. Kuipers, Effect of pressure on gas–solid flow behavior in dense gas-fluidized beds: A discrete particle simulation study, *Powder Technol.* 127 (2002) 173–184.
- [10] P. Basu, S.A. Fraser, Circulating Fluidized Bed Boilers, Springer, New York, 1991 pp. 229–253.
- [11] M. Trainer, E.Y. Hsie, S.A. McKeen, R. Tallamraju, D.D. Parrish, F.C. Fehsenfeld, S.C. Liu, Impact of natural hydrocarbons on hydroxyl and peroxy radicals at a remote site, *J. Geophys. Res. Atmos.* 92 (2012) 11879–11894.
- [12] D.D. Parrish, M. Trainer, E.J. Williams, D.W. Fahey, G. Hübner, C.S. Eubank, S.C. Liu, P.C. Murphy, D.L. Albritton, F.C. Fehsenfeld, Measurements of the NO_x–O₃ photostationary state at Niwot Ridge, Colorado, *J. Geophys. Res. Atmos.* 91 (2012) 5361–5370.
- [13] B. Leckner, Fluidized bed combustion: Mixing and pollutant limitation, *Prog. Energy Combust. Sci.* 24 (1998) 31–61.
- [14] L. Arnesto, H. Boerrigter, A. Bahillo, J. Otero, N₂O emissions from fluidised bed combustion. The effect of fuel characteristics and operating conditions, *Fuel* 82 (2003) 1845–1850.
- [15] B. Valentim, M.J. Lemos De Sousa, P. Abelha, D. Boavida, I. Gulyurtlu, Combustion studies in a fluidised bed — The link between temperature, NO_x and N₂O formation, char morphology and coal type, *Int. J. Coal Geol.* 67 (2006) 191–201.
- [16] K. Svoboda, M. Pohorelý, Influence of operating conditions and coal properties on NO_x and N₂O emissions in pressurized fluidized bed combustion of subbituminous coals, *Fuel* 83 (2004) 1095–1103.
- [17] Y. Lu, A. Jahkola, I. Hippien, J. Jalovaara, The emissions and control of NO_x and N₂O in pressurized fluidized bed combustion, *Fuel* 71 (1992) 693–699.
- [18] Y. Lu, I. Hippien, A. Jahkola, Control of NO_x and N₂O in pressurized fluidized-bed combustion, *Fuel* 74 (1995) 317–322.
- [19] K. Svoboda, M. Pohorelý, M. Hartman, Effects of operating conditions and dusty fuel on the NO_x, N₂O, and CO emissions in PFB co-combustion of coal and wood, *Energy Fuel* 17 (2003) 1091–1099.
- [20] Y. Lu, Laboratory studies on devolatilization and char oxidation under PFBC conditions. 2. Fuel nitrogen conversion to nitrogen oxides, *Energy Fuel* 10 (1996) 357–363.
- [21] L.A.C. Tarelho, M.A.A. Matos, F.J.M.A. Pereira, Influence of limestone addition on the behaviour of NO and N₂O during fluidised bed coal combustion, *Fuel* 85 (2006) 967–977.
- [22] L.F. de Diego, C.A. Londono, X.S. Wang, B.M. Gibbs, Influence of operating parameters on NO_x and N₂O axial profiles in a circulating fluidized bed combustor, *Fuel* 75 (1996) 971–978.
- [23] J. Andries, J.G.M. Becht, P.D.J. Hoppelsteyn, Pressurized fluidized bed combustion and gasification of coal using flue gas recirculation and oxygen injection, *Energy Convers. Manag.* 38 (1997) 117–122.
- [24] S.A. Channiwala, P.P. Parikh, A unified correlation for estimating HHV of solid, liquid and gaseous fuels, *Fuel* 81 (2002) 1051–1063.
- [25] F. Winter, C. Wartha, G. Löffler, H. Hofbauer, The NO and N₂O formation mechanism during devolatilization and char combustion under fluidized-bed conditions, *Symp. Combust.* 26 (1996) 3325–3334.
