#### 2609

# A KINETIC EVALUATION ON NO<sub>2</sub> FORMATION IN THE POST-FLAME REGION OF PRESSURIZED OXY-COMBUSTION PROCESS

#### by

# Xuebin WANG<sup>a,b</sup>\*, Gaofeng DAI<sup>a</sup>, Gregory S. YABLONSKY<sup>c</sup>, Milan VUJANOVIĆ<sup>a</sup>, and Richard L. AXELBAUM<sup>b</sup>

 <sup>a</sup> MOE Key Laboratory of Thermo-Fluid Science and Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi, China
<sup>b</sup> Department of Energy, Environmental and Chemical Engineering, Consortium for Clean Coal Utilization, Washington University in St. Louis, St. Louis, Mo., USA
<sup>c</sup> Parks College of Engineering, Aviation and Technology, Saint Louis University, St. Louis, Mo., USA
<sup>d</sup> Faculty of Mechanical Engineering and Naval Architecture, University of Zagreb, Zagreb, Croatia Original scientific paper https://doi.org/10.2298/TSCI200415236W

Pressurized oxy-combustion is a promising technology that can significantly reduce the energy penalty associated with first generation oxy-combustion for  $CO_2$ capture in coal-fired power plants. However, higher pressure enhances the production of strong acid gases, including  $NO_2$  and  $SO_3$ , aggravating the corrosion threat during flue gas re-circulation. In the flame region, high temperature  $NO_x$ exists mainly as NO, while conversion from NO to  $NO_2$  happened in post-flame region. In this study, the conversion of  $NO \rightarrow NO_2$  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  $(O_2/H_2O)$ , and minor or trace species  $(CO/SO_x)$ on  $NO_2$  formation are studied. The calculation results show that when pressure is increased from 1 to 15 bar,  $NO_2$  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  $HO_2$  in the oxidation of NO. A higher water vapor content accelerates NO<sub>2</sub> formation in all cases by providing more O and HO<sub>2</sub> radicals. The addition of CO or SO<sub>2</sub> also promotes the formation of NO<sub>2</sub>. The NO<sub>2</sub> formation in a pressurized oxy-combustion furnace can be over 10 times that of an atmospheric air-combustion furnace.

Key words: NO<sub>2</sub>, pressurized oxy-combustion, detailed mechanism, post-flame region

## Introduction

Oxy-coal combustion is one of the routes for controlling CO<sub>2</sub> emissions from coal combustion, however, first-generation oxy-combustion technologies, operated under atmos-

<sup>\*</sup> Corresponding author, e-mail: wxb005@mail.xjtu.edu.cn

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 oxycombustion, whereas, high pressure enhances the production of strong acid gases, including NO<sub>2</sub>, aggravating the low temperature corrosion. Another motivation in terms of the importance of NO<sub>2</sub> in POC, is closely related with a new developed technology of integrated SO<sub>x</sub>/NO<sub>x</sub> removal during GPU process at elevated pressures [4]. In this technology, only when NO<sub>2</sub> is formed in gas phase, it is able to active the fast dissolution of NO<sub>x</sub> in liquid [5], and to oxidize SO<sub>2</sub> into SO<sub>3</sub> or oxidize H<sub>2</sub>SO<sub>3</sub> into H<sub>2</sub>SO<sub>4</sub> under the interaction between SO<sub>x</sub>/NO<sub>x</sub> in gas or liquid, respectively [6].

The NO<sub>2</sub> formation is more significant at lower temperature (in the post-flame region) and higher pressure [7]. However, the formation of NO<sub>2</sub> receive little attention in combustion process, since NO<sub>2</sub> is unstable at high temperatures, regardless of pressure, and only a neglectable amount can be produced in post-flame area at atmospheric pressure [8]. There are few studies on specific formation of NO<sub>2</sub> formation in post-flame region at elevated pressure, except for the studies of slow conversion kinetics of NO  $\rightarrow$  NO<sub>2</sub> in atmosphere chemistry [9] and in post-flame region at atmospheric pressure [10], and the related interaction of NO<sub>2</sub> during gas fuel oxidation process [11].

