

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

Xuebin WANG^{1,2,}, Gaofeng DAI¹, Gregory S. YABLONSK³, Milan Vujanović⁴,*

Richard L. AXELBAUM²

1. MOE Key Laboratory of Thermo-Fluid Science and Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi, 710049, China
2. Department of Energy, Environmental & Chemical Engineering, Consortium for Clean Coal Utilization, Washington University in St. Louis, St. Louis, MO 63130, USA
3. Parks College of Engineering, Aviation & Technology, Saint Louis University, St. Louis, MO 63103, USA
4. Faculty of Mechanical Engineering and Naval Architecture, University of Zagreb, Zagreb, 10000, Croatia

*Corresponding Author Email: wxb005@mail.xjtu.edu.cn

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 recirculation. In the flame region, high temperature NO_x 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/SO_x) 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, e.g., at 15 bar and 1300°C, equilibrium is reached in 1 millisecond and the NO₂/NO is about 0.8%. The formation and destruction of NO₂ is generally through the reversible reactions: NO+O+M=NO₂+M, HO₂+NO=NO₂+OH, and NO+O₂=NO₂+O. 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. Finally, NO₂ formation in a Pressurized oxy-combustion furnace is compared with that in a practical atmospheric air-combustion furnace and the comparison show that 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.

Nomenclature

ASU	Air separation unit	POC	Pressurized oxy-combustion
FGR	Gas recirculation	PFR	Plug flow reactor
GPU	Gas processing unit	ROP	Rate of production
HHV	High heating value	SPOC	Staged Pressurized Oxy-Combustion process
JSR	Jet-stirred reactor		

1. Introduction

Oxy-coal combustion is one of the routes for controlling CO₂ emissions from coal combustion, however, first-generation oxy-combustion technologies, operated under atmospheric 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 (ASU), flue gas recirculation (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 Pressurized Oxy-Combustion 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].

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 NO₂, aggravating the low-temperature corrosion. Another motivation in terms of the importance of NO₂ in POC, is closely related with a new developed technology of integrated SO_x/NO_x 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_x in liquid [5], and to oxidize SO₂ into SO₃ or oxidize H₂SO₃ into H₂SO₄ under the interaction between SO_x/NO_x in gas or liquid, respectively [6].

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

neglectable 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 HO₂ to OH through HO₂+NO=NO₂+OH (R1) and a catalytic recycle reaction through NO₂+H=NO+OH (R2). 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 et.al [16] and Liu et.al [17] also pointed that in circulating fluidized bed the high CO₂ concentration could inhabit the calcination of limestone, which will increase the formation of NO_x.

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 not be neglected.

All the above studies have ensured the impact of NO_x 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 SO_x 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 pressurized oxy-combustion. The conversion of NO → NO₂ has been kinetically evaluated under representative post-flame conditions of pressurized oxy-combustion after validating an updated detailed mechanism. The effects of residence time, temperature, pressure, major species (O₂/H₂O), and minor or trace species (CO/SO_x) on NO₂ formation are studied. Sensitivity analysis and reaction pathway analysis are conducted to demonstrate the interaction mechanism, respectively.

2. Modeling Approach

2.1 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 (JSR) [22] wrapped with ceramic wool and located inside a stainless-steel pressure resistant jacket allowing operation up to 10 atm. The effect of NO or NO₂ addition on H₂ oxidation in this reactor were analyzed and their experimental results are plotted in Fig.1(a).

