Experimental Study of NO\textsubscript{x} Formation in a High-Steam Atmosphere During a Pressurized Oxygen-Fuel Combustion Process

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ABSTRACT: Pressurized oxy-fuel combustion is considered to be one of the most promising carbon capture technologies due to its low energy consumption and high carbon capture rate. Part of the combustion-supporting environment is composed of circulating flue gas, so the concentration of steam in the carrier gas is higher than that of conventional combustion. However, as an important factor in this technology, steam has not been mentioned in the vast majority of studies. In this study, combustion experiments simulating wet flue gas recycling were performed in a pressurized tube furnace to analyze the effects of the steam ratio (0–40%), oxygen concentration (21–50%), and pressure (0.1–0.6 MPa) on the formation of NO\textsubscript{x}. The results show that increased system pressure significantly inhibits NO emissions during the oxy-fuel combustion process. Meanwhile, the increase of the injected steam concentration enriches the various radical pool compositions in the carrier gas, inhibiting the formation of NO and N\textsubscript{2}O. In contrast, the increase of the combustion temperature promotes and inhibits the formation of NO and N\textsubscript{2}O, respectively, during oxy-fuel pressurized combustion. Moreover, elevated oxygen concentration enhances the oxidation of the carrier gas, leading to an increase in NO emissions.

1. INTRODUCTION

Global energy-related CO\textsubscript{2} emissions increased by 1.6% in 2017 after three consecutive years of flattening, and data collected in early 2017 indicate that emissions will continue to grow in the next few years.\textsuperscript{1} This scenario is, therefore, distant from the development trajectory to achieve global environment goals. Meanwhile, the share of electricity, which is increasingly becoming the preferred power resource, in global energy consumption is increasing. Electrification can result in the improvement of air quality; however, if it is to fully release its potential capabilities and achieve climate goals, further steps are needed to achieve a low carbon supply. If these steps are not properly executed, the sources of carbon dioxide emissions may only shift from the terminal sector to upstream.

Among the sources of greenhouse gases, represented by CO\textsubscript{2}, coal-fired power plants are considered the main source of their emission. To alleviate the increasing (and already severe) environmental pressure, researchers have studied many carbon capture and storage (CCS) methods, in which oxy-fuel combustion is one of the most promising ones.\textsuperscript{2} In this process, a mixture of pure oxygen and recycled flue gas (RFG) is used instead of air to balance the temperature inside the burner. The flue gas produced by the oxy-combustion contains a high concentration of carbon dioxide (close to 90% under dry conditions),\textsuperscript{2} thereby facilitating its purification, compression, transportation, and storage afterward. However, pressure changes between the air separation unit (ASU), the combustion furnace, and the compression purification unit (CPU) result in reduced efficiency of these processes.
To reduce pressure loss, pressurized oxy-fuel combustion technology was developed. The process is conducted under high pressure, reducing the energy loss, caused by pressure changes in various parts of the system, when compared with the atmospheric oxy-fuel combustion system. Furthermore, the condensation temperature of the steam in the flue gas, which is conducive to the recovery and utilization of latent heat of vaporization, is also increased.

Although a large number of researchers have conducted extensive and in-depth research on the migration characteristics of nitrogen and NO\textsubscript{x} emissions in oxy-fuel combustion for the past 20 years, the influence of pressure in the system still needs to be explored. The design and construction of the experimental system are difficult due to high-pressure conditions; therefore, in recent years, research has mainly focused on economic analysis and numerical simulation of the system, while only a few involve experimental work. Some scholars studied the effects of pressure on the conversion of NO\textsubscript{x} under traditional conditions and concluded that an increase in pressure will reduce NO\textsubscript{x} emissions. Lasek et al.\textsuperscript{8,9} used a laboratory-scale fluidized bed with supercharging capacity to study the effect of pressure on pollutant emissions during continuous combustion. Their conclusions indicate that in an O\textsubscript{2}/CO\textsubscript{2} environment, a pressure elevation will suppress NO\textsubscript{x} and SO\textsubscript{2} emissions. Duan et al.\textsuperscript{10} used a 10 kW\textsubscript{th} bubbling fluidized-bed reactor to study the effects of pressure, combustion environment, and fuel type on the emissions of gaseous pollutants. The experimental results show that the concentrations of NO, N\textsubscript{2}O, and SO\textsubscript{2} decrease with the increase of pressure. Furthermore, the concentrations of NO and SO\textsubscript{2} increase with temperature, while the concentration of N\textsubscript{2}O decreases under the same conditions. Pang et al.\textsuperscript{11} also obtained similar conclusions when studying NO\textsubscript{x} emissions using a 15 kW\textsubscript{th} pressurized fluidized bed. Duan et al.\textsuperscript{12} studied the coal pyrolysis process, and their experimental results show that the increase in pressure promotes coal pyrolysis, producing more HCN and NH\textsubscript{3}. Gül et al.\textsuperscript{13} used a 500 kW\textsubscript{th} pressurized bubbling fluidized-bed gasifier for 80 h of continuous gasification experiments, providing valuable insights into the application of large-scale gasification systems. Steam enrichment in the carrier gas is an inevitable result of flue gas recirculation technology. In the atmospheric environment, the influence of steam on the combustion process has been studied by a large number of scholars. The results show that wet flue gas can change the combustion reaction path, accelerate the consumption of char, CO oxidation, and inhibit the formation of NO\textsubscript{x}.\textsuperscript{5–7} Few scholars have, however, focused on the influence of steam during pressurized oxy-fuel combustion.