Glarborg et al. [12] experimentally and numerically studied the impact of NO and NO<sub>2</sub> 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 HO<sub>2</sub> to OH through HO<sub>2</sub> + NO = NO<sub>2</sub> + OH (R1) and a catalytic recycle reaction through  $NO_2 + H = NO + OH$  (R2). The  $NO_2$  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 NO<sub>2</sub> 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 +  $+ O + M = NO_2 + M$  (R3), NO  $+ O_2 = NO_2 + O$  (R4), NO<sub>2</sub>  $+ HO_2 = HONO + O_2$  (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  $\rightarrow$  NO<sub>2</sub> 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 NO<sub>2</sub> on the ignition of CH<sub>4</sub> and  $C_2H_6$  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 CO<sub>2</sub> concentration could inhabit the calcination of limestone, which will increase the formation of NO<sub>x</sub>.

Hori *et al.* [10] studied the promotion effect of hydrocarbons on the NO  $\rightarrow$  NO<sub>2</sub> conversion in an atmospheric pressure flow reactor at 600-1100 K. It was found that hydrocarbons oxidize NO to NO<sub>2</sub> predominantly through R1, and hydrocarbon oxidation leads to additional HO<sub>2</sub> production, and the effectiveness of hydrocarbon on the NO  $\rightarrow$  NO<sub>2</sub> conversion dependents strongly on fuel type and temperature. Mueller *et al.* [18] further studied the interaction between SO<sub>2</sub> and NO in the CO/H<sub>2</sub>O/O<sub>2</sub>/NO/SO<sub>2</sub> 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  $\rightarrow$  NO<sub>2</sub> increases, the interaction *via* SO<sub>2</sub> + NO<sub>2</sub> = SO<sub>3</sub> + NO (R7) also becomes important and cannot not be neglected.

All the mentioned studies have ensured the impact of  $NO_x$  on multi species oxidation through several recycling reaction pathways. The impacts are closely related to  $HO_2$ , 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 SO<sub>x</sub> 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  $NO_2$  emission from traditional air combustion [20].

This study aims to clarify the NO<sub>2</sub> formation mechanism in POC. The conversion of NO  $\rightarrow$  NO<sub>2</sub> 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 (O<sub>2</sub>/H<sub>2</sub>O), and minor or trace species (CO/SO<sub>x</sub>) on NO<sub>2</sub> 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 NO<sub>2</sub> 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 NO<sub>2</sub> addition on H<sub>2</sub> oxidation in this reactor were analyzed and their experimental results are plotted in fig. 1(a).

Mueller *et al.* [18] studied the effect of trace  $SO_2$  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: H<sub>2</sub>O, 5%; O<sub>2</sub>, 4%; CO, 3%; CO<sub>2</sub>, 3%; NO, 5%; NO<sub>2</sub>, 5%, and SO<sub>2</sub>, 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 SO<sub>x</sub> and NO<sub>x</sub> in POC condition, in which, the mechanism of sulfur and SO<sub>x</sub>/NO<sub>x</sub> 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 is 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 NO<sub>2</sub> 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 NO<sub>x</sub>, CO, and SO<sub>x</sub>.



Figure 1. Mechanism validating by comparison with the data in literatures; (a) 1 second, 10 atm., 1% H<sub>2</sub>, Case 1: 220 ppm NO, 0.333% O<sub>2</sub>; Case 2: 65 ppm NO<sub>2</sub>, 1% O<sub>2</sub> [15] and (b) 950 K, 0.51% CO, 0.75% O<sub>2</sub>, 0.49% H<sub>2</sub>O, 97 ppm NO, 500 ppm SO<sub>2</sub> [10]

#### 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% O<sub>2</sub>, 15% H<sub>2</sub>O, trace CO/SO<sub>2</sub>, while CO<sub>2</sub> 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. Wang, X., et al.: A Kinetic Evaluation on NO<sub>2</sub> Formation in the Post-Flame Region of ... THERMAL SCIENCE: Year 2021, Vol. 25, No. 4A, pp. 2609-2620

	8	-	
Parameters	Ranges	Units	Variable gas composition
Temperature	700-1300	[°C]	1000 ppm NO, 5% O <sub>2</sub> , 15% H <sub>2</sub> O, CO <sub>2</sub> as balance gas
Pressure	1-15	[bar]	1000 ppm NO, 5% O <sub>2</sub> , 15% H <sub>2</sub> O, CO <sub>2</sub> as balance gas
O2	0-15	[%]	1000 ppm NO, 15% H <sub>2</sub> O, CO <sub>2</sub> as balance gas
H <sub>2</sub> O	1-25	[%]	1000 ppm NO, 5% O <sub>2</sub> , CO <sub>2</sub> as balance gas
СО	0-10000	[ppm]	1000 ppm NO, 5% O <sub>2</sub> , 15% H <sub>2</sub> O, CO <sub>2</sub> as balance gas
SO <sub>2</sub>	0-5000	[ppm]	1000 ppm NO, 5% O <sub>2</sub> , 15% H <sub>2</sub> O, CO <sub>2</sub> as balance gas