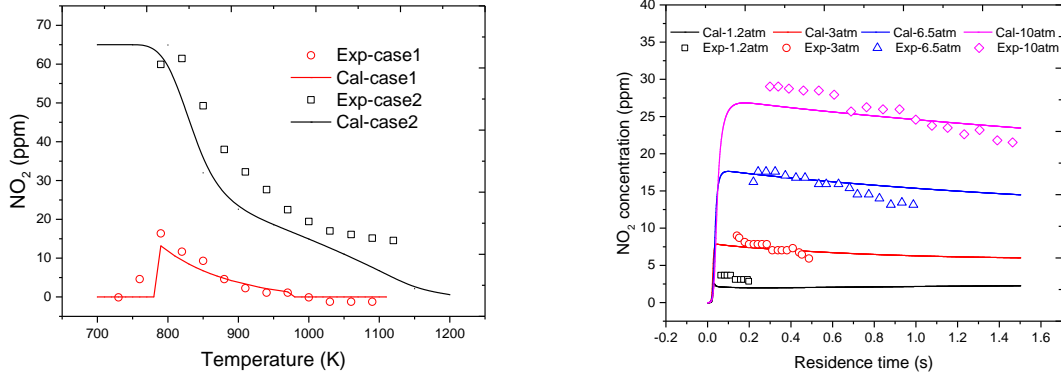
Mueller et al. [18] studied the effect of trace SO₂ and NO on CO oxidation in a pressurized flow reactor [23], which can produce a homogenous, premixed, highly dilute, one-dimensional gas flow at sufficient initial temperatures to initiate chemical reaction of the mixture. The high-pressure experimental 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.

2.2 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. 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_x and NO_x in POC condition, in which, the mechanism of sulfur and SO_x/NO_x interaction are added from Glarborg et al [25]. The full mechanism includes 80 species and 464 steps. CHEMKIN is a software package whose 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 analyse 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 NO_x, CO, and SO_x.



(a) 1 s, 10 atm, 1% H₂, case1: 220 ppm NO, 0.333% O₂; case2: 65 ppm NO₂, 1% O₂ [15]

(b) 950 K, 0.51% CO, 0.75% O₂, 0.49% H₂O, 97 ppm NO, 500 ppm SO₂ [10]

Fig.1: Mechanism validating by comparison with the data in literatures

2.3 Test conditions

The conditions used are taken according to the real post-flame conditions of pressurized oxy-combustion (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 Table 1. The residence time ranges from 0.01 s to 10 s, 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.

Parameters	Ranges	Units	Variable gas composition
Temperature	700-1300	°C	1000 ppm NO, 5% O ₂ , 15% H ₂ O, CO ₂ as balance gas
Pressure	1-15	bar	1000 ppm NO, 5% O ₂ , 15% H ₂ O, CO ₂ as balance gas
O ₂	0-15	%	1000 ppm NO, 15% H ₂ O, CO ₂ as balance gas
H ₂ O	1-25	%	1000 ppm NO, 5% O ₂ , CO ₂ as balance gas
CO	0-10000	ppm	1000 ppm NO, 5% O ₂ , 15% H ₂ O, CO ₂ as balance gas
SO ₂	0-5000	ppm	1000 ppm NO, 5% O ₂ , 15% H ₂ O, CO ₂ as balance gas

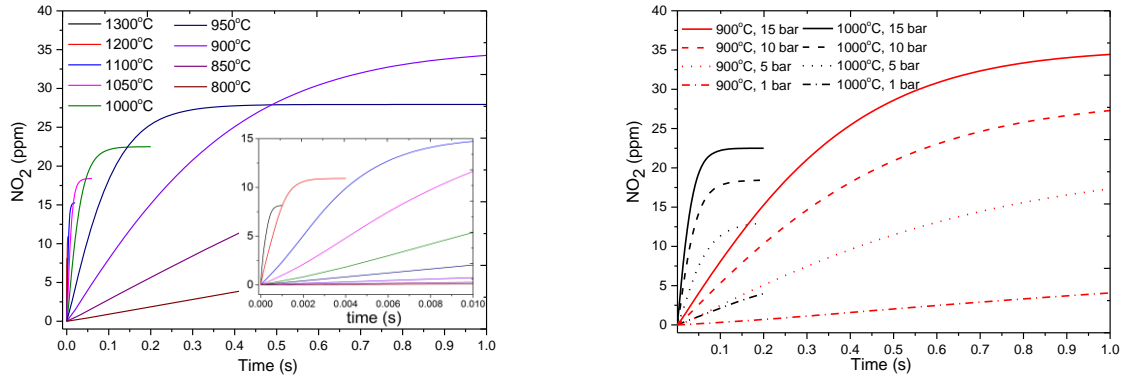
3. Results and Discussion

3.1 Effect of pressure and temperature

The effects of pressure and temperature on NO₂ formation in a pressurized PFR is 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 1bar to 15bar. Under POC conditions, the NO₂ formation are several times higher than the atmospheric air-combustion.

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.