Higher concentrations of steam in pressurized oxy-fuel combustion technology can seriously affect the conversion of fuel-N, but research on this aspect is still in a relatively initial phase. Although pressurized oxy-fuel combustion is a very attractive method of combustion, important issues in this area have not been resolved. This article describes the test results obtained using a pressurized tube furnace with a longer constant-temperature section, focusing on the effects of pressure and temperature on NO\textsubscript{x} emissions when steam is involved.

2. RESULTS AND DISCUSSION

2.1. Effect of Pressure on NO Emissions. Figure 1 shows the measured NO emissions in an oxy-fuel combustion experiment in a simulated pressurized furnace. Figure 1a shows the emission process of NO. The emission curve in the figure shows two distinct peaks. During the combustion of volatiles, higher pressure delays the appearance of an emission peak and lowers the maximum value of the peak. During the char combustion process, affected by higher pressure, the emission peak value decreases and the emission peak shifts left. It is evident from the yield curve of NO that higher pressure reduces the burnout time, improves the combustion rate, and inhibits the generation rate of NO.

Figure 1b shows the change of total emissions. For the four types of simulated dry flue gas recycling, which are different based on the O\textsubscript{2} and CO\textsubscript{2} concentrations, NO emissions present varying degrees of decline, indicating that the internal pressure of the tube influences the inhibition of NO. As a result, under high-pressure conditions, the reduction of NO emissions is expected; however, this condition will also affect the migration of fuel-N during the combustion process.

The increase in pressure reduces the molecular diffusion rate,\textsuperscript{10} which prolongs the residence time of NO and NO\textsubscript{x} precursors, delaying their detachment from the coal surface. Furthermore, the partial pressure of each gas is also increased, accelerating the chemical reaction rate and leading to the reaction of NO with char and CO. Moreover, a high-pressure condition promotes the gasification reaction of char with CO\textsubscript{2},\textsuperscript{10} which results in enhanced reducibility around the fuel. In addition, it also promotes the conversion of fuel-N and the yield of NO\textsubscript{x} precursors, such as HCN and NH\textsubscript{3}.\textsuperscript{17,18} These components reduce the amount of NO due to reactions 2, 3, 4,
and 5,19 which is also a possible reason for high pressure to inhibit the NO emission during the oxy-fuel combustion experiment.

\[ \text{NH} + \text{NO} \rightarrow \text{N}_2 + \text{OH} \quad (1) \]
\[ \text{NH}_2 + \text{NO} \rightarrow \text{N}_2 + \text{H}_2\text{O} \quad (2) \]
\[ \text{HCN} + \text{O} \rightarrow \text{NCO} + \text{H} \quad (3) \]
\[ \text{NCO} + \text{NO} \rightarrow \text{N}_2\text{O} + \text{CO} \quad (4) \]

2.2. Effect of Temperature on NOx Emissions. In the simulated oxy-fuel combustion experiment, the furnace temperature significantly affects the formation of NOx. Figure 2 shows the effect of the reaction temperature on the measured NOx emissions under two different pressure conditions. As shown in Figure 2a, the increase in temperature promotes NO emission, under both reaction pressures, in the simulated pressurized oxygen-enriched combustion experiment.

In traditional oxy-fuel combustion experiments, it is concluded that an increase in temperature would promote NO emissions. Similar results are obtained in the simulated pressurized oxy-fuel combustion experiments, as the high temperature promotes the coal pyrolysis to release more NOx precursors.20 Moreover, high temperatures contribute to the opening of more nitrogen sites in the char matrix,21 leading to the conversion of fuel-N to NOx precursors through the gasification reaction with CO2.22 Combined with the excess oxygen in the environment, it shows a growth trend in NO emissions eventually.

