A KINETIC EVALUATION ON NO₂ FORMATION IN THE POST-FLAME REGION OF PRESSURIZED OXY-COMBUSTION PROCESS

by

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Pressurized oxy-combustion is a promising technology that can significantly reduce the energy penalty associated with first generation oxy-combustion for CO₂ capture in coal-fired power plants. However, higher pressure enhances the production of strong acid gases, including NO₂ and SO₃, aggravating the corrosion threat during flue gas re-circulation. In the flame region, high temperature NOₓ exists mainly as NO, while conversion from NO to NO₂ happened in post-flame region. In this study, the conversion of NO → NO₂ has been kinetically evaluated under representative post-flame conditions of pressurized oxy-combustion after validating the mechanism (80 species and 464 reactions), which includes nitrogen and sulfur chemistry based on GRI-MECH 3.0. The effects of residence time, temperature, pressure, major species (O₂/H₂O), and minor or trace species (CO/SOₓ) on NO₂ formation are studied. The calculation results show that when pressure is increased from 1 to 15 bar, NO₂ is increased from 1 to 60 ppm, and the acid dew point increases by over 80 °C. Higher pressure and temperature greatly reduce the time required to reach equilibrium. With increasing pressure and decreasing temperature, O plays a much more important role than HO₂ in the oxidation of NO. A higher water vapor content accelerates NO₂ formation in all cases by providing more O and HO₂ radicals. The addition of CO or SO₂ also promotes the formation of NO₂. The NO₂ formation in a pressurized oxy-combustion furnace can be over 10 times that of an atmospheric air-combustion furnace.

Key words: NO₂, pressurized oxy-combustion, detailed mechanism, post-flame region

Introduction

Oxy-coal combustion is one of the routes for controlling CO₂ emissions from coal combustion, however, first-generation oxy-combustion technologies, operated under atmos-
pheric pressure suffered a significant energy penalty in net generating efficiency of more than 10 percentage points. This is primarily due to the auxiliary energy consumption from the air separation unit, flue gas re-circulation (FGR), and gas processing unit (GPU). A promising new technology is pressurized oxy-combustion (POC), which can increase the plant efficiency by recovering the latent heat in the flue gas moisture and coupled it back with the steam cycle [1]. Since 2000, POC technologies have been developed by ThermoEnergy/CANMET and ETEA/ENEL, with the highest net plant efficiency around 33.5% high heating value (HHV).

In recent years, research at Washington University in St. Louis has proposed a unique POC process aiming at minimize the recycled flue gas through fuel staging combustion [2]. The process is termed the staged POC process (SPOC), and has a net efficiency of 35.7-36.7% HHV, which is only 4 percentage points lower than that of normal air combustion [3].

The POC appears to be a promising way to increase the net efficiency of oxy-combustion, whereas, high pressure enhances the production of strong acid gases, including NO, aggravating the low temperature corrosion. Another motivation in terms of the importance of NO in POC, is closely related with a new developed technology of integrated SOₓ/NOₓ removal during GPU process at elevated pressures [4]. In this technology, only when NO₂ is formed in gas phase, it is able to active the fast dissolution of NO in liquid [5], and to oxidize SO₂ into SO₃ or oxidize H₂SO₃ into H₂SO₄ under the interaction between SOₓ/NOₓ in gas or liquid, respectively [6].

The NO₂ formation is more significant at lower temperature (in the post-flame region) and higher pressure [7]. However, the formation of NO₂ receive little attention in combustion process, since NO₂ is unstable at high temperatures, regardless of pressure, and only a negligible amount can be produced in post-flame area at atmospheric pressure [8]. There are few studies on specific formation of NO₂ formation in post-flame region at elevated pressure, except for the studies of slow conversion kinetics of NO → NO₂ in atmosphere chemistry [9] and in post-flame region at atmospheric pressure [10], and the related interaction of NO₂ during gas fuel oxidation process [11].

Glarborg et al. [12] experimentally and numerically studied the impact of NO and NO₂ on CO oxidation at atmospheric pressure in the temperature range of 800-1400 K. It was found that low-concentration of NO enhances CO oxidation in the 900-1100 K range by converting NO₂ to OH through NO₂ + NO = NO₂ + OH (R1) and a catalytic recycle reaction through NO₂ + H = NO + OH (R2). The NO₂ is much more efficient than NO in removing radicals and has a strong inhibiting effect on CO oxidation. They also illustrated that the presence of NO₂ impurities may significantly affect the experiments containing NO. Rasmussen et al. [13] continued this study at 20-100 bar and 600-900 K in a pressurized flow reactor. It was found that at elevated pressure, besides R1 and R2, the effect of the recycling reactions NO + O + M = NO₂ + M (R3), NO + O₂ = NO₂ + O (R4), NO₂ + HO₂ = HONO + O₂ (R5), and HONO + M = NO + OH + M (R6) also become important. Mueller et al. [14] also observed the similar results, and their further measurement at elevated pressures show that the overall effect of NO on fuel oxidation and the conversion of NO → NO₂ depend strongly on pressure and stoichiometry (oxygen concentration). The model predictions using the detailed mechanism are in good agreement with the experimental data over the wide temperature and pressure ranges.