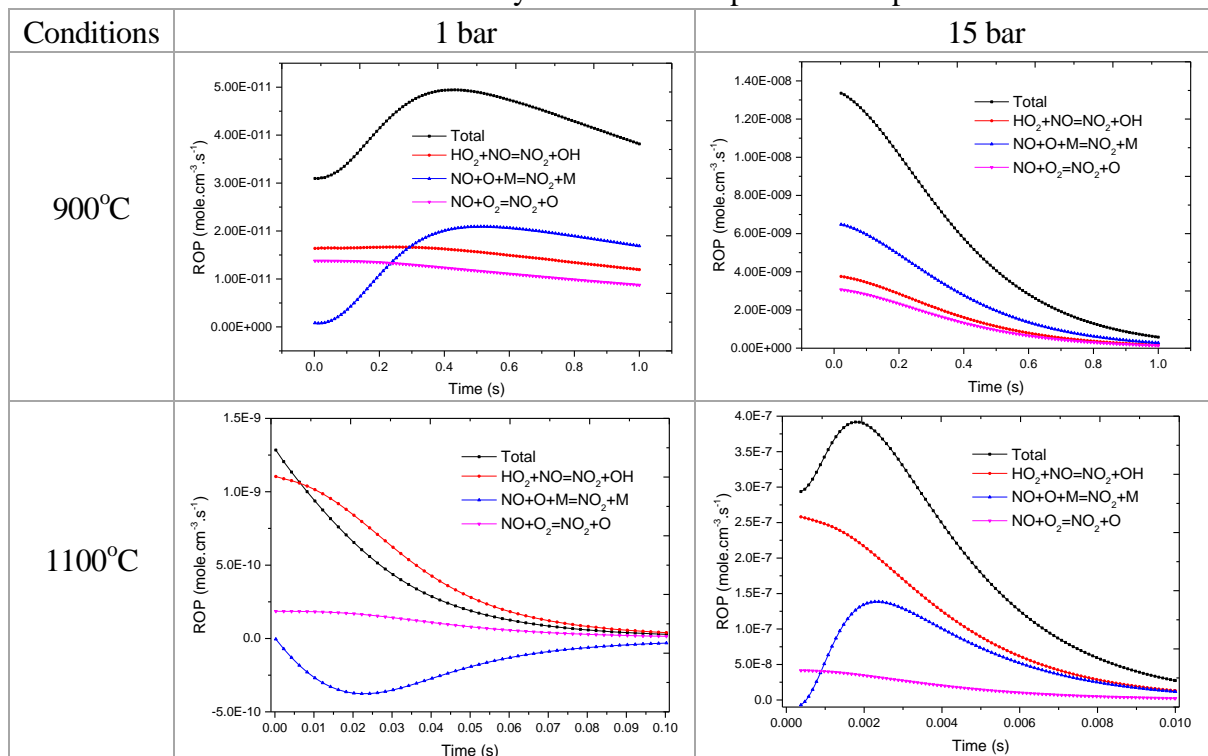


(a) Effect of temperature at 15 bar

(b) Effect of pressure at 900 and 1000°C

Fig.2 NO₂ formation along the residence time at different temperatures and pressures (1000 ppm NO, 5% O₂, 15% H₂O, CO₂ as balance)

Table 2: ROP analysis at varied temperature and pressure.



3.2 Effect of O_2 and H_2O

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_2 formation is shown in Fig. 3(b). Similar to O_2 , the increasing in concentration also accelerates the formation of NO_2 and shortens the time to reach equilibrium; however, it does not affect the equilibrium point for NO_2 yield.

At 1 bar and 900 °C, NO_2 formation is mainly via R3, R4, R1. In contrast, at 15 bar, R1 can be a little stronger than R4. R1 can become important than R3 and R4 at 15bar and 1300 °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.