Figure 2b presents the relationship between N2O emissions and temperature in the simulated pressurized oxy-fuel combustion experiment. For both reaction pressures, the emission of N2O is drastically reduced when the tube temperature is increased. This phenomenon is mainly caused due to the decomposition reaction of N2O (reaction 6),23 and the reaction rate increases with temperature. In addition, more free radicals (H and OH radicals), which are produced at higher temperatures, consume part of N2O through reactions 7 and 8.24 Furthermore, the high-temperature condition promotes the reduction of more N2O by char,25 leading to the decrease of N2O.

\[ \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O} \quad (5) \]
\[ \text{N}_2\text{O} + \text{H} \rightarrow \text{N}_2 + \text{OH} \quad (6) \]
\[ \text{N}_2\text{O} + \text{OH} \rightarrow \text{N}_2 + \text{HO}_2 \quad (7) \]

Figure 3 shows the trend of the fuel-N conversion rate in the pressurized oxy-fuel combustion experiment at different temperatures. Considering an increase in temperature from 700 to 900 °C, the fuel-N conversion rate reduces from 20 to 11.8% under atmospheric conditions, and from 16.9 to 9.7% at 0.4 MPa. This phenomenon is mainly due to the strong inhibition of N2O formation in a high-temperature environment during the pressurized combustion experiment.

2.3. Effect of Oxygen Concentration on NO Emissions. Figure 4 shows the effect of oxygen concentration on the NO emission in the simulated pressurized oxy-fuel combustion experiment. In the emission curves of Figure 4a, both curves display only one emission peak. Furthermore, the higher oxygen concentration increased the value of the emission peak and shortened the burnout time. In the yield curves of Figure 4a, affected by oxygen concentration, the NO formation rate becomes faster, and final emissions increase.

This phenomenon could be explained as follows: the increase in oxygen concentration of the environment strengthens the oxidation capacity of the simulated flue gas recycling. The increase in oxygen concentration accelerates the combustion reaction and also promotes the consumption of products, such as char, CO, and other products,28 which inhibits the NO generation. The high concentration of oxygen, therefore, results in the formation of more NO in the simulated traditional oxygen-enriched combustion experiments.
In Figure 4b, the five types of simulated flue gas recycling experiments present a more uniform trend that increasing oxygen concentration would cause an increase in NO emissions during the pressurized oxy-fuel combustion. However, it is worth noting that the growth tendency of NO emissions is very small. One possible reason is that the reaction rate increases due to the increase in environmental pressure. Furthermore, the long pipeline at a constant temperature enables sufficient time for the reaction to occur, causing a large number of NOx precursors to be fully oxidized to NO.

2.4. Effect of Steam Concentration on NOx Emissions.

Steam affects the combustion of the flame and interacts with char in the flame zone. In addition, it has a significant influence on the concentrations of certain free radicals, which indirectly affects the nitrogen migration pathway. Moreover, the diversification of the free radical pool composition becomes richer due to the presence of steam.

Figure 5 shows the measured NO emissions in the pressurized oxy-fuel combustion experiments with the simulated recycling wet flue gas. In Figure 5a, the injection of steam changes the emission curve, the curve changes from a double peak to a single peak. The presence of steam delays the appearance of the emission peak and lowers the maximum value of the peak. It is evident from the yield curve of NO that steam reduced the burnout time and inhibited the emissions and the generation rate of NO.

As shown in Figure 5b, the NO emissions at the outlet significantly decrease with the injection of steam, indicating that it could inhibit the NO formation. By comparing each of these six cases, it is possible to conclude that the inhibitory effect on NO emissions, considering the same initial steam concentration, increases with pressure. Moreover, the minimum emission (1.17 mg) of NO in the wet recycling is lower than that in the dry recycling (1.78 mg), indicating that the presence of steam enhances the inhibition effect of the operating pressure on NO formation.

There are several reasons to explain the above phenomena. Compared with the activation energy of the reaction between coal and CO2, the activation energy of the reaction between coal and steam is lower, 31 so steam can accelerate the consumption of coal. Through the self-decomposition reaction (reaction 9),27 the injected steam could produce plenty of OH and H radicals. The reduction of NO by H radicals is represented by the following steps: NO → HNO → NH → N2O → N2.28 Meanwhile, steam would simultaneously react with the O radical, forming OH (reaction 10),29 leading to a sharp increase of the OH/O ratio. Although the flue gas enriched with O radicals promotes the formation of NO, a large amount of OH radicals will consume the O radicals through reaction 11,27 weakening the formation of NO. Moreover, the direct contribution of steam to the formation of NO is particularly small; therefore, the presence of steam could overall inhibit the NO formation obviously.

