# CO<sub>2</sub> effects on NO reburning by methane in a jet-stirred reactor: Experiments and modeling

Wenhao Li, Pengfei Li, Kai Wang, Fan Hu, Lu Liu State Key Laboratory of Coal Combustion, School of Energy and Power Engineering, Huazhong University of Science and Technology Wuhan, Hubei, China

# 1 Abstract

New experimental results on the NO reduction by CH<sub>4</sub> in both N<sub>2</sub> and CO<sub>2</sub> atmospheres are obtained in a jet-stirred reactor. Experiments are conducted in the temperature range of 600 - 1323 K at 1 atm. The experiments are simulated using an updated reaction mechanism and the simulations are highly consistent with the experiments. The NO-reburning in the CO<sub>2</sub> atmosphere is reduced by 40% - 60%, relative to that in the N<sub>2</sub> atmosphere. The inhibition of methane oxidation under high CO<sub>2</sub> concentrations is responsible for the decrease of the NO reduction efficiency. The main reaction pathways of the NO reduction in the N<sub>2</sub> atmosphere are: NO ( $\rightarrow$  HCNO)  $\rightarrow$  HCN  $\rightarrow$  NCO  $\rightarrow$  N<sub>2</sub> and NO  $\rightarrow$  HNCO  $\rightarrow$  NH<sub>2</sub>  $\rightarrow$  NNH  $\rightarrow$  N<sub>2</sub>, while the primary path in the CO<sub>2</sub> atmosphere is: NO ( $\rightarrow$  H<sub>2</sub>CN)  $\rightarrow$  HCN  $\rightarrow$  CH<sub>3</sub>CN  $\rightarrow$  NCO  $\rightarrow$  N<sub>2</sub> due to the chemical effect of CO<sub>2</sub>.

# 2 Introduction

Oxy-fuel combustion [1] is one of the most promising new combustion technologies which is achieved by a strong recirculation of exhausted gases. Such a strategy implies that high contents of  $CO_2$  interact with the reactants oxidation chemistry which can significantly reduce  $NO_x$  emissions. However, other  $NO_x$ reduction techniques are still needed in many combustion systems to achieve greater reduction. Reburning [2] is a low-cost and effective  $NO_x$  reduction technology that has proven to be effective in air combustion and can reduce  $NO_x$  emissions by more than 50%. It is worth mentioning that Normann [3] pointed out that reburning technology is a promising option for both traditional and oxy-fuel combustion in his review. Although there are some reburning studies [4-5] in the  $CO_2$  atmosphere in recent years, basic experimental data and further kinetic studies are still scarce.

The jet-stirred reactor is an ideal continuous stirred reactor (0-dimensional) and is suitable for gas-phase kinetics studies. The distributions of thermal and species are uniform inside the reactor due to the high-speed jets of the JSR nozzles. Therefore, the reactions in the JSR occur in a nearly homogeneous

#### Wenhao Li

environment and can approximate locally occurring at one point of the space. To our best knowledge, there are no reports on the NO-reburning experiment of a JSR under high  $CO_2$  concentrations. Moreover, the experimental data for the correction and optimization of the nitrogen chemical mechanism under high  $CO_2$  concentrations is very scarce. The present study aims to fill the gaps.

Therefore, the purpose of this paper is to carry out reburning experiments and kinetic simulation studies under high  $CO_2$  concentrations in a jet-stirred reactor. Methane was used as the research object to study the  $CO_2$  effects on NO reburning.

# **3** Experimental setup and Kinetic model



Figure 1. Schematic diagram of the experimental apparatus.

Figure 1 displays the photo of the JSR. The main structure of the JSR is a 40 mm diameter sphere made by quartz and the reactor volume is approximately 60 cm<sup>3</sup>. The preheated mixed gas is injected into the reactor through the internal four nozzles. The diameter of each nozzle is only 1 mm and thus the initial velocity of the injection jet is sufficiently high. Consequently, the thermal and species distributions inside the reactor are nearly uniform. The JSR is installed and fixed in an electric heating oven with a thermal power of 1.5 kW and the reaction temperature is controlled by the oven. The heating oven is insulated with high-purity alumina fiber and is heated by ferrochromium-doped iron-chromium-aluminum alloy heating wires. High-purity gases (purity above 99.999%) are used in the experiment. The flow rate of gases is accurately controlled by mass flowmeter controllers with the error of  $\pm 0.3\%$  of full scale. The exhaust species concentrations after the reaction are measured on-line by using a portable Fourier infrared flue gas analyzer (DX4000) supplied by the Swedish company Gasmet. The concentrations of CH<sub>4</sub>, O<sub>2</sub>, CO<sub>2</sub>, NO, CO, HCN, NO<sub>2</sub>, and N<sub>2</sub>O can be measured simultaneously, and the measurement error is estimated to be  $\pm 1\%$ .

