Article

NO$_x$ Emissions and Nitrogen Fate at High Temperatures in Staged Combustion

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Abstract: Staged combustion is an effective technology to control NO$_x$ emissions for coal-fired boilers. In this paper, the characteristics of NO$_x$ emissions under a high temperature and strong reducing atmosphere conditions in staged air and O$_2$/CO$_2$ combustion were investigated by CHEMKIN. A methane flame doped with ammonia and hydrogen cyanide in a tandem-type tube furnace was simulated to detect the effects of combustion temperature and stoichiometric ratio on NO$_x$ emissions. Mechanism analysis was performed to identify the elementary steps for NO$_x$ formation and reduction at high temperatures. The results indicate that in both air and O$_2$/CO$_2$ staged combustion, the conversion ratios of fuel-N to NO$_x$ at the main combustion zone exit increase as the stoichiometric ratio rises, and they are slightly affected by the combustion temperature. The conversion ratios at the burnout zone exit decrease with the increasing stoichiometric ratio at low temperatures, and they are much higher than those at the main combustion zone exit. A lot of nitrogen compounds remain in the exhaust of the main combustion zone and are oxidized to NO$_x$ after the injection of a secondary gas. Staged combustion can lower NO$_x$ emissions remarkably, especially under a high temperature ($\geq$1600 °C) and strong reducing atmosphere (SR $\leq$ 0.8) conditions. Increasing the combustion temperature under strong reducing atmosphere conditions can raise the H atom concentration and change the radical pool composition and size, which facilitate the reduction of NO to N$_2$. Ultimately, the increased OH/H ratio in staged O$_2$/CO$_2$ combustion offsets part of the reducibility, resulting in the final NO$_x$ emissions being higher than those in air combustion under the same conditions.

Keywords: chemical simulation; NO$_x$ emission; staged combustion; high temperature; strong reducing atmosphere

1. Introduction

Nitrogen oxides (NO$_x$) are one of the most predominant pollutants in coal-fired boilers. Because NO$_x$ can endanger human health severely and cause acid rain, there is an increasing public demand for reducing NO$_x$ emissions. Many countries have promulgated new NO$_x$ emission limits [1–4]. In China, the allowed NO$_x$ emissions should be below 100 mg of NO$_x$/Nm$^3$ (6% O$_2$) for all coal-fired power plants after 2014. In the European Union, the NO$_x$ emission limit is expected to be lowered to 200 mg of NO$_x$/Nm$^3$ (6% O$_2$) for power plants over 500 MW$_e$ by the year of 2016.

To achieve these stringent NO$_x$ emission limits, a combination of two or more NO$_x$ reduction techniques has to be used [5,6]. Currently, commercially available NO$_x$ reduction techniques include air staging, reburning, low-nitrogen burner [7], selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR). Among them, air staging, reburning and low-nitrogen burner are low
NO\textsubscript{x} combustion techniques, whereas SCR and SNCR are post-combustion NO\textsubscript{x} reduction technologies employed to offer varying degrees of NO\textsubscript{x} control capability. Because of high capital and operating costs, ammonia leakage, deactivation of the catalyst, and relatively narrow temperature windows for post-combustion NO\textsubscript{x}-reduction technologies [8–13], it is more desirable in practice to remove as much NO\textsubscript{x} as possible during combustion to alleviate the dependency on SCR and SNCR.

Air staging is the most widely used NO\textsubscript{x} control technique during combustion in pulverized coal boilers, which employs a main combustion zone and a burnout zone within the furnace region (see Figure 1) [5,14,15]. About 80% of air flow enters the main combustion zone where pulverized coal burns under substoichiometric conditions, i.e., reducing atmosphere conditions. The balance of the required air for complete combustion is introduced to the burnout zone through overfire air (OFA) ports. In the main combustion zone, the deficiency of oxygen can accelerate CH\textsubscript{m} (with \(m = 1, 2, \text{ and } 3\)) and NH\textsubscript{m} (with \(n = 0, 1, \text{ and } 2\)) to reduce generated NO\textsubscript{x} to N\textsubscript{2} [16]. After the balance of oxygen is supplied to the burnout zone, a small amount of fuel NO\textsubscript{x} will be formed here, as most of the fuel-N has been converted into N\textsubscript{2} or NO\textsubscript{x}. Meanwhile, the generation of thermal NO\textsubscript{x} is also inhibited. As a result, lower emissions of NO\textsubscript{x} are achieved at the furnace exit.