Furthermore, regarding the heterogeneous experiments with the simulated wet flue gas recycling, the activation energy of the coal char gasification with steam is generally lower than that with CO2. As a result, the injection of steam improves the concentration of CO in the flue gas, further enhancing the reducibility of the carrier gas.30
In addition, over the flame zone, steam affects both free radical pools and coal char particles. In recent years, the combustion behavior of char in the steam-enriched combustion environment has been intensively studied. Due to the deep penetration of \( \text{H}_2\text{O} \) within the intraparticle region,\(^{31} \) the gasification reaction of steam and char enlarges the surface area of the pores at the surface of the coal char particle, accelerating the overall char−NO reduction rate. The elevation pressure contributes to the extension of the residence time; therefore, the injection of steam is further responsible for the reduction of the NO generation.

Figure 6 shows the effect of temperature on the NO\(_x\) emissions in a pressurized oxygen-enriched combustion system with the simulated wet flue gas recycling. In Figure 6a, the injection of steam is responsible for the reduction of the formation of NO. In addition, the inhibitory effect (0.68 mg) at 900 °C is higher than that at 800 °C (0.52 mg), indicating that the increase in temperature slightly strengthened the reducibility of the wet flue gas due to its concentration of free radicals. Although high temperature promotes the formation of NO, considering a constant initial steam concentration, the concentration of free radicals in the wet flue gas will also be improved.\(^{28} \) As a result, high-temperature conditions will overall enhance the suppression effect of the steam, which indirectly affects the formation of NO.

Figure 6b shows the impact of initial steam concentration on the formation of N\(_2\)O in the pressurized oxy-fuel combustion experiment. Two trends of N\(_2\)O formation, caused by temperature changes in the fixed bed, are observed. At an environmental temperature of 800 °C, the variation trend of N\(_2\)O is affected by steam, the total emissions decreased from 1.47 to 0.34 mg, and the trend gradually flattened. As mentioned above, the injection of steam in the wet flue gas greatly increases the content of these two kinds of free radicals that consume N\(_2\)O through reactions 7 and reactions 7,\(^{24} \) respectively. Moreover, the CO produced by the pyrolysis reaction also consumes a portion of N\(_2\)O.\(^{32} \)

The N\(_2\)O emission measured at an environmental temperature of 900 °C in the pressurized oxy-fuel combustion experiment is much lower than that at 800 °C. Although the emission of this component at the outlet decreased, the injection of steam at the inlet slightly affects its formation. This phenomenon may be due to the small amount of N\(_2\)O generated in the combustion experiment, resulting in an inapparent suppression of steam. The inhibitory effect of high-temperature conditions on the N\(_2\)O formation is more significant than that of steam.

Figure 7 shows the fuel-N conversion rate in the pressurized oxy-fuel combustion experiment with the simulated wet flue gas recycling. With increasing steam concentrations in the simulated recycling wet flue gas, the fuel-N conversion rate shows different trends depending on the experimental temperatures. In contrast, the steam concentration shows a more significant influence at a bed temperature of 800 °C, due to the inhibition of steam in the formation of N\(_2\)O. At 900 °C, due to the low N\(_2\)O emission caused by high temperatures, the effect of steam on the fuel-N conversion rate is reflected in the inhibition of NO formation.
concentration, and steam concentration, on the NO combustion parameters, such as temperature, pressure, oxygen from the results of this study, are as follows:

In this study, pressurized oxy-fuel combustion experiments were conducted at horizontal tube furnace facilities under laboratory conditions. The effects generated by different combustion parameters, such as temperature, pressure, oxygen concentration, and steam concentration, on the NO formation were systematically studied. The main conclusions, obtained from the results of this study, are as follows:

(1) The pressure increase promotes the char gasification reaction to produce more reducing gas and accelerates the reaction rate. In addition, higher pressure reduces the molecular diffusion coefficient and prolongs the residence time, so that NO is reduced around the fuel. Eventually, the increase in pressure suppresses NO emissions.

(2) In the simulated pressurized oxy-fuel combustion experiment, both pressure conditions analyzed show similar results (NO and N₂O emissions are increased and suppressed, respectively) as those obtained with the increase of temperature. As N₂O is rapidly decomposed in a high-temperature environment, the conversion rate of fuel-N decreases with temperature.

(3) With an increase in the O₂ concentration, the burnout time of coal becomes shorter, the formation rate of NO becomes faster, and the emissions of NO in the pressurized oxy-fuel combustion experiment with the simulated dry flue gas recycling slightly increase.