Gersen et al. [15] studied the effect of NO₂ on the ignition of CH₄ and C₂H₆ in a rapid compression machine (25-50 bar), and indicated that the generation of chain-initiating OH radicals through reactions R1 and R2 is one of the most important routes. Krzywanski and Novak [16] and Liu and Gibbs [17] also pointed that in circulating fluidized bed the high CO₂ concentration could inhibit the calcination of limestone, which will increase the formation of NOₓ.
Hori et al. [10] studied the promotion effect of hydrocarbons on the NO → NO₂ conversion in an atmospheric pressure flow reactor at 600-1100 K. It was found that hydrocarbons oxidize NO to NO₂ predominantly through R1, and hydrocarbon oxidation leads to additional HO₂ production, and the effectiveness of hydrocarbon on the NO → NO₂ conversion depends strongly on fuel type and temperature. Mueller et al. [18] further studied the interaction between SO₂ and NO in the CO/H₂O/O₂/NO/SO₂ system, at pressures and temperatures ranging from 0.5-10.0 bar and 950-1040 K, respectively. They concluded that at higher pressures, where the conversion ratio of NO → NO₂ increases, the interaction via SO₂ + NO₂ = SO₃ + NO (R7) also becomes important and cannot be neglected.

All the mentioned studies have ensured the impact of NO₂ on multi species oxidation through several recycling reaction pathways. The impacts are closely related to HO₂, H, OH, and other intermediate radicals, and are strongly dependent on pressure, temperature and atmosphere. In POC process, the flue gas composition in the post-flame region is far different from that in traditional air combustion [19], e.g., the SO₂ concentration is higher by several times; the moisture content depends on warm or cold FGR recycling. Besides of the elevated pressure, the temperature distribution and residence time in post-flame region can also be much different depending on the furnace design. These prominent differences in POC process, indicate a potential different NO₂ emission from traditional air combustion [20].

This study aims to clarify the NO₂ formation mechanism in POC. The conversion of NO → NO₂ has been kinetically evaluated under representative post-flame conditions of POC after validating an updated detailed mechanism. The effects of residence time, temperature, pressure, major species (O₂/H₂O), and minor or trace species (CO/SO₂) on NO₂ formation are studied. Sensitivity analysis and reaction pathway analysis are conducted to demonstrate the interaction mechanism, respectively.

**Modeling approach**

*Experimental reference*

Up to now, only two valuable groups related to NO₂ production at high pressure were reported in the literature. Dayma and Dagaut [21] used a spherical fused silica jet-stirred reactor [22] wrapped with ceramic wool and located inside a stainless-steel pressure resistant jacket allowing operation up to 10 atmosphere. The effect of NO or NO₂ addition on H₂ oxidation in this reactor were analyzed and their experimental results were plotted in fig. 1(a).

Mueller et al. [18] studied the effect of trace SO₂ and NO on CO oxidation in a pressurized flow reactor [23], which can produce a homogenous, premixed, highly dilute, 1-D gas flow at sufficient initial temperatures to initiate chemical reaction of the mixture. The high pressure experimental results were plotted in fig. 1(b). The uncertainties in these measurements are: H₂O, 5%; O₂, 4%; CO, 3%; CO₂, 3%; NO, 5%; NO₂, 5%, and SO₂, 3% of the reading.