Table 1. The range of tested temperature, pressure, and specie concentration

#### **Results and discussion**

## Effect of pressure and temperature

The effects of pressure and temperature on NO<sub>2</sub> 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 NO<sub>2</sub>/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 NO<sub>2</sub> formation reduces, which means that high temperature is favorable for the NO<sub>2</sub> formation. The influence of pressure on the NO<sub>2</sub> formation is shown in fig. 2(b). At both 900 °C and 1000 °C, NO<sub>2</sub> formation is enhanced as the pressure increases from 1 bar to 15 bar. Under POC conditions, the NO<sub>2</sub> formation are several times higher than the atmospheric air-combustion (AAC), tab. 2.



Figure 2. The NO<sub>2</sub> formation along the residence time at different temperatures and pressures (1000 ppm NO, 5% O<sub>2</sub>, 15% H<sub>2</sub>O, CO<sub>2</sub> as balance); (a) effect of temperature at 15 bar and (b) effect of pressure at 900 and 1000 °C

The ROP analysis indicates that the formation of NO<sub>2</sub> is mainly through R1, R3, R4, and R5 by the oxidation by HO<sub>2</sub>, O, and O<sub>2</sub>, 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 NO<sub>2</sub>, and most of the NO<sub>2</sub> is produced through R1 by the oxidation of HO<sub>2</sub>, where the effect of reaction  $O_2 + H_2O = OH + HO_2$  (R8) is important. However, with decreasing temperature and increasing pressure, R3 runs forward and promotes  $NO_2$  formation, and at certain conditions, its contribution to  $NO_2$  is larger than that of R1.



Table 2. The ROP analysis at varied temperature and pressure

## Effect of O2 and H2O

Effect of  $O_2$  concentration on  $NO_2$  formation in POC is shown in fig. 3(a). With the increasing in  $O_2$  concentration from 0.1% to 15%, the equilibrium  $NO_2$  yield increases with  $O_2$  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  $H_2O$  concentration in flue gas can vary dramatically. The effect of  $H_2O$  concentration on NO<sub>2</sub> formation is shown in fig. 3(b). Similar to O<sub>2</sub>, the increasing in concentration also accelerates the formation of NO<sub>2</sub> and shortens the time to reach equilibrium; however, it does not affect the equilibrium point for NO<sub>2</sub> yield.

At shown in tab. 3, at 1 bar and 900 °C, NO<sub>2</sub> formation is mainly via R3, R4, R1. In contrast, R1 can be a little stronger than R4 when the H<sub>2</sub>O concentration is 15%. In wet recycling R1 can become important than R3 and R4 at 15 bar, and 1100 °C.

The promotion of both  $O_2$  and  $H_2O$  on  $NO_2$  formation is due to the enhancement of OH and  $HO_2$  formation through R8.

 $<sup>1 - \</sup>text{total}, 2 - \text{HO}_2 + \text{NO} = \text{NO}_2 + \text{OH}, 3 - \text{NO} + \text{O} + \text{M} = \text{NO}_2 + \text{M}, 4 - \text{NO} + \text{O}_2 = \text{NO}_2 + \text{O}_2 + \text$ 





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)

# Effect of CO and SO<sub>2</sub>

The effects of CO on NO<sub>2</sub> formation during POC are shown in fig. 4(a). With increasing the CO concentration, a large amount of NO<sub>2</sub> 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 concertation of CO decreases while NO<sub>2</sub> formation increases

quickly, indicating that CO consumption promotes NO<sub>2</sub> formation. To elaborate the NO<sub>2</sub> formation mechanism, the reaction is divided into A and B region by the NO<sub>2</sub> peak.



Figure 4. Effect of CO concentration on NO<sub>2</sub> formation; (a) NO<sub>2</sub> profile at different CO concentrations and (b) simutaneous profile of CO and NO<sub>2</sub> (CO = 1000 ppm)

The ROP and sensitivity analysis on NO<sub>2</sub> 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 =  $= CO_2 + H$  (R9), while the conversion of NO  $\rightarrow$  NO<sub>2</sub> is through the oxidation by HO<sub>2</sub> through R1. At the starting stage of CO oxidation, the large consumption of OH promotes the forward reaction of R1. With the consumption of HO<sub>2</sub> and the increase in NO<sub>2</sub>, the ROP of R1 producing NO<sub>2</sub> decreases while that of R5 and R6 consuming NO<sub>2</sub> is enhanced, which results in a subsequent decrease of NO<sub>2</sub>.