(4) In the experiment with the simulated wet flue gas recycling, the formation process of NO is changed by the influence of steam and the injected steam can significantly reduce the formation of NO, and the conversion rate of fuel nitrogen. Furthermore, the inhibition effect caused by steam is amplified as the steam concentration increases. The effect of steam on the N₂O formation in higher temperature experiments, however, is not significant.

3. CONCLUSIONS

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4. EXPERIMENTAL SECTION

4.1. Experimental Setup. In this study, a pressurized tube furnace was designed and built to execute the experiments, as shown in Figure 8. The experimental device consisted of a feeding device, an electric heating furnace, a fixed-bed reactor, a gas supply system, and a flue gas analyzer. High-purity O₂ and CO₂ gases were supplied through the gas steel sheets to the mixing chamber and their flow rate was controlled by a mass flow meter. Meanwhile, the steam in the mixing chamber was provided by a steam-generating device. The mixed gas stream was preheated to 200 °C in the mixing chamber and was thereafter sent to the reaction tube. In this experiment, the total flow rate of the mixed gas was set to 3 L/min under atmospheric temperature and pressure conditions. The tail gas entered the tail mixing chamber after passing through a filter unit loaded with anhydrous calcium chloride. The tail gas was diluted with nitrogen gas, at 6 L/min, and, thereafter, was sent to the flue gas analyzer. The electric heating furnace used a silicon carbon rod as the heating element, and six sets of temperature control devices were evenly distributed along the furnace to ensure that the temperature distribution in the section was constant and uniform. The reaction tube was made of 310S stainless steel and had an inner diameter of 50 mm, a length of 1500 mm, a constant-temperature section of more than 1200 mm, and a maximum temperature and load condition of 1000 °C and 1 MPa, respectively. The feed push rod was arranged at the joint and was connected by a flexible seal for feeding in a high-pressure environment. The pressure inside the tube was regulated by an X-tec universal backpressure valve. Fourier transform infrared (FTIR) spectroscopy (Antaris IGS, Thermo Fisher Scientific Inc.) was employed to monitor the flue gas, and its measurement accuracy for NO, N₂O, and SO₂ is 0.01 ppm.

4.2. Materials and Parameters. The material used in the experiment was Shanxi bituminous coal with a particle size ranging from 0.1 to 0.3 mm. The coal sample was dried at a constant temperature (110 °C) for 2 h and then sealed and stored. The coal analysis results are shown in Table 1. Table 2 details the experimental test conditions for all experiments.

4.3. Methods. First, the electric heater was turned on and the horizontal tube furnace and the mixing chamber were heated to the specified temperature, respectively. When the temperature reached the required level, a quartz boat loaded with 1 g of sample was placed at the inlet of the tube (where the temperature is below 110 °C). After sealing the left side of the tube furnace, the required proportion of gas was passed...
and the backpressure valve was adjusted to the required pressure. When the temperature and pressure of the reactor were stable, the left joint was loosened slightly, the sample rod was pushed quickly to send the quartz boat into the central reaction zone, and then the sleeve joint was quickly locked to complete the sample feeding work. The pressure loss did not exceed 0.01 MPa during the sample feeding process. The exhaust gas was diluted with N2 (6 L/min) and then allowed to enter the flue gas analyzer.

4.4. Data Processing. The reaction temperature does not exceed 1000 °C, and N2 is replaced by CO2, so no thermal NOx and prompt NOx will be produced in the experiment. It is considered that the nitrogen oxides collected in the experiment are all coming from fuel NOx. The fuel NOx conversion rate formula is as follows

\[
C_N = \frac{M_N \times (V_1 + V_2) \times \left( \int_0^t Q_{NO} \, dt + 2 \int_0^t Q_{N_2O} \, dt \right) \times \frac{T_1}{T_2}}{V_m \times m_o \times w_N}
\]

(11)

where \(C_N\) is the conversion rate (%) of the N element in the sample. \(M_N\), \(M_{NO}\), and \(M_{N_2O}\) are the molar masses of N, NO, and N2O, respectively (g/mol). \(V_1\) is the dry carrier gas flow at normal temperature and pressure, and \(V_2\) is the dilution gas flow. \(Q_{NO}\) and \(Q_{N_2O}\) are the volume concentrations of flue gas per unit time at room temperature (ppm). \(T_1\) is room temperature and \(T_2\) is 0 °C. \(V_m\) is the molar volume of gas, \(m_o\) is the total mass of the sample (mg), \(w_N\) is the nitrogen mass fraction in the sample (%), and \(t\) denotes the time.

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Notes

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