- [26] R. Abe, H. Sasatsu, T. Harada, N. Misawa, I. Saitou, Prediction of emission gas concentration from pressurized fluidized bed combustion (PFBC) of coal under dynamic operation conditions, *Fuel* 80 (2001) 135–144.
- [27] T. Hulgaard, J.K. Dam, Homogeneous nitrous oxide formation and destruction under combustion conditions, *AIChE J.* 39 (1993) 1342–1354.
- [28] J.C. Kramlich, J.A. Cole, J.M. McCarthy, W.S. Lanier, J.A. McSorley, Mechanisms of nitrous oxide formation in coal flames, *Combust. Flame* 77 (1989) 375–384.
- [29] P. Kilpinen, M. Hupa, Homogeneous N₂O chemistry at fluidized bed combustion conditions: A kinetic modeling study, *Combust. Flame* 85 (1991) 94–104.
- [30] J.P. Hämäläinen, M.J. Aho, Effect of fuel composition on the conversion of volatile solid fuel-N to N₂O and NO, *Fuel* 74 (1995) 1922–1924.
- [31] J.A. Miller, C.T. Bowman, Mechanism and modeling of nitrogen chemistry in combustion, *Prog. Energy Combust. Sci.* 15 (1989) 287–338.
- [32] F. Winter, in: G. Yue, H. Zhang, C. Zhao, Z. Luo (Eds.), Formation and reduction of pollutants in CFBC: From heavy metals, particulates, alkali, NO_x, N₂O, SO_x, HCl, Springer Berlin Heidelberg, Berlin, Heidelberg 2010, pp. 43–48.
- [33] M.J. Aho, K.M. Paakkinen, P.M. Pirkonen, P. Kilpinen, M. Hupa, The effects of pressure, oxygen partial pressure, and temperature on the formation of N₂O, NO, and NO₂ from pulverized coal, *Combust. Flame* 102 (1995) 387–400.
- [34] P. Kilpinen, S. Kallio, J. Kontinen, V. Barišić, Char-nitrogen oxidation under fluidised bed combustion conditions: Single particle studies, *Fuel* 81 (2002) 2349–2362.
- [35] T. Joutsenoja, J. Saastamoinen, M. Aho, R. Hernberg, Effects of pressure and oxygen concentration on the combustion of different coals, *Energy Fuel* 13 (1999) 130–145.
- [36] J. Tomeczek, S. Gil, Volatiles release and porosity evolution during high pressure coal pyrolysis, *Fuel* 82 (2003) 285–292.
- [37] G.G. De Soete, Heterogeneous N₂O and NO formation from bound nitrogen atoms during coal char combustion, *Symp. Combust.* 23 (1991) 1257–1264.
- [38] X. Jiang, X. Huang, J. Liu, X. Han, NO_x emission of fine- and superfine- pulverized coal combustion in O₂/CO₂ atmosphere, *Energy Fuel* 24 (2010) 6307–6313.
- [39] S. Lin, Y. Suzuki, H. Hatano, Effect of pressure on NO_x emission from char particle combustion, *Energy Fuel* 16 (2002) 634–639.
- [40] A. Reidick, H. Kremer, Pollutant formation during coal combustion in a CFB test furnace, *Symp. Combust.* 26 (1996) 3309–3315.
- [41] S. Ergun, A.A. Orning, Fluid flow through randomly packed columns and fluidized beds, *Ind. Eng. Chem.* 41 (1949) 1179–1184.
- [42] C.Y. Wen, Y.H. Yu, A generalized method for predicting the minimum fluidization velocity, *AIChE J.* 12 (1966) 610–612.
- [43] H. Zhou, Y. Huang, G. Mo, Z. Liao, K. Cen, Experimental investigations of the conversion of fuel-N, volatile-N and char-N to NO_x and N₂O during single coal particle fluidized bed combustion, *J. Energy Inst.* 90 (2017) 62–72.
- [44] G. Löffler, D. Andahazy, C. Wartha, F. Winter, H. Hofbauer, NO_x and N₂O formation mechanisms — A detailed chemical kinetic modeling study on a single fuel particle in a laboratory-scale fluidized bed, *J. Energy Resour. Technol.* 123 (2001) 228–235.