Table 1. Experimental conditions in the present work						
	inlet streams					т
case	$CH_4$	NO	$O_2$	$CO_2$	$\Phi$	I K
	ppm	ppm	vol%	vol%		
1	5000	1000	2	0	0.5	600-1323
2	5000	1000	2	30	0.5	600-1323
3	5000	1000	0.7	0	1.43	600-1323
4	5000	1000	0.7	30	1.43	600-1323

Table 1. Experimental conditions in the present work

The experiment was carried out under the pressure of 1 atm and the temperature range was 600 K-1323 K. The total flow rate of the reactants was controlled at 1 L/min, while the concentration of methane was controlled at 5000 ppm. The specific operating conditions were as shown in Table 1.

#### Wenhao Li

#### CO<sub>2</sub> effects on NO reburning

Numerical predictions were simulated using the PSR model from Chemkin-PRO. The AURORA code [6] was used for PSR chemical kinetic analysis. In this paper, the mechanism developed by Glarborg [7] in 2018 is selected as the basis and some modifications and updates are made. The mechanism includes the oxidation mechanism of  $C_1$  hydrocarbons, HCN and NH<sub>3</sub>, and the reactions describing the interaction between hydrocarbons and nitrogen-containing components. For consistency, the experiment may still require some modifications and optimizations to account for the effects of high  $CO_2$  concentrations. Therefore, in the current work we have added some different reactions related to  $CO_2$  that are not included in the initial mechanism and may work in a  $CO_2$  atmosphere. At the same time, based on our experimental results and considering the previous literature research, we also added some reactions about reburning and further modified and optimized some sensitive reactions. The simulation using the modified mechanism is in good agreement compared with our experimental results. The modified mechanism consists of 151 components and 1408 reactions and the complete mechanism can be obtained from the author.

## **3** Results

Experiments were carried out in a jet-stirred reactor with a temperature range varying from 600 K to 1323 K under fuel-lean and fuel-rich conditions. Figure 2(a) and 2(b) shows the O<sub>2</sub> and CO profiles with increasing temperature under fuel-lean and fuel-rich conditions. The simulation results using the updated mechanism are basically consistent with the experimental data. As shown in Figures 2, clearly, with the increase of temperature the O<sub>2</sub> consumption slows down in the CO<sub>2</sub> atmosphere compared with that in the N<sub>2</sub> atmosphere, especially under the fuel-rich condition: as the temperature rises from 600 K to 1323 K, the O<sub>2</sub> concentration drops from 0.7% to 0.07% in the N<sub>2</sub> atmosphere while it reduces to 0.23% in the CO<sub>2</sub> atmosphere. This phenomenon implies that methane requires a higher temperature to be fully oxidized in the CO<sub>2</sub> atmosphere than that in the N<sub>2</sub> atmosphere. This finding is consistent with previous investigation on oxy-fuel combustion [4] and can be considered as the inhibition of CH<sub>4</sub> oxidation by the high content of CO<sub>2</sub>. The reason is, the high concentration of CO<sub>2</sub> can suppress the forward reaction of H + O<sub>2</sub>  $\leftrightarrow$  O + OH during combustion.



27th ICDERS - July 28th - August 2nd, 2019 - Beijing, China



Figure 2. Components profiles with increasing temperature under (a) fuel-lean condition ( $\Phi = 0.5$ , case 1 and case 2 in Table 1), and (b) fuel-rich condition ( $\Phi = 1.43$ , case 3 and case 4 in Table 1). Comparison between experimental data (symbols) and model predictions (lines).

Figure 2 also shows the experimental and numerical results of the concentrations of NO and HCN and the NO reduction efficiency with temperature in  $N_2$  and  $CO_2$  atmospheres. Note that in the NO-reburning process, NO is not completely reduced to  $N_2$  and may be converted to other nitrogenous contaminants. The concentrations of NO<sub>2</sub>,  $N_2O$ , NH<sub>3</sub> and HCN are measured in the present experiment. It is found that the concentrations of nitrogen-containing components, with the exception of HCN, are always lower than 10 ppm during the reaction. Hence, the sum of the concentrations of NO and HCN is used as a standard for evaluating the reduction efficiency of NO. Equation (1) shows the definition of the NO reduction efficiency:

NO Reduction Efficiency (%) =  $100\% \times (IFN - TFN) / IFN$  (1)