Figure 5. The ROP and sensitivity analysis on NO<sub>2</sub> formation (1000 ppm NO, 5% O<sub>2</sub>, 15% H<sub>2</sub>O, 900 °C, 15 bar); (a) ROP and (b) sensitivity

The effects of SO<sub>2</sub> on NO<sub>2</sub> formation in POC are shown in fig. 6. It can be seen that the increase in SO<sub>2</sub> concentration promotes the formation of NO<sub>2</sub>, and a large amount of SO<sub>3</sub> is accompanied. The ROP analysis of NO<sub>2</sub> and SO<sub>3</sub> are shown in figs. 7(a) and 7(b), respectively. The NO<sub>2</sub> is mainly produced through the oxidation of NO by HO<sub>2</sub> with the production of OH, while consumed by SO<sub>2</sub> so as to enhance the formation of SO<sub>3</sub>. The SO<sub>3</sub> formation is mainly through the oxidation of HOSO<sub>2</sub> by O<sub>2</sub> with the production of HO<sub>2</sub>. In related to the formation of HOSO<sub>2</sub>, the consumption of OH is necessary. The production and consumption of OH, HO<sub>2</sub> acts like *catalyst*, which promotes the formation of NO<sub>2</sub> and SO<sub>3</sub>. The interaction between SO<sub>x</sub> and NO<sub>x</sub> at elevated pressures can be explained by a cycle which consists of three reactions





Figure 6. Effect of SO<sub>2</sub> concentration on NO<sub>2</sub> formation (1000 ppm NO, 5% O<sub>2</sub>, 15% H<sub>2</sub>O, 900 °C, 15 bar; SO<sub>3</sub> – dash line, NO<sub>2</sub> – solid line); (a) 900°C, 1 bar and (b) 900°C, 15 bar;  $1 - SO_2 = 0$  ppm,  $2 - SO_2 = 100$  ppm,  $3 - SO_2 = 500$  ppm,  $4 - SO_2 = 1000$  ppm



Figure 7. The ROP analysis on NO<sub>2</sub> and SO<sub>3</sub> formation when SO<sub>2</sub> is added (1000 ppm NO, 5% O<sub>2</sub>, 15% H<sub>2</sub>O, 900 °C, 15 bar); (a) NO<sub>2</sub> and (b) SO<sub>3</sub>

# Comparison of NO<sub>2</sub> 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 O*<sub>2</sub> and H<sub>2</sub>O, and Effects of CO and SO<sub>2</sub>, and according to the boiler temperature profiles shown in fig. 8 [30], the NO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> formation is negligible at sufficiently high temperature, *e.g.*, at 15 bar and 1100 °C, the equilibrium of NO/NO<sub>2</sub> system is reached in 10 milliseconds.
- For all cases studied, there was less than 4% conversion from NO to NO<sub>2</sub> within 1 second. The formation and destruction of NO<sub>2</sub> is generally through the reactions: NO + O + + M = NO<sub>2</sub> + M, HO<sub>2</sub> + NO = NO<sub>2</sub> + OH, and NO + O<sub>2</sub> = NO<sub>2</sub> + O. At the higher temperatures (*e.g.*, 1100 °C), the oxidation of NO by HO<sub>2</sub> and the reaction O<sub>2</sub> + H<sub>2</sub>O = OH + HO<sub>2</sub> become more important. At these temperatures and at lower pressures, NO<sub>2</sub> is reduced via NO + O + + M = NO<sub>2</sub> + M, in contrast of producing NO<sub>2</sub> at higher pressures.
- A higher water vapor content accelerates NO<sub>2</sub> formation in all cases by providing more O and HO<sub>2</sub> radicals. The addition of CO or SO<sub>2</sub> accelerates the formation of NO<sub>2</sub>. The effect of CO is mainly through the reaction  $CO + OH = H + CO_2$ . The effect of SO<sub>2</sub> is mainly through the reaction  $HOSO_2 + O_2 = HO_2 + SO_3$ , which produces HO<sub>2</sub> for NO oxidation. The direct interaction of SO<sub>2</sub> + NO<sub>2</sub> = SO<sub>3</sub> + NO inhibits NO<sub>2</sub> formation. At higher pressure and lower temperature (*e.g.*, 1100 °C and 1 bar) the influence of SO<sub>2</sub> on NO<sub>2</sub> formation is small.
- The NO<sub>2</sub> 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<sub>2</sub> formation and reduction should be taken into consideration in a POC.