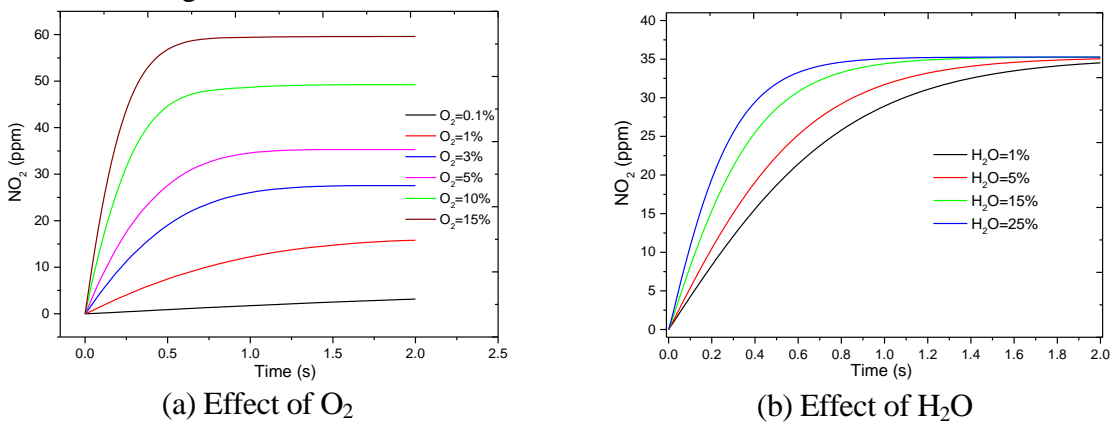


Fig.3 Effect of O_2 (a) and H_2O (b) (1000 ppm NO, 900°C, 15 bar)

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

Conditions	1% H_2O (dry recycling)	15% H_2O (wet recycling)
900°C		
1100°C		

3.3 Effect of CO and SO₂

The effects of CO on NO₂ formation during POC is shown in Fig. 4(a). With increasing the CO concentration, a large amount of NO₂ is produced within about 0.1 s, 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 NO₂ 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.

The ROP and sensitivity analysis on NO₂ formation in the stage A and B is shown in Fig. 5(a) and (b), respectively. 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.

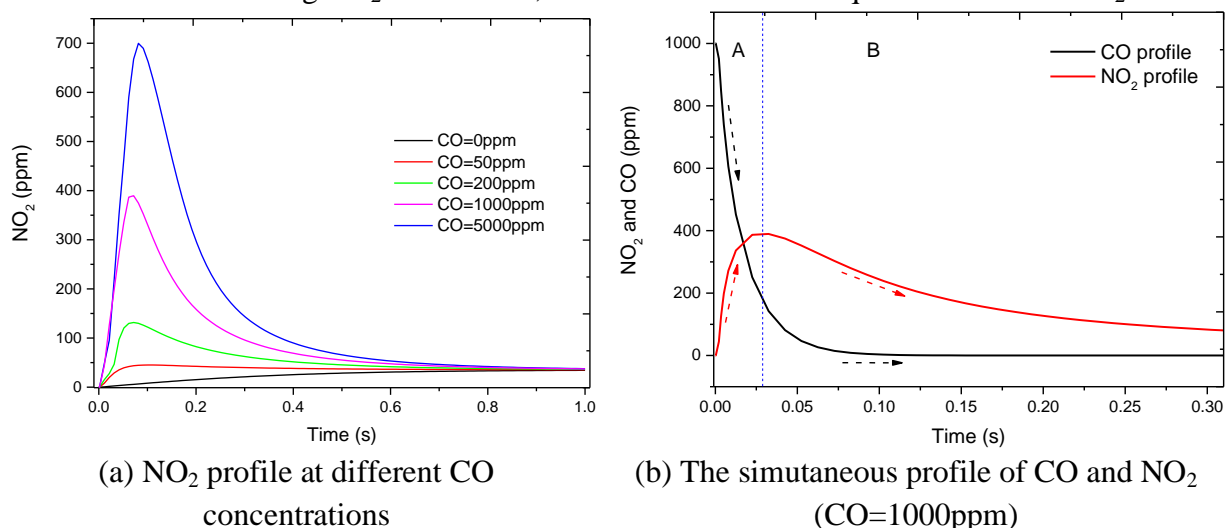


Fig.4 Effect of CO concentration on NO₂ formation
(1000 ppm NO, 5% O₂, 15% H₂O, 900°C, 15 bar)