![Figure 1. Pulverized coal boiler air-staged combustion NO\textsubscript{x} control system.](image)

Many research efforts have been devoted to the characteristics of NO\textsubscript{x} formation and reduction in staged air combustion [1,3,16–22]. The results revealed that NO\textsubscript{x} emissions are mostly determined by coal properties, combustion temperature, stoichiometric ratio (SR) and residence time. Some investigators [17,22] reported that stoichiometric ratio can strongly affect the generation of NO\textsubscript{x}, and the conversion ratio of fuel-N to NO\textsubscript{x} falls with the decreasing stoichiometric ratio under reducing atmosphere conditions (SR < 1). Taniguchi et al. [1,19] detected the impact of combustion temperature on NO\textsubscript{x} emissions in a drop-tube furnace system used to simulate the air-staged combustion characteristics of actual pulverized coal boilers. They agreed that raising the temperature of the main combustion zone under reducing atmosphere conditions helps the reduction of NO\textsubscript{x}. This viewpoint is also supported by some other research work [21]. Thus, it is found that a high temperature or strong reducing atmosphere in the main combustion zone can lower NO\textsubscript{x} emissions. In other words, to achieve the minimal NO\textsubscript{x} emissions in staged air combustion, the combustion temperature should be raised as high as possible and the stoichiometric ratio should be reduced as far as possible simultaneously in
the main combustion zone. Bai et al. [16] examined NO\textsubscript{x} emission levels of various coals under high temperature and strong reducing atmosphere conditions in a vertical tandem-type drop-tube furnace system. Their results verified the NO\textsubscript{x} removal potential of this combustion method.

Creating high temperature and strong reducing atmosphere conditions in staged air combustion to lower NO\textsubscript{x} emissions has a promising prospect. The slag-tap furnace is expected to be the most appropriate application for the combustion method owing to the following two aspects: The first is the high combustion temperature. For example, the gas temperature within the cyclone barrel is more than 1650 °C in cyclone-fired boilers [23]. The second is the decreased ash melting temperature under strong reducing atmosphere conditions [24]. The slag-tap furnace prefers to fire the coals having low ash melting temperatures without severe slagging. Moreover, there are also some other furnaces featuring high combustion temperatures [5,21].

O\textsubscript{2}/CO\textsubscript{2} combustion is one of the most promising CO\textsubscript{2}-capture technologies in thermal power generation [25–28]. Studies have shown that staged combustion can also lower the NO\textsubscript{x} emissions in O\textsubscript{2}/CO\textsubscript{2} combustion [16,20,26,29]. Thus, NO\textsubscript{x} formation and reduction under high temperatures and strong reducing atmosphere conditions in staged O\textsubscript{2}/CO\textsubscript{2} combustion are also worthy being explored.

A number of researchers [4,6,20,30–35] have investigated the processes of NO\textsubscript{x} formation and reduction in staged air and O\textsubscript{2}/CO\textsubscript{2} combustion to date. However, these studies were performed under the conditions of relatively low temperature or relatively high stoichiometric ratio. There are very few studies on the reaction mechanisms for NO\textsubscript{x} under high temperatures and strong reducing atmosphere conditions, which differ from those under conventional conditions of staged combustion. Meanwhile, how to co-ordinate the combustion temperature and stoichiometric ratio to achieve the most suitable conditions for NO\textsubscript{x} reduction is still unclear and insufficiently understood. Therefore, it is of great significance to study how the high temperature and strong reducing atmosphere conditions influence the NO\textsubscript{x} formation and reduction in staged combustion.

In the present study, the characteristics of NO\textsubscript{x} formation and reduction under high temperature and strong reducing atmosphere conditions in staged air combustion were investigated numerically by CHEMKIN. A methane flame doped with ammonia and hydrogen cyanide for fuel-N in a tandem-type tube furnace was simulated to probe the effects of combustion temperature and stoichiometric ratio on the NO\textsubscript{x} emissions. Based on the calculations, the elementary steps for NO\textsubscript{x} formation and reduction at the high temperature were identified. In addition, NO\textsubscript{x} formation and reduction in staged O\textsubscript{2}/CO\textsubscript{2} combustion were also examined.

2. Numerical Approach

2.1. Reactors and Models

The simulations were carried out for a tandem-type tube furnace consisting of two identical tube reactors. The tube furnace is shown schematically in Figure 2a. The inside diameter and heating length of the tube reactor are 38 mm and 600 mm, respectively. The heaters are arranged around the tube reactors to control the reaction temperatures. The primary gas, which includes CH\textsubscript{4}, NH\textsubscript{3}, HCN and air (O\textsubscript{2}/CO\textsubscript{2}), is introduced into the tube reactor 1 where methane burns under different temperatures and stoichiometric conditions. Meanwhile, NH\textsubscript{3} and HCN are converted into NO or N\textsubscript{2}. Subsequently, the secondary gas, i.e., supplementary air or O\textsubscript{2}/CO\textsubscript{2}, is injected as OFA from the connection between the tube reactor 1 and 2. The residual fuel burns out in the tube reactor 2. Therefore, the tube furnace can be employed to describe the characteristics of NO\textsubscript{x} formation and reduction in staged combustion with the tube reactor 1 and 2 regarded as the main combustion zone and the burnout zone, respectively.