#### Acknowledgment

The authors gratefully acknowledge the financial support of the National Natural Science Foundation of China (Nos. 51676157, 51761125012), the U.S. Dept. of Energy (Award # DE-FE0009702), and the Consortium for Clean Coal Utilization (CCCU) at Washington University in St. Louis.

Wang, X., et al.: A Kinetic Evaluation on NO<sub>2</sub> Formation in the Post-Flame Region of ... THERMAL SCIENCE: Year 2021, Vol. 25, No. 4A, pp. 2609-2620

#### Nomenclature

AAC - atmospheric air-combustion

FGR – gas re-circulation

- GPU gas processing unit
- HHV high heating value

#### References

 Axelbaum, R. L., et al., Advances in Pressurized Oxy-Combustion for Carbon Capture, CornerStone, 4. (2016), 2, pp. 52-56

POC

PFR – plug flow reactor

ROP - rate of production

SPOC - staged POC

- pressurized oxy-combustion

- [2] Gopan, A., et al., Process Design and Performance Analysis of a Staged, Pressurized Oxy-Combustion (SPOC) Power Plant for Carbon Capture, Applied Energy, 125 (2014), July, pp. 179-188
- [3] Gopan, A., et al., Effect of Operating Pressure and Fuel Moisture on Net Plant Efficiency of a Staged, Pressurized Oxy-Combustion Power Plant, International Journal of Greenhouse Gas Control, 39 (2015), Aug., pp. 390-396
- [4] Murciano, L. T., et al., Sour Compression Process for the Removal of SO<sub>x</sub> and NO<sub>x</sub> from Oxyfuel-Derived CO<sub>2</sub>, Energy Procedia, 4 (2011), Dec., pp. 908-916
- [5] Ting, T., et al., Laboratory Investigation of High Pressure NO oxidation to NO<sub>2</sub> and Capture with Liquid and Gaseous Water Under Oxy-Fuel CO<sub>2</sub> Compression Conditions, International Journal of Greenhouse Gas Control, 18 (2013), Oct., pp. 15-22
- [6] Normann, F., et al., Nitrogen and Sulphur Chemistry in Pressurised Flue Gas Systems: A Comparison of Modelling and Experiments, International Journal of Greenhouse Gas Control, 12 (2013), Jan., pp. 26-34
- [7] Morrison, M., et al., Rate and Mechanism of Gas-Phase Oxidation of Parts-Per-Million Concentrations of Nitric Oxide, Industrial & Engineering Chemistry Fundamentals, 5 (1966), 2, pp. 175-181
- [8] Atkinson, R., et al., Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Part 1-Gas Phase Reactions of Ox, HO<sub>x</sub>, NO<sub>x</sub>, and SO<sub>x</sub> species, Atmospheric Chemistry and Physics Discussions, 3 (2003), 6, pp. 6179-6699
- [9] Greig, J. P., Hall, Thermal Oxidation of Nitric Oxide at Low Concentrations, *Transactions of the Fara*day Society, 63 (1967), pp. 655-661
- [10] Hori, M., et al., An Experimental and Kinetic Calculation of the Promotion Effect of Hydrocarbons on the NO-NO<sub>2</sub> Conversion in a Flow Reactor, Symposium (International) on Combustion, *Elsevier*, 27 (1998), 1, pp. 389-396
- [11] Rasmussen, C. L., *et al.*, Sensitizing Effects of NO<sub>x</sub> on CH<sub>4</sub> Oxidation at High Pressure, *Combustion and Flame*, 154 (2008), 3, pp. 529-545
- [12] Glarborg, P., et al., Interactions of CO, NO<sub>x</sub> and H<sub>2</sub>O Under Post-Flame Conditions, *Combustion science and technology*, 110 (1995), 1, pp. 461-485
- [13] Rasmussen, C. L., et al., Experimental Measurements and Kinetic Modeling of CO/H<sub>2</sub>/O<sub>2</sub>/NO<sub>x</sub> Conversion at High Pressure, International Journal of Chemical Kinetics, 40 (2008), 8, pp. 454-480
- [14] Mueller, M., et al., Flow Reactor Studies and Kinetic Modeling of the H<sub>2</sub>/O<sub>2</sub>/NO<sub>x</sub> and CO/H2O/O2/NOx Reactions, International Journal of Chemical Kinetics, 31 (1999), 10, pp. 705-724
- [15] Gersen, S., et al., Ignition-Promoting Effect of NO<sub>2</sub> on Methane, Ethane and Methane/Ethane Mixtures in a Rapid Compression Machine, Proceedings of the Combustion Institute, 33 (2011), 1, pp. 433-440
- [16] Krzywanski, J. W., Nowak, Neurocomputing Approach for the Prediction of NO<sub>x</sub> Emissions from CFBC in Air-Fired and Oxygen-Enriched Atmospheres, *Journal of Power Technologies*, 97 (2017), 2, pp. 75-84
- [17] Liu, H., Gibbs, B. M., The Influence of Limestone Addition at Different Positions on Gaseous Emissions from a Coal-Fired Circulating Fluidized Bed Combustor, *Fuel*, 77 (1998), 14, pp. 1569-1577
- [18] Mueller, M., et al., Kinetic Modeling of the CO/H<sub>2</sub>O/O<sub>2</sub>/NO/SO<sub>2</sub> System: Implications for High-Pressure Fall-Off in the SO<sub>2</sub> + O (+M) = SO<sub>3</sub> (+M) Reaction, International Journal of Chemical Kinetics, 32. (2000), 6, pp. 317-339
- [19] Pang, L., et al., Experimental Investigation of Oxy-coal Combustion in a 15 kWth Pressurized Fluidized Bed Combustor, Energy and Fuels, 33 (2019), 3, pp. 1694-1703
- [20] Duan, Y., et al., Observation of Simultaneously Low CO, NO<sub>x</sub>, and SO<sub>2</sub> Emission During Oxycoal Combustion in a Pressurized Fluidized Bed, *Fuel*, 242 (2019), Apr., pp. 374-381