In Equation (1), IFN (initial fraction of N) represents the concentration of NO initially added, and TFN (total fraction of N) stands for the sum of the concentrations of NO and HCN. As shown in Figure 2, less than 30% of NO is reduced in both  $N_2$  and  $CO_2$  atmospheres under the fuel-lean condition, and the concentration of HCN is less than 20 ppm. However, under the fuel-rich condition (Figure 4b), the NO reduction efficiency can be greater than 30% in both  $N_2$  and  $CO_2$  atmosphere is significantly lower than that at the  $N_2$  atmosphere when the reburning chemistry at the  $CO_2$  atmosphere is significantly lower than that at the  $N_2$  atmosphere and temperatures above about 1100 K at the  $CO_2$  atmosphere. Especially, under the fuel-rich condition the NO reduction efficiency in the  $CO_2$  atmosphere is reduced by about 50% compared with that in the  $N_2$  atmosphere at temperatures above 1200 K. The inhibition of methane oxidation under high  $CO_2$  concentrations can be responsible for the decrease of the NO reduction efficiency, because the reduced oxidation process results in only a small amount of hydrocarbon radicals (CH<sub>3</sub>, HCCO, CH<sub>2</sub>, etc.) that can take part in the NO-reburning reactions. In addition, with the decrease of the NO concentration more HCN is formed, which implies that HCN is an important intermediate in the NO reduction process.

To further analyze how the NO reburning occurs in different atmospheres, detailed simulation analyses of NO reduction pathways are conducted under the fuel-rich ( $\Phi = 1.43$ ) condition at 1300 K in both N<sub>2</sub> and

#### Wenhao Li

CO<sub>2</sub> atmospheres with the normalized reaction rate of production (ROP). The detailed NO reduction paths are shown in Figure 3.

It can be seen from Fig. 3(a) that the NO reduction in the N<sub>2</sub> atmosphere mainly achieves through the following reaction. First, NO reacts with hydrocarbon radicals CH<sub>3</sub> and HCCO to form HCN, or reacts with HCCO and CH<sub>2</sub> to form HCNO, which is then decomposed into HCN. Then HCN is oxidized by O to form NCO, and NCO reacts with NO to form N<sub>2</sub> to achieve reduction of NO, or the realization of NO reduction adopts another path: NO first reacts with CH<sub>2</sub> to form HNCO, HNCO then reacts with H radicals to become NH<sub>2</sub>, NH<sub>2</sub> reacts with NO to form NNH, and NNH finally decomposes into N<sub>2</sub> to achieve final reduction. From Fig. 3(b), it can be seen that the NO reduction in the CO<sub>2</sub> atmosphere mainly passes through the following reaction. First, NO reacts with CH<sub>3</sub> and HCCO to form HCN, or reacts with CH<sub>3</sub> to form H<sub>2</sub>CN and then converts to HCN, Then HCN reacts with CH<sub>3</sub> to become CH<sub>3</sub>CN, and CH<sub>3</sub>CN is further oxidized to NCO by O. Finally, NCO reacts with NO to form N<sub>2</sub> to achieve reduction of NO.



(b) CO<sub>2</sub> atmosphere

Figure 3 NO reduction pathway diagram under fuel-rich condition ( $\Phi$ =1.43) at 1300K.

Combined with the above analysis, it can be found that the NO reduction in N<sub>2</sub> atmosphere mainly passes through two paths: NO ( $\rightarrow$  HCNO)  $\rightarrow$  HCN  $\rightarrow$  NCO  $\rightarrow$  N<sub>2</sub> and NO  $\rightarrow$  HNCO  $\rightarrow$  NH<sub>2</sub>  $\rightarrow$  NNH  $\rightarrow$  N<sub>2</sub>. And