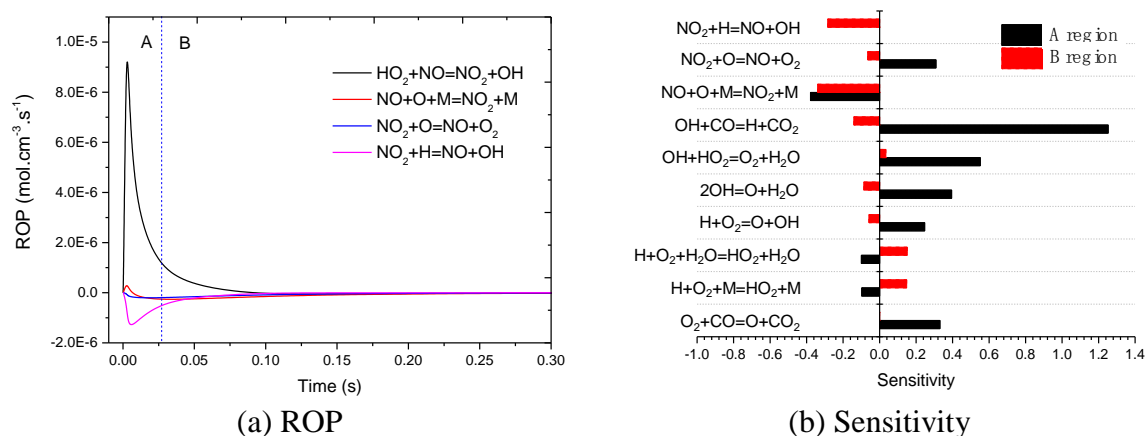


Fig.5 ROP and sensitivity analysis on NO₂ formation
(1000 ppm NO, 5% O₂, 15% H₂O, 900°C, 15 bar)

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 Fig.7(a) and (b), respectively. 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. 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 SO_x and NO_x at elevated pressures can be explained by a cycle which consists of three reactions HO₂+NO=NO₂+OH (R1), SO₂+OH+M=HOSO₂+M (R10), HOSO₂+O₂=HO₂+SO₃ (R11) with the global reaction NO+SO₂+O₂=NO₂+SO₃ (R12) [29].

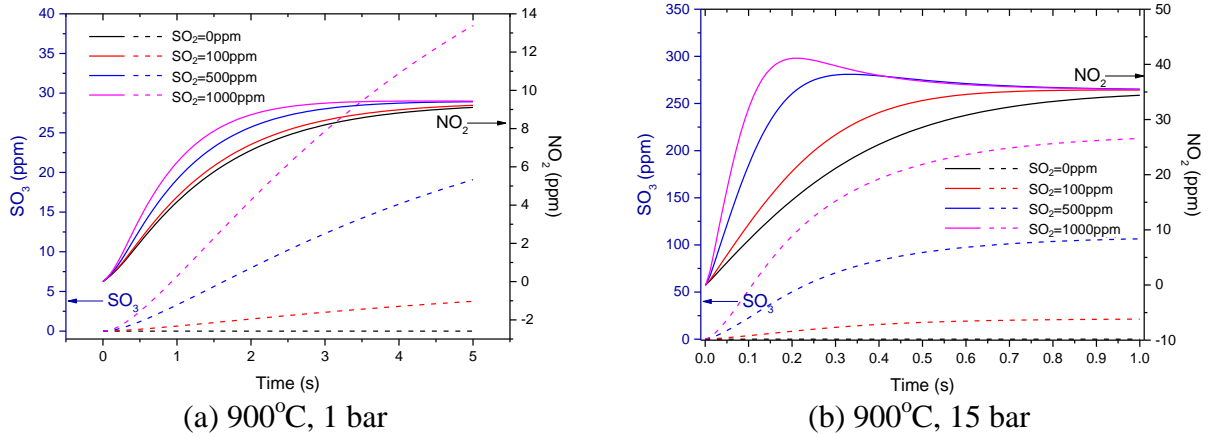


Fig.6 Effect of SO₂ concentration on NO₂ formation
(1000 ppm NO, 5% O₂, 15% H₂O, 900°C,15 bar; SO₃-dash line, NO₂-solid line)