*Gas-phase model*

In this study, a detailed gas-phase mechanism including nitrogen and sulfur chemistry based on GRI-MECH 3.0 was adopted for the evaluating calculation. The GRI-MECH 3.0 is an optimized mechanism designed to model natural gas combustion, including NO formation and reburn chemistry [24]. To understand the interaction of SO₂ and NO in POC condition, in which, the mechanism of sulfur and SO₂/NO₂ interaction are added from Glarborg et
al. [25]. The full mechanism includes 80 species and 464 steps. The CHEMKIN is a software package with purpose to facilitate the formation, solution, and interpretation of problems involving elementary gas-phase chemical kinetics. It provides a flexible and powerful tool for incorporating complex chemical kinetics into simulations of fluid dynamics [26]. Plug flow reactor (PFR) is a continuous reaction flow model in CHEMKIN software package, which is used to simulate the post flame region and analyze the products with respect to the residence time. In this model, it is assumed that there is no back mixing in the flow direction and there is good mixing in each reactor section perpendicular to the flow direction, so the mass diffusion is ignorable [27]. Rate of production (ROP) analysis are useful tools in interpreting detailed chemical kinetics calculations and can provide a better understanding of the contribution of each reaction [28]. Sensitivity analysis is also another useful tool in understanding the role of each reaction. This method can find out the rate-limiting reactions and analyze the importance of each reaction in the whole system.

Two representative experimental result from Dayma and Dagaut [21] are compared with the predicted results by the mechanism in this study. As shown in fig. 1(a), the predicted results agree well with the experimental data at either fuel-rich or fuel-lean condition. Mueller et al. [18] measured NO2 emissions at 1.2 bar, 3 bar, 6.5 bar, and 10 bar, which are plotted in fig. 1(b) to compare with the calculation results of this model. The comparison indicates that the mechanism used in this study is able to predict the interaction among NOx, CO, and SOx.

![Figure 1. Mechanism validating by comparison with the data in literatures; (a) 1 second, 10 atm, 1% H2, Case 1: 220 ppm NO, 0.333% O2; Case 2: 65 ppm NO2, 1% O2; (b) 950 K, 0.51% CO, 0.75% O2, 0.49% H2O, 97 ppm NO, 500 ppm SO2]({})

**Test conditions**

The conditions used are taken according to the real post-flame conditions of POC (1-15 bar, 700-1100 °C), and with the composition of 1000 ppm NO, 5% O2, 15% H2O, trace CO/SO2, while CO2 is injected as the balance gas to simulate the oxy-combustion atmosphere. The tested ranges of pressure, temperature, and specie concentration are listed in tab. 1. The residence time ranges from 0.01 seconds to 10 seconds, depending on the temperature and pressure. Gopan et al. [3] found that when the pressure is higher than 16 bar, the effect of pressure on the net plant efficiency is small. Therefore, the pressure range in this paper is selected with 1-15 bar.
Table 1. The range of tested temperature, pressure, and specie concentration

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Ranges</th>
<th>Units</th>
<th>Variable gas composition</th>
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</thead>
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<tr>
<td>Temperature</td>
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<td>1000 ppm NO, 5% O₂, 15% H₂O, CO₂ as balance gas</td>
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<tr>
<td>Pressure</td>
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<td>bar</td>
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<td>O₂</td>
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<td>%</td>
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<td>1-25</td>
<td>%</td>
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<td>ppm</td>
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<td>SO₂</td>
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Results and discussion

Effect of pressure and temperature

The effects of pressure and temperature on NO₂ formation in a pressurized PFR are shown in fig. 2. Higher pressure and temperature are seen to greatly reduce the time required to reach equilibrium, e.g., at 15 bar and 1300 °C, equilibrium is reached in 1 millisecond and the NO₂/NO is about 0.8%; while at 1 bar and 800 °C, it needs more than 100 seconds to reach equilibrium. As shown in fig. 2(a), at 15 bar, as the temperature increases from 1000 °C to 1300 °C the time up to the equilibrium of NO₂ formation reduces, which means that high temperature is favorable for the NO₂ formation. The influence of pressure on the NO₂ formation is shown in fig. 2(b). At both 900 °C and 1000 °C, NO₂ formation is enhanced as the pressure increases from 1 bar to 15 bar. Under POC conditions, the NO₂ formation are several times higher than the atmospheric air-combustion (AAC), tab. 2.

The ROP analysis indicates that the formation of NO₂ is mainly through R1, R3, R4, and R5 by the oxidation by HO₂, O, and O₂, respectively. However, the contributions of these three reactions strongly depend on pressure and temperature. At atmospheric pressure and high temperature, R3 runs backwards and consumes NO₂, and most of the NO₂ is produced through R1 by the oxidation of HO₂, where the effect of reaction O₂ + H₂O = OH + HO₂ (R8) is important. However, with decreasing temperature and increasing pressure, R3 runs forward...
and promotes NO₂ formation, and at certain conditions, its contribution to NO₂ is larger than that of R1.