Indeed, some key processes in real boilers such as strong turbulence, devolatilization, char combustion and thermal radiation are simplified for the purpose of seeking elementary steps for N conversion at high temperatures. During pulverized coal combustion, considerable fractions of C and N conversion occur in the gas phase. When pulverized coal is ignited in the furnace, the volatiles in coal are first released and then mixed with air for homogeneous combustion. Hydrocarbons
are the important components of the volatiles. Compared with the real combustion process of pulverized coal, the transformation of Char-N and heterogeneous reduction of NO\(_x\) are not considered. This simplification certainly brings deviation for direct prediction of NO\(_x\) emissions in practice, and its influence depends on the amount of the coal volatiles. In this study, although methane combustion simulation cannot fully reflect the N conversion during coal combustion, it can still reveal NO\(_x\) formation and reduction in the homogeneous combustion.

![Diagram](image)

**Figure 2.** Schematic diagram of simulation object: (a) tube furnace of staged combustion; (b) reaction process modeling, 1—external source of inlet gas i, 2—plug flow reactor i, 3—external source of inlet gas ii, 4—non-reactive gas mixer, 5—plug flow reactor ii, 6—outlet flow of reactor.

The simulations were performed using a chemical kinetics modeling code CHEMKIN. It provides a feasible and powerful tool to understand reaction processes involving elementary gas-phase chemical kinetics [30–32,34,36–38]. Proper models were chosen to simulate the tube furnace and a corresponding reaction process diagram was developed in Figure 2b. Two external source of inlet gas models were used to introduce the primary and secondary gases into the reaction system. Moreover, two plug flow reactor (PFR) models were employed to describe the combustion processes in the tube reactor 1 and 2, respectively. The PFR model assumes that no mixing occurs in the flow direction while perfect mixing occurs in the direction perpendicular to the flow [39,40]. Many researchers have applied it to simulate the complex physical and chemical phenomena in tube reactors. A non-reactive gas mixer model was used to replace the connection between the two tube reactors. The reaction system ended up with an outlet flow of reactor model. All the models above completely constituted the simulation object.

### 2.2. Reaction Mechanism

There are three mechanisms responsible for the NO\(_x\) formation in combustion systems: thermal NO\(_x\), prompt NO\(_x\) and fuel NO\(_x\). In the present study, the production of NO is far more than those of other nitrogen oxides, thus, only NO is taken into account in our results. The thermal NO\(_x\) is formed by the direct oxidation of nitrogen from the combustion air at a very high temperature (>1800 K). This reaction process can be expressed by the extended Zeldovich mechanism as follows [41]:

\[
\begin{align*}
\text{N}_2 + \text{O} & \rightarrow \text{NO} + \text{N} \\
\text{N} + \text{O}_2 & \rightarrow \text{NO} + \text{O} \\
\text{N} + \text{OH} & \rightarrow \text{NO} + \text{H}
\end{align*}
\]
The prompt NO\textsubscript{x} are generated by the reaction of atmospheric nitrogen with hydrocarbon radicals in fuel-rich conditions. The key reactions are written by [42]:

\begin{align*}
N_2 + \text{CH} & \rightarrow \text{HCN} + N \quad (4) \\
N_2 + \text{CH}_2 & \rightarrow \text{HCN} + \text{NH} \quad (5)
\end{align*}

Subsequently, these resultants are oxidized to NO quickly. The fuel NO\textsubscript{x} are produced by the oxidation of nitrogen bound in the fuel and generally account for more than 80% of the total NO\textsubscript{x} production in large pulverized coal boilers [41]. NH\textsubscript{3} and HCN are the dominant intermediates during the conversion of fuel-N to NO or N\textsubscript{2}. As a result, the overall reactions of the fuel NO\textsubscript{x} formation can be given by:

\begin{align*}
\text{NH}_3 + \text{O}_2 & \rightarrow \text{NO} + \ldots \quad (6) \\
\text{HCN} + \text{O}_2 & \rightarrow \text{NO} + \ldots \quad (7)
\end{align*}

In addition, the generated NO is also reduced to N\textsubscript{2} simultaneously, which mainly depends on the local environment. The final NO\textsubscript{x} emissions are the comprehensive result of these actions, and a detailed reaction mechanism is needed to predict it.