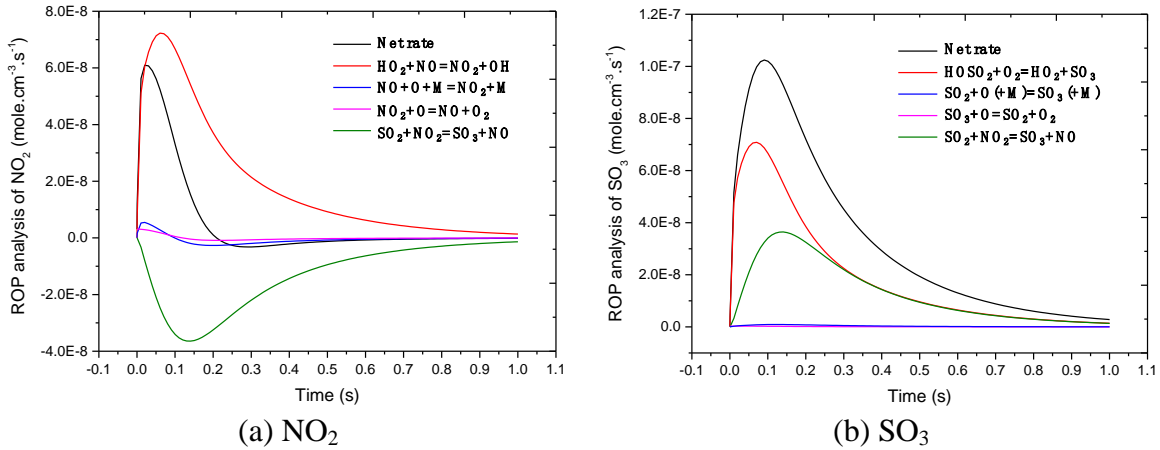


Fig.7: ROP analysis on NO₂ and SO₃ formation when SO₂ is added
(1000 ppm NO, 5% O₂, 15% H₂O, 900°C,15 bar)

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

Based on the analysis results in 3.1-3.3, and according to the boiler temperature profiles shown in Fig. 8 [30], the NO₂ formation is evaluated in a practical atmospheric air-combustion (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.

The results, plotted in Fig.9, show that for the sub-bituminous coal, the NO₂ 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.

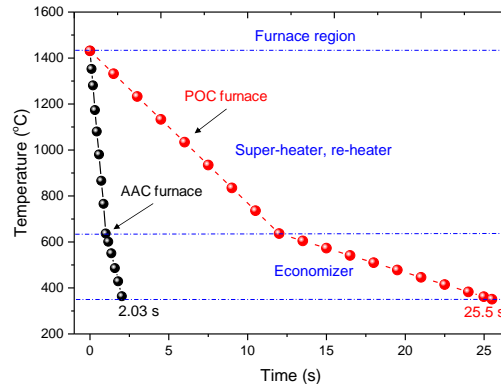


Fig.8 Temperature profile in pulverized coal boilers of air-combustion [30] and pressurized oxy-combustion [32]

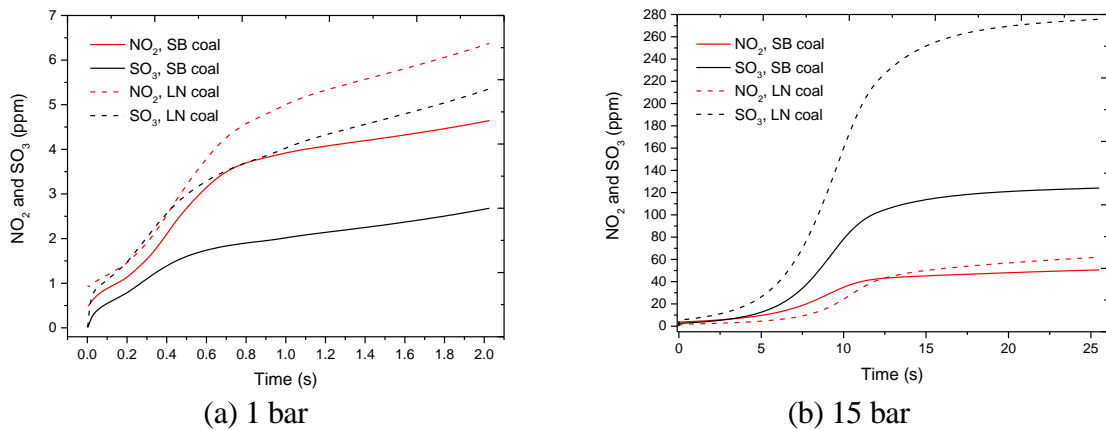


Fig.9: NO_2 formation in pulverized coal boilers of air-combustion (1 bar) and pressurized oxy-combustion (15 bar)