- [21] Dayma, G. P., Dagaut, Effects of Air Contamination on the Combustion of Hydrogen effect of NO and NO<sub>2</sub> Addition on Hydrogen Ignition and Oxidation Kinetics, *Combustion science and technology*, 178 (2006), 10-11, pp. 1999-2024
- [22] Dagaut, P., et al., A Jet-Stirred Reactor for Kinetic Studies of Homogeneous Gas-Phase Reactions at Pressures Up to Ten Atmospheres (≈1 MPa), Journal of Physics E Scientific Instruments, 19 (1986), 3, p. 207
- [23] Allen, M. T., et al., The Decomposition of Nitrous Oxide at 1.5 P 10.5 atm and 1103 T 1173 K, International Journal of Chemical Kinetics, 27 (1995), 9, pp. 883-909
- [24] Smith, G. P., et al., GRI-Mech 3.0, 1999, URL http://www.me. berkeley. edu/gri\_mech., 2011
- [25] Glarborg, P., et al., Impact of SO<sub>2</sub> and NO on CO Oxidation Under Post-Flame Conditions, International Journal of Chemical Kinetics, 28 (1996), 10, pp. 773-790
- [26] Kee, R. J., et al., CHEMKIN-III: A FORTRAN Chemical Kinetics Package for the Analysis of Gas-Phase Chemical and Plasma Kinetics, Report, SAND 96-8216, UNT, USA, 1996
- [27] Wang, X., et al., Kinetic Investigation of the SO<sub>2</sub> Influence on NO Reduction Processes During Methane Reburning, Asia-Pacific Journal of Chemical Engineering, 5 (2010), 6, pp. 902-908
- [28] Bendtsen, A. B., et al., Visualization Methods in Analysis of Detailed Chemical Kinetics Modelling, Computers & Chemistry, 25 (2001), 2, pp. 161-170
- [29] Wang, X., et al., Synergistic SO<sub>x</sub>/NO<sub>x</sub> Chemistry Leading to Enhanced SO<sub>3</sub> and NO<sub>2</sub> Formation During Pressurized Oxy-Combustion, *Reaction Kinetics Mechanisms and Catalysis*, 123 (2018), 2, pp. 313-322
- [30] Senior, C. L., et al., Gas-Phase Transformations of Mercury in Coal-Fired Power Plants, Fuel Processing Technology, 63 (2000), 2, pp. 197-213
- [31] Tan, Y., *et al.*, Combustion Characteristics of Coal in a Mixture of Oxygen and Recycled Flue Gas, *Fuel*, 85 (2006), 4, pp. 507-512
- [32] Gao, Z., *et al.*, Heat Transfer Characteristics of Boiler Convective Heating Surface Under Pressurized Oxygen-fuel Combustion Conditions [J], *Proceedings of the CSEE*, 32 (2012), 23, pp.1-8