A GRI-Mech 3.0 reaction mechanism was adopted in this paper, which involves 53 species and 325 elementary chemical reactions [43]. The purpose of this mechanism is to model natural gas combustion, including NO formation and reduction and reburn chemistry. The three NO\textsubscript{x} formation mechanisms above are all included in this mechanism. Species concentrations in reaction systems are calculated from the net rate of production for each species by chemical reaction. Reaction rate constants are determined by the modified Arrhenius expression [32]:

\begin{equation}
k = AT^\beta \exp\left(-\frac{E}{RT}\right)\end{equation}

where \(A\) is the pre-exponential factor, \(T\) is the reaction temperature, \(\beta\) is the correction factor, \(E\) is the activation energy and \(R\) is the molar gas constant. The reverse reaction rate constants derive from the forward reaction rate constants and appropriate equilibrium constants. Under this mechanism, the rate of production (ROP) and first-order sensitivity analyses were used to interpret the kinetic results [32,34,36,44]. The ROP analysis can provide the information of the rates of formation and consumption for each species involved in the mechanism. The first-order sensitivity analysis is able to obtain the first-order sensitivity coefficient defined as:

\begin{equation}
\kappa = \frac{\delta Y_j / Y_j}{\delta A_i / A_i}
\end{equation}

where \(Y_j\) is the mole fraction for the \(j\)th species and \(A_i\) is the pre-exponential factor for the \(i\)th reaction. The coefficient reflects the relative change in the predicted concentration for \(j\)th species caused by increasing the reaction rate constant for the \(i\)th reaction.

3. Data Analysis and Simulation Conditions

The stoichiometric ratio (SR) is often used to express combustion conditions, which is represented in this study by:

\begin{equation}
\text{SR} = \frac{V_{\text{O}_2}/V_{\text{CH}_4}}{(V_{\text{O}_2}/V_{\text{CH}_4})_{\text{st}}}
\end{equation}

where \(V\) is the volume flow rate and the subscript \(\text{st}\) denotes the stoichiometric condition. The conversion ratio of fuel-N to NO\textsubscript{x} (NO\textsubscript{x} CR) is defined as:

\begin{equation}
\text{NO}_x \text{ CR} = \frac{\text{Exhaust NO}_x \text{ volume flow rate}}{\text{Inflow fuel – N volume flow rate}}\end{equation}
where the Inflow fuel-N volume flow rate is the sum of NH$_3$ and HCN volume flow rates.

Nine different stoichiometric ratios in the main combustion zone (0.5–1.2, 2) were used to study the effect of the SR on the characteristics of NO$_x$ emissions, as shown in Table 1. The C/N mole ratios in these cases were all selected as 85. The reaction temperature in the main combustion zone varies from 1200 to 1800 °C, while that in the burnout zone varies from 1100 to 1400 °C. To compare with air-staged combustion, NO$_x$ emissions in staged O$_2$/CO$_2$ and O$_2$/Ar combustion were also investigated with the O$_2$ concentrations set at the same value (21%).

Table 1. Simulation conditions for staged combustion in the tandem-type tube furnace.

| SR (Main Combustion Zone) | 0.5 | 0.6 | 0.7 | 0.8 | 0.9 | 1   | 1.1 | 1.2 | 2   |
|---------------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Primary gas (Ncm$^3$/min): |     |     |     |     |     |     |     |     |     |
| CH$_4$                     | 735 | 612.5 | 525 | 459.4 | 408.3 | 367.5 | 334.1 | 306.2 | 183.8 |
| O$_2$                      | 735 | 735 | 735 | 735 | 735 | 735 | 735 | 735 | 735 |
| N$_2$ (CO$_2$ or Ar)       | 2765 | 2765 | 2765 | 2765 | 2765 | 2765 | 2765 | 2765 | 2765 |
| NH$_3$                     | 3.46 | 2.88 | 2.47 | 2.16 | 1.92 | 1.73 | 1.57 | 1.44 | 0.86 |
| HCN                        | 5.19 | 4.32 | 3.71 | 3.24 | 2.88 | 2.59 | 2.36 | 2.16 | 1.30 |
| Secondary gas (Ncm$^3$/min): |     |     |     |     |     |     |     |     |     |
| O$_2$                      | 1029 | 735 | 525 | 367.5 | 245 | 147 | 66.8 | 0 | 0 |
| N$_2$ (CO$_2$ or Ar)       | 3871 | 2765 | 1973 | 1382.5 | 921.7 | 553 | 251.4 | 0 | 0 |
| SR$_{global}$              | 1.2 | 1.2 | 1.2 | 1.2 | 1.2 | 1.2 | 1.2 | 1.2 | 2 |