Table 2. The ROP analysis at varied temperature and pressure

<table>
<thead>
<tr>
<th>Conditions</th>
<th>1 bar</th>
<th>15 bar</th>
</tr>
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<td><img src="image2.png" alt="Graph" /></td>
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<tr>
<td>1100 °C</td>
<td><img src="image3.png" alt="Graph" /></td>
<td><img src="image4.png" alt="Graph" /></td>
</tr>
</tbody>
</table>

1 – total, 2 – HO₂ + NO = NO₂ + OH, 3 – NO + O + M = NO₂ + M, 4 – NO + O₂ = NO₂ + O

Effect of O₂ and H₂O

Effect of O₂ concentration on NO₂ formation in POC is shown in fig. 3(a). With the increasing in O₂ concentration from 0.1% to 15%, the equilibrium NO₂ yield increases with O₂ concentration to the power of 0.5, and the time to reach equilibrium is also reduced.

In the POC system, depending on dry or wet FGR and coal type, the H₂O concentration in flue gas can vary dramatically. The effect of H₂O concentration on NO₂ formation is shown in fig. 3(b). Similar to O₂, the increasing in concentration also accelerates the formation of NO₂ and shortens the time to reach equilibrium; however, it does not affect the equilibrium point for NO₂ yield.

At shown in tab. 3, at 1 bar and 900 °C, NO₂ formation is mainly via R3, R4, R1. In contrast, R1 can be a little stronger than R4 when the H₂O concentration is 15%. In wet recycling R1 can become important than R3 and R4 at 15 bar, and 1100 °C.

The promotion of both O₂ and H₂O on NO₂ formation is due to the enhancement of OH and HO₂ formation through R8.
Figure 3. Effect of $O_2$ (a) and $H_2O$ (b) (1000 ppm NO, 900 °C, 15 bar); (a) effect of $O_2$ and (b) effect of $H_2O$

Table 3. The ROP analysis comparison between low- and high-moisture conditions (15 bar)

<table>
<thead>
<tr>
<th>Conditions</th>
<th>1% H$_2$O (dry recycling)</th>
<th>15% H$_2$O (wet recycling)</th>
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<tbody>
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<td><img src="chart1.png" alt="Graph" /></td>
<td><img src="chart2.png" alt="Graph" /></td>
</tr>
<tr>
<td>1100 °C</td>
<td><img src="chart3.png" alt="Graph" /></td>
<td><img src="chart4.png" alt="Graph" /></td>
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</tbody>
</table>

**Effect of CO and SO$_2$**

The effects of CO on NO$_2$ formation during POC are shown in fig. 4(a). With increasing the CO concentration, a large amount of NO$_2$ is produced within about 0.1 seconds, and then gradually decreases into the equilibrium yield without CO addition. As shown in fig. 4(b), at initial time, the concentration of CO decreases while NO$_2$ formation increases.
quickly, indicating that CO consumption promotes NO₂ formation. To elaborate the NO₂ formation mechanism, the reaction is divided into A and B region by the NO₂ peak.

Figure 4. Effect of CO concentration on NO₂ formation; (a) NO₂ profile at different CO concentrations and (b) simultaneous profile of CO and NO₂ (CO = 1000 ppm)

The ROP and sensitivity analysis on NO₂ formation in the stage A and B is shown in figs. 5(a) and 5(b), respectively. The CO is mainly oxidized by OH through CO + OH = = CO₂ + H (R9), while the conversion of NO → NO₂ is through the oxidation by HO₂ through R1. At the starting stage of CO oxidation, the large consumption of OH promotes the forward reaction of R1. With the consumption of HO₂ and the increase in NO₂, the ROP of R1 producing NO₂ decreases while that of R5 and R6 consuming NO₂ is enhanced, which results in a subsequent decrease of NO₂.

Figure 5. The ROP and sensitivity analysis on NO₂ formation (1000 ppm NO, 5% O₂, 15% H₂O, 900 °C, 15 bar); (a) ROP and (b) sensitivity

The effects of SO₂ on NO₂ formation in POC are shown in fig. 6. It can be seen that the increase in SO₂ concentration promotes the formation of NO₂, and a large amount of SO₃ is accompanied. The ROP analysis of NO₂ and SO₃ are shown in figs. 7(a) and 7(b), respectively. The NO₂ is mainly produced through the oxidation of NO by HO₂ with the production of OH, while consumed by SO₂ so as to enhance the formation of SO₃. The SO₃ formation is mainly through the oxidation of HOSO₂ by O₂ with the production of HO₂. In related to the formation of HOSO₂, the consumption of OH is necessary. The production and consumption of OH, HO₂ acts like catalyst, which promotes the formation of NO₂ and SO₃. The interaction between SOₓ and NOₓ at elevated pressures can be explained by a cycle which consists of three reactions...