the main path of NO reduction in the CO<sub>2</sub> atmosphere is: NO ( $\rightarrow$  H<sub>2</sub>CN)  $\rightarrow$  HCN  $\rightarrow$  CH<sub>3</sub>CN  $\rightarrow$  NCO  $\rightarrow$  N<sub>2</sub>. Through further analysis we found that the CH<sub>4</sub> oxidation in a high concentration of CO<sub>2</sub> is mainly through CH<sub>4</sub>  $\rightarrow$  CH<sub>3</sub> ( $\rightarrow$  CH<sub>2</sub>OH)  $\rightarrow$  CH<sub>2</sub>O  $\rightarrow$  HCO  $\rightarrow$  CO  $\rightarrow$  CO<sub>2</sub>, and the pathways of CH<sub>4</sub>  $\rightarrow$  CH<sub>3</sub>  $\rightarrow$  CH<sub>2</sub> $\rightarrow$  HCO  $\rightarrow$  CO  $\rightarrow$  CO<sub>2</sub> and the pathways of CH<sub>4</sub>  $\rightarrow$  CH<sub>3</sub>  $\rightarrow$  CH<sub>2</sub> $\rightarrow$  HCO  $\rightarrow$  CO  $\rightarrow$  CO<sub>2</sub> and CH<sub>4</sub>  $\rightarrow$  CH<sub>3</sub>  $\rightarrow$  C<sub>2</sub>H<sub>6</sub>  $\rightarrow$  C<sub>2</sub>H<sub>5</sub>  $\rightarrow$  C<sub>2</sub>H<sub>4</sub>  $\rightarrow$  C<sub>2</sub>H<sub>3</sub>  $\rightarrow$  C<sub>2</sub>H<sub>2</sub>  $\rightarrow$  HCCO  $\rightarrow$  CO  $\rightarrow$  CO<sub>2</sub> are suppressed. So the generation of hydrocarbon radical CH<sub>2</sub> and HCCO is reduced, thereby inhibiting the reaction HCCO + NO  $\leftrightarrow$  HCNO + CO and CH<sub>2</sub> + NO  $\leftrightarrow$  HCNO + H so that the pathway of NO  $\rightarrow$  HCNO is suppressed and the pathway of NO  $\rightarrow$  H<sub>2</sub>CN by reaction CH<sub>3</sub> + NO  $\leftrightarrow$  H<sub>2</sub>CN + OH is strengthen ; At the same time, the inhibition of the main chain branching reaction HCN + O  $\leftrightarrow$ NCO + H, which weakens the pathway of HCN conversion to NCO thus strengthens the conversion of HCN  $\rightarrow$  CH<sub>3</sub>CN; Finally, the inhibition of CH<sub>2</sub> radical generation also suppresses the reaction CH<sub>2</sub> + NO  $\leftrightarrow$ HNCO + H, which reduces the importance of NO  $\rightarrow$  HNCO  $\rightarrow$  NH<sub>2</sub>  $\rightarrow$  NNH  $\rightarrow$  N<sub>2</sub> in the CO<sub>2</sub> atmosphere.

## 4 Conclusions

In this paper, a jet-stirred reactor is applied to obtain new experimental results for the NO reduction by  $CH_4$  in  $N_2$  and  $CO_2$  atmospheres. The differences in the reburning process between  $N_2$  and  $CO_2$  atmospheres are investigated experimentally and numerically. The following conclusions are drawn:

(1) The inhibition of  $CH_4$  oxidation observed at high  $CO_2$  levels in the experiment can be the reason for the lower NO reduction efficiency in the  $CO_2$  atmosphere, because the slower oxidation process resulting in only a small amount of hydrocarbon radicals ( $CH_3$ , HCCO, etc.) can be used to reduce NO in reburning.

(2) The NO reduction in the N<sub>2</sub> atmosphere mainly passes through two pathways: NO ( $\rightarrow$  HCNO)  $\rightarrow$  HCN  $\rightarrow$  NCO  $\rightarrow$  N<sub>2</sub> and NO  $\rightarrow$  HNCO  $\rightarrow$  NH<sub>2</sub>  $\rightarrow$  NNH  $\rightarrow$  N<sub>2</sub>. And the main path of NO reduction in the CO<sub>2</sub> atmosphere is: NO ( $\rightarrow$  H<sub>2</sub>CN)  $\rightarrow$  HCN  $\rightarrow$  CH<sub>3</sub>CN  $\rightarrow$  NCO  $\rightarrow$  N<sub>2</sub>.

## References

[1] Stanger R, Wall T, Spörl R, Paneru M, Grathwohl S, Weidmann M, Scheffknecht G, McDonald D, Myöhänen K, Ritvanen J, Rahiala S, Hyppänen T, Mletzko J, Kather A, Santos S. (2015). Oxyfuel combustion for  $CO_2$  capture in power plants. International Journal of Greenhouse Gas Control. 40: 55.

[2] Smoot LD, Hill SC, Xu H. (1998). NO<sub>x</sub> control through reburning. Prog. Energy Combust. Sci. 24: 385.

[3] Normann F, Andersson K, Leckner B, Johnsson F. (2009). Emission control of nitrogen oxides in the oxy-fuel process. Prog. Energy Combust. Sci. 35: 385.

[4] Mendiara T, Glarborg P. (2009). Ammonia chemistry in oxy-fuel combustion of methane. Combustion and Flame. 156 : 1937.

[5] Gimenez-Lopez J, Aranda V, Millera A, Bilbao R, Alzueta MU. (2011). An experimental parametric study of gas reburning under conditions of interest for oxy-fuel combustion. Fuel Process. Technol. 92: 582.

[6] Meeks E, Grcar JF, Kee RJ, Moffat HK. (1996). AURORA: A FORTRAN program for modeling well stirred plasma and thermal reactors with gas and surface reactions. Office of Scientific Technical Information Technical Reports.

[7] Glarborg P, Miller JA, Ruscic B, Klippenstein SJ. (2018). Modeling nitrogen chemistry in combustion. Prog. Energy Combust. Sci. 67: 31.