Reaction temperature: 1200–1800 °C (Main combustion zone); 1100–1400 °C (Burnout zone)

4. Results and Discussion

4.1. Model Validation

In order to obtain creditable and reasonable simulation results, a comparison between different reaction mechanisms and models was carried out in Figure 3. An updated reaction mechanism of Glarborg et al. and a premixed flame model (PFM) were also taken into consideration in the present study. The updated Glarborg reaction mechanism includes 97 species and 779 elementary chemical reactions, and is able to predict the experimental results correctly [32]. The PFM can compute species and temperature profiles in steady-state burner-stabilized premixed laminar flames. Figure 3 gives the predicted results of three cases: PFR model and GRI-Mech 3.0 reaction mechanism, PFR model and updated Glarborg reaction mechanism, PFM model and GRI-Mech 3.0 reaction mechanism [45]. The calculation was conducted under the SR of 0.7 and the reaction temperature varying from 1200 to 1800 °C; the other conditions are listed in Table 1. On the whole, the predicted volume flow rates of NH$_3$, HCN and NO at the main combustion zone exit show similar trends in the three cases. Although there are some differences between the reaction mechanisms and models, these results are comparable. Especially at high temperatures, a good agreement is observed. Therefore, the above-described numerical approach is valid.

4.2. Characteristics of NO$_x$ Emissions in Staged Air Combustion

Figure 4 shows the NO$_x$ CRs at the main combustion zone and burnout zone exits in the staged air combustion. The NO$_x$ CRs at the main combustion zone exit increase when the SR rises, and the reaction temperature seems to have little influence on the NO$_x$ CRs. However, the NO$_x$ CRs at the burnout zone exit are significantly affected by the SR and reaction temperature in the main combustion zone. When the reaction temperature is low, the NO$_x$ CRs decrease with the increasing SR. Comparing the NO$_x$ CRs of the main combustion zone exit and the burnout zone exit, a large quantity of NO$_x$ is produced after the injection of secondary gas, which means a lot of nitrogen compounds exist in the exhaust of the main combustion zone. This point will be proved and discussed in Figure 5. The smaller the SR is, the higher the number of nitrogen compounds. Contrastingly, for the high reaction temperature, the final NO$_x$ emission levels are quite low. A minimal difference is found in the NO$_x$ CRs between the main combustion zone exit and the burnout zone exit, which means most
of the fuel-N has been converted into NO$_x$ or N$_2$ and few nitrogen compounds remain at the main combustion zone exit. In addition, the lower NO$_x$ emission levels are found at a high temperature (≥1600 °C) and strong reducing atmosphere (SR ≤ 0.8) conditions.

The sums of NH$_3$, HCN, and NO$_x$ at the main combustion zone and burnout zone exits in staged air combustion are shown in Figure 5. At the main combustion zone exit, the NO$_x$ emissions are low, while the sum of NH$_3$, HCN, and NO$_x$ is quite high when the reaction temperature is set as 1200 °C. A large amount of NH$_3$ and HCN remain in the primary combustion exhaust. With the secondary gas introduced, the remaining NH$_3$ and HCN are almost entirely oxidized to NO$_x$. Therefore, at the burnout zone exit, very little NH$_3$ and HCN exist, and the sum of NH$_3$, HCN, and NO$_x$ is approximately equal to the NO$_x$ emissions. The final NO$_x$ emissions depend on the sum of nitrogen compounds in the primary combustion exhaust. To limit the NO$_x$ emissions as much as possible by air staging, it is of great significance to obtain a minimum sum of NH$_3$, HCN, and NO$_x$ in the main combustion zone, i.e., converting more fuel-N to N$_2$ in terms of N balance. With the reaction temperature in the main combustion zone rising, the final NO$_x$ emissions decrease. When the temperature is higher than 1600 °C, the final NO$_x$ emissions attain a minimum level.
Figure 4. Conversion ratio of fuel-N to NO\textsubscript{x} in staged air combustion (reaction temperature in the burnout zone: 1100 °C): (a) main combustion zone exit; (b) burnout zone exit.

Figure 5. Sums of NH\textsubscript{3}, HCN and NO\textsubscript{x} at the exits in staged air combustion (reaction temperature in the burnout zone: 1100 °C).