5. Conclusion

- (1) 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.
- (2) 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: $\text{NO} + \text{O} + \text{M} = \text{NO}_2 + \text{M}$, $\text{HO}_2 + \text{NO} = \text{NO}_2 + \text{OH}$, and $\text{NO} + \text{O}_2 = \text{NO}_2 + \text{O}$. At the higher temperatures (e.g., 1100°C), the oxidation of NO by HO_2 and the reaction $\text{O}_2 + \text{H}_2\text{O} = \text{OH} + \text{HO}_2$ become more important. At these temperatures and at lower pressures, NO_2 is reduced via $\text{NO} + \text{O} + \text{M} = \text{NO}_2 + \text{M}$, in contrast of producing NO_2 at higher pressures.
- (3) 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 $\text{CO} + \text{OH} = \text{H} + \text{CO}_2$. The effect of SO_2 is mainly through the reaction $\text{HOSO}_2 + \text{O}_2 = \text{HO}_2 + \text{SO}_3$, which produces HO_2 for NO oxidation. The direct interaction of $\text{SO}_2 + \text{NO}_2 = \text{SO}_3 + \text{NO}$ 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.

- (4) NO₂ 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 NO₂ formation and reduction should be taken into consideration in a pressurized oxy-combustion furnace.

Acknowledgement

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.

References

- [1] Axelbaum, R.L., *et al.*, Advances in Pressurized Oxy-Combustion for Carbon Capture, *CornerStone*, 4. (2016), 2, pp. 52–56
- [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), 125, 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), pp. 390-396
- [4] Murciano, L.T., *et al.*, Sour compression process for the removal of SO_x and NO_x from oxyfuel-derived CO₂, *Energy Procedia*, 4. (2011), pp. 908-916
- [5] Ting, T., *et al.*, Laboratory investigation of high pressure NO oxidation to NO₂ and capture with liquid and gaseous water under oxy-fuel CO₂ compression conditions, *International Journal of Greenhouse Gas Control*, 18. (2013), 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), 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 O_x, HO_x, NO_x and SO_x 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 Faraday 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-NO₂ conversion in a flow reactor, Symposium (International) on Combustion, 1998, 27, pp. 389-396
- [11] Rasmussen, C.L., *et al.*, Sensitizing effects of NO_x on CH₄ oxidation at high pressure, *Combustion and Flame*, 154. (2008), 3, pp. 529-545
- [12] Glarborg, P., *et al.*, Interactions of CO, NO_x and H₂O 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/H₂/O₂/NO_x 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 H₂/O₂/NO_x and CO/H₂O/O₂/NO_x reactions, *International Journal of Chemical Kinetics*, 31. (1999), 10, pp. 705-724
- [15] Gersen, S., *et al.*, Ignition-promoting effect of NO₂ 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_x emissions from CFBC in air-fired and oxygen-enriched atmospheres, *Journal of Power Technologies*, 97. (2017), pp. 75-84
- [17] Liu, H., B.M. Gibbs, 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/H₂O/O₂/NO/SO₂ system: Implications for high - pressure fall - off in the SO₂+ O (+ M)= SO₃ (+ 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_x and SO₂ emission during oxycoal combustion in a pressurized fluidized bed, *Fuel*, 242. (2019), pp. 374-381
- [21] Dayma, G., P. Dagaut, Effects of air contamination on the combustion of hydrogen—effect of NO and NO₂ 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 SO₂ 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, United States, 1996.
- [27] Wang, X., *et al.*, Kinetic investigation of the SO₂ influence on NO reduction processes during methane reburning, *Asia - Pacific Journal of Chemical Engineering*, 5. (2010), 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_x/NO_x chemistry leading to enhanced SO₃ and NO₂ 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

Submitted: 15.04.2020.
Revised: 31.07.2020.
Accepted: 02.08.2020.