\[
\text{HO}_2 + \text{NO} = \text{NO}_2 + \text{OH} \quad \text{(R1)},
\text{SO}_2 + \text{OH} + \text{M} = \text{HOSO}_2 + \text{M} \quad \text{(R10)},
\text{HOSO}_2 + \text{O}_2 = \text{HO}_2 + \text{SO}_3 \quad \text{(R11) with the global reaction NO} + \text{SO}_2 + \text{O}_2 = \text{NO}_2 + \text{SO}_3 \quad \text{(R12)} \quad [29].
\]

Figure 6. Effect of SO₂ concentration on NO₂ formation (1000 ppm NO, 5% O₂, 15% H₂O, 900 °C, 15 bar; SO₃ – dash line, NO₂ – solid line); (a) 900°C, 1 bar and (b) 900°C, 15 bar; 1 – SO₂ = 0 ppm, 2 – SO₂ = 100 ppm, 3 – SO₂ = 500 ppm, 4 – SO₂ = 1000 ppm

Figure 7. The ROP analysis on NO₂ and SO₃ formation when SO₂ is added (1000 ppm NO, 5% O₂, 15% H₂O, 900 °C, 15 bar); (a) NO₂ and (b) SO₃

Comparison of NO₂ formation in the post-flame region of pulverized coal boilers in air-combustion and POC

Based on the analysis results in sections Effect of pressure and temperature, Effects of O₂ and H₂O, and Effects of CO and SO₂, and according to the boiler temperature profiles shown in fig. 8 [30], the NO₂ formation is evaluated in a practical AAC furnace and a POC furnace. Because the flue gas volume is compressed proportionally with pressure, the residence time in the POC furnace is much longer. The initial gas composition is from the measurement by Tan et al. [31], including bituminous (SB) and lignite (LN) coals.

Figure 8. Temperature profile in pulverized coal boilers of air-combustion [30] and POC [32]
The results, plotted in fig. 9, show that for the sub-bituminous coal, the NO$_2$ yield reaches 51 ppm, which is over 10 times that of the AAC furnace (4.6 ppm). Similar results can also be observed in lean coal. This strong promotion of NO$_2$ formation is mainly due to the longer residence time and the enhancement of reactions R3 and R12 at elevated pressures.

**Figure 9.** The NO$_2$ formation in pulverized coal boilers of air-combustion (1 bar) and POC (15 bar); (a) 1 bar and (b) 15 bar

**Conclusion**

- Higher pressure and temperature greatly reduce the time required to reach equilibrium, such that NO$_2$ formation is negligible at sufficiently high temperature, e.g., at 15 bar and 1100 °C, the equilibrium of NO/NO$_2$ system is reached in 10 milliseconds.
- For all cases studied, there was less than 4% conversion from NO to NO$_2$ within 1 second. The formation and destruction of NO$_2$ is generally through the reactions: NO + O + + M = NO$_2$ + M, HO$_2$ + NO = NO$_2$ + OH, and NO + O$_2$ = NO$_2$ + O. At the higher temperatures (e.g., 1100 °C), the oxidation of NO by HO$_2$ and the reaction O$_2$ + H$_2$O = OH + HO$_2$ become more important. At these temperatures and at lower pressures, NO$_2$ is reduced via NO + O + + M = NO$_2$ + M, in contrast of producing NO$_2$ at higher pressures.
- A higher water vapor content accelerates NO$_2$ formation in all cases by providing more O and HO$_2$ radicals. The addition of CO or SO$_2$ accelerates the formation of NO$_2$. The effect of CO is mainly through the reaction CO + OH = H + CO$_2$. The effect of SO$_2$ is mainly through the reaction HOSO$_2$ + O$_2$ = HO$_2$ + SO$_3$, which produces HO$_2$ for NO oxidation. The direct interaction of SO$_2$ + NO$_2$ = SO$_3$ + NO inhibits NO$_2$ formation. At higher pressure and lower temperature (e.g., 1100 °C and 1 bar) the influence of SO$_2$ on NO$_2$ formation is small.
- The NO$_2$ formation in a POC furnace can be over 10 times that of an AAC furnace, such that increase the acid dew point and aggravate the low-temperature corrosion. It is suggested that NO$_2$ formation and reduction should be taken into consideration in a POC.

**Acknowledgment**

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Nomenclature

AAC – atmospheric air-combustion
FGR – gas re-circulation
GPU – gas processing unit
HHV – high heating value
PFR – plug flow reactor
POC – pressurized oxy-combustion
SPOC – staged POC

References