Figure 6 illustrates the NO\textsubscript{x} emissions under the oxidizing atmosphere condition (SR ≥ 1) in air combustion. Considering the formation of the thermal NO\textsubscript{x}, a simulation of O\textsubscript{2}/Ar combustion was
performed for comparison. Most of the fuel-N is easily oxidized to NO\textsubscript{x} by the excess O\textsubscript{2}. When the combustion temperature is higher than 1500 °C, the thermal NO\textsubscript{x} begins to be markedly produced. As the combustion temperature and SR rise, the emissions of the thermal NO\textsubscript{x} increase rapidly.

\begin{equation}
\text{H + CO}_2 \rightarrow \text{OH} + \text{CO} \quad \text{(12)}
\end{equation}

**Figure 6.** Comparison of NO\textsubscript{x} emissions between air combustion and O\textsubscript{2}/Ar combustion under oxidizing atmosphere conditions.

The effect of the reaction temperature in the burnout zone (\(T_2\)) on the NO\textsubscript{x} emissions in air staging is shown in Figure 7. The reaction temperature in the main combustion zone (\(T_1\)) is selected as 1500 °C. There is minimal difference in the final NO\textsubscript{x} CR when \(T_2\) varies from 1100 to 1400 °C. In other words, \(T_2\) nearly has no effect on the formation of NO\textsubscript{x}. Therefore, it is important to control the NO\textsubscript{x} formation and reduction in the main combustion zone instead of the burnout zone.

**Figure 7.** Effect of reaction temperature in the burnout zone on the NO\textsubscript{x} emissions in staged air combustion.

4.3. **Characteristics of NO\textsubscript{x} Emissions in Staged O\textsubscript{2}/CO\textsubscript{2} Combustion**

Figure 8 presents the effects of the SR and combustion temperature on the NO\textsubscript{x} emissions in the staged O\textsubscript{2}/CO\textsubscript{2} combustion. The variation trends of the NO\textsubscript{x} CRs are similar to those in the staged air combustion. However, a significant difference in the exact NO\textsubscript{x} emission value between O\textsubscript{2}/CO\textsubscript{2} combustion and air combustion is found due to the existence of a great deal of CO\textsubscript{2}. In the O\textsubscript{2}/CO\textsubscript{2} combustion, the CO\textsubscript{2} concentration is so high that the chemical reaction 12 is observably facilitated [30,37]:
Here, CO\(_2\) cannot be considered as an inert gas anymore. The chemical reaction 12 diminishes the H atom concentration and increases the concentration of OH radicals, which impacts the NO\(_x\) formation and reduction strongly. Compared with the staged air combustion, the NO\(_x\) CR at the main combustion zone exit increases markedly, and the range of the SR and combustion temperature (under which a significant amount of NH\(_3\) and HCN remain in the primary combustion exhaust) is narrow. At low temperatures (\(\leq 1400\) °C), a significant amount of NH\(_3\) and HCN remain at the main combustion zone exit. Their sum rises rapidly with the decreasing SR and combustion temperature. Similarly, the lower final NO\(_x\) emission levels appear at high temperatures (\(\geq 1500\) °C), and the higher combustion temperature and the smaller SR lead to lower NO\(_x\) emissions. Furthermore, the final NO\(_x\) emissions in the staged O\(_2\)/CO\(_2\) combustion are higher than those in the staged air combustion at the same high temperature and strong reducing atmosphere conditions. This conclusion is consistent with Mendiara et al.’s research results [32,36]. Because of the chemical reaction 12, the OH/H ratio increases, which is equivalent to providing an oxidizing agent in the combustion atmosphere. Therefore, the oxidation of NH\(_3\) and HCN to NO\(_x\) is promoted.

**Figure 8.** Conversion ratio of fuel-N to NO\(_x\) in staged O\(_2\)/CO\(_2\) combustion (reaction temperature in the burnout zone: 1100 °C): (a) main combustion zone exit; (b) burnout zone exit.

Figure 9 compares the NO\(_x\) emissions of staged air and O\(_2\)/CO\(_2\) combustion under different atmosphere conditions. In O\(_2\)/CO\(_2\) combustion, staged combustion is also able to decrease the NO\(_x\) emissions enormously, but the emission reduction is less than that in air staging. Under the oxidizing atmosphere condition, the NO\(_x\) emission levels are quite high in both air combustion and O\(_2\)/CO\(_2\)
combustion. Moreover, CO\(_2\) can reduce the O:H radical pool and tends to inhibit the NO\(_x\) formation from fuel-N and, thus, the NO\(_x\) emissions in O\(_2\)/CO\(_2\) combustion are lower than those in air combustion. When under the reducing atmosphere condition, as the SR falls, the NO\(_x\) CR in O\(_2\)/CO\(_2\) combustion decreases while that in air combustion reduces first and then increases. The NO\(_x\) CR of O\(_2\)/CO\(_2\) combustion has a minimum of 7.1% at the SR of 0.5, while that of air combustion reaches a minimum of 4.7% at the SR of 0.7. These results denote that staged air combustion is more practical for limiting the NO\(_x\) emissions than staged O\(_2\)/CO\(_2\) combustion.

Another interesting finding in Figure 9 is that there are two reverse trends for staged air combustion and O\(_2\)/CO\(_2\) combustion at a smaller SR. The chemical reaction 12 can affect reducibility of combustion atmosphere strongly. At a smaller SR, a certain amount of NH\(_3\) and HCN remain in the primary combustion exhaust for staged air combustion when the temperature is not so high (here 1500 °C), then the NO\(_x\) CR increases after these NH\(_3\) and HCN are oxidized to NO\(_x\) by the OFA. While for staged O\(_2\)/CO\(_2\) combustion, the atmosphere is much less reductive at the same SR; only a small amount of NH\(_3\) and HCN remain when the temperature is 1500 °C. Moreover, the smaller SR is, the more significant the effect of reducibility.

4.4. Mechanism Analysis

According to the ROP analysis, a reaction path diagram reflecting the main reaction pathways for the conversion of NH\(_3\) and HCN to NO or N\(_2\) in staged air and O\(_2\)/CO\(_2\) combustion is proposed in Figure 10. The combustion temperature is 1600 °C and the SR is 0.7 during the calculation. The solid lines represent reaction pathways important in air combustion, while the dashed lines express those only significant in O\(_2\)/CO\(_2\) combustion. It can be seen from the reaction path diagram that NO is directly reduced to N\(_2\) mainly through the following reactions:

\[
N + NO \rightarrow N_2 + O \quad (13)
\]
\[
NH + NO \rightarrow N_2 + OH \quad (14)
\]
\[
NCO + NO \rightarrow N_2 + CO_2 \quad (15)
\]

Besides, part of NO first forms nitrogen intermediates NNH and N\(_2\)O, and they are then converted into N\(_2\) by:

\[
NH + NO \rightarrow NNH + O \quad (16)
\]
\[
\text{NNH} + \text{H} \rightarrow \text{H}_2 + \text{N}_2 \quad (17)
\]
\[
\text{NNH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{N}_2 \quad (18)
\]
\[
\text{NNH} \rightarrow \text{N}_2 + \text{H} \quad (19)
\]
\[
\text{NH} + \text{NO} \rightarrow \text{N}_2\text{O} + \text{H} \quad (20)
\]
\[
\text{NCO} + \text{NO} \rightarrow \text{N}_2\text{O} + \text{CO} \quad (21)
\]
\[
\text{N}_2\text{O} + \text{H} \rightarrow \text{N}_2 + \text{OH} \quad (22)
\]
\[
\text{N}_2\text{O}(+\text{M}) \rightarrow \text{N}_2 + \text{O}(+\text{M}) \quad (23)
\]

Figure 10. Reaction path diagram for the fuel-N conversion under a high temperature and strong reducing atmosphere conditions in staged air and O$_2$/CO$_2$ combustion.

Major reactions for NH$_3$ consumption are the interactions with H, O and OH radicals:
\[
\text{NH}_3 + \text{H} \rightarrow \text{NH}_2 + \text{H}_2 \quad (24)
\]
\[
\text{NH}_3 + \text{O} \rightarrow \text{NH} + \text{OH} \quad (25)
\]
\[
\text{NH}_3 + \text{OH} \rightarrow \text{NH}_2 + \text{H}_2\text{O} \quad (26)
\]

Main reactions for HCN removal are listed as follows:
\[
\text{HCN} + \text{OH} \rightarrow \text{NH}_2 + \text{CO} \quad (27)
\]
\[
\text{HCN} + \text{O} \rightarrow \text{NH} + \text{CO} \quad (28)
\]
\[
\text{HCN} + \text{O} \rightarrow \text{NCO} + \text{H} \quad (29)
\]
\[
\text{HCN} + \text{OH} \rightarrow \text{HOCN} + \text{H} \quad (30)
\]
\[
\text{HCN} + \text{OH} \rightarrow \text{HNCO} + \text{H} \quad (31)
\]
\[
\text{HCN} + \text{M} \rightarrow \text{H} + \text{CN} + \text{M} \quad (32)
\]
HCN + OH → CN + H₂O  \hspace{1cm} (33)

There are also some important nitrogen intermediates formed during the conversion of NH₃ and HCN, such as NCO, NH, NH₂, and HNO. Whether the fuel-N is finally converted into NO or N₂ depends on the formation and evolution of these nitrogen intermediates, which are significantly affected by the presence of H, O and OH radicals in the reaction atmosphere. Determined by the combustion temperature and SR, different concentrations of H, O and OH radicals lead to different NOₓ emissions. Under the high temperature and strong reducing atmosphere conditions, the H atom concentration is increased, and the OH/H ratio and O/H ratio are decreased correspondingly. As a result, the reactions by which the nitrogen intermediates are oxidized to NO are inhibited, while those promoting the NO reduction to N₂ are enhanced. For O₂/CO₂ combustion, reaction 12 is considered to be responsible for the impact of high CO₂ concentration. It can compete with reaction 34 for H \[30,37\], which changes the concentrations of H, O and OH radicals in the reaction atmosphere.

\[ \text{H} + \text{O}_2 \to \text{O} + \text{OH} \hspace{1cm} (34) \]

Figure 11 gives the results of a first-order sensitivity analysis for N₂ at the SR of 0.7 in air combustion. Here, the effect of temperature on N₂ production is detected emphatically. The first-order sensitivity coefficients of some reactions are negative at a low temperature, while they become positive at a high temperature, which means that these reactions play important roles in the reduction of NOₓ to N₂. With the increasing temperature, the function of these reactions switches from inhibiting N₂ production to facilitating it. This is because the increasing rate constant of each reaction induced by the higher temperature changes the radical pool composition and size in the reaction atmosphere. Moreover, N₂ is mostly sensitive to the reactions that generate or consume H and CH₃ radicals under the high temperature and strong reducing atmosphere conditions. For instance, increasing the rate of reaction 34 will promote NOₓ reduction. Similarly, Figure 12 displays the first-order sensitivity analysis for N₂ in O₂/CO₂ combustion. Due to reaction 12, some reactions for CH₃ consumption become bottlenecks in N₂ formation, besides reaction 34.

**Figure 11.** First-order sensitivity analysis for N₂ at different temperatures in air combustion (SR = 0.7).
Figure 12. First-order sensitivity analysis for N\textsubscript{2} at different temperatures in O\textsubscript{2}/CO\textsubscript{2} combustion (SR = 0.7).

5. Conclusions

In this study, a methane flame doped with ammonia and hydrogen cyanide for fuel-N in a tandem-type tube furnace was simulated to investigate the characteristics of NO\textsubscript{x} emissions under a high temperature and strong reducing atmosphere conditions in staged air and O\textsubscript{2}/CO\textsubscript{2} combustion by CHEMKIN. The effects of combustion temperature and stoichiometric ratio on the NO\textsubscript{x} emissions were examined, and the elementary steps for NO\textsubscript{x} formation and reduction at high temperatures were identified. The following conclusions can be drawn:

In both staged air and staged O\textsubscript{2}/CO\textsubscript{2} combustion (SR < 1), the NO\textsubscript{x} CRs at the main combustion zone exit increase as the SR rises, and they are slightly affected by the combustion temperature. The NO\textsubscript{x} CRs at the burnout zone exit decrease with the increasing SR at low temperatures, and they are much higher than those at the main combustion zone exit. Here, a lot of nitrogen compounds remain in the exhaust of the main combustion zone and can be easily oxidized to NO\textsubscript{x} with the injection of secondary gas. Staged combustion can lower the NO\textsubscript{x} emission levels significantly, especially under a high temperature (≥1600 °C) and strong reducing atmosphere (SR ≤ 0.8) conditions. Increasing the combustion temperature under strong reducing atmosphere conditions can raise the H atom concentration and change the radical pool composition and size. Therefore, the reactions by which NO is reduced to N\textsubscript{2} are facilitated. In addition, the increased OH/H ratio through reaction 12 offsets part of the reducibility in staged O\textsubscript{2}/CO\textsubscript{2} combustion, resulting in the final NO\textsubscript{x} emissions in O\textsubscript{2}/CO\textsubscript{2} combustion being higher than those in air combustion at the same high temperature and strong reducing atmosphere conditions.

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Nomenclature

- $A$: pre-exponential factor (L/(mol·s))
- $E$: activation energy (kJ/mol)
- $k$: reaction rate constant (L/(mol·s))
- $NO_x$: conversion ratio of fuel-N to NOx (%)
- $R$: molar gas constant (kJ/(mol·K))
- $SR$: stoichiometric ratio (-)
- $T$: reaction temperature (K)
- $V$: volume flow rate (Ncm³/min)
- $Y$: mole fraction (-)
- $\beta$: correction factor (-)
- $\kappa$: first-order sensitivity coefficient (-)
- $i$: index for reaction
- $j$: index for species
- $st$: stoichiometric condition

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