Experimental Investigation of NOx Reduction by Urea Solution Injection in Fuel-rich Zone of Coal Combustion

Degui Bi$^1$, Zhongxiao Zhang$^{1, *}$, Zhixiang Zhu$^1$, Jiancong Dong$^1$ and Tuo Zhou$^2$

$^1$School of Mechanical Engineering, Shanghai JiaoTong University, Shanghai, 200240, PR China
$^2$Institute of Engineering Thermophysics, Chinese Academy of Sciences, Beijing 100190, China
Email: bidegui1103@163.com

Abstract. Experiments were carried out in an electrically heated vertical tandem-type drop-tube furnace system to evaluate the influence of stoichiometric ratio (SR), normalized stoichiometric ratio (NSR) and temperature (T) on NOx reduction by urea solution in coal combustion. The results indicated that, SR was the deciding factor for NOx reduction by ammonia under high temperatures. The reduction efficiency was improved with the increase of NSR. There was a significant reduction in NOx emission with increase in temperature under reducing conditions. However, ammonia had the tendency to get oxidized to NO, in presence of excess O2 in the combustion zone at high temperature.

1. Introduction
NOx emitted from utility boilers makes contributions to environmental pollution problems. Many countries have lowered their NOx emission limits in flue gases. For example, in the European Union the permissible NOx emission has been reduced to below 200 mg of NO2/m3 (6% O2), after 2016[1]. In China, by 2014, the permissible NOx emission was controlled to less than 100 mg/Nm3 at 6%O2 for all power plants [2]. There are numerous well-established methods, such as air staging, staged fuel combustion, selective non-catalytic reduction (SNCR), and selective catalytic reduction (SCR). SNCR is a conceptually simple process for reducing NOx emissions and has therefore been the most widely adopted method in coal-fired power plants [3-4]. However, in SNCR technology, a serious limitation of the SNCR for NOx reduction is the requirement of a narrow temperature window [5], developing new NOx control technologies is quite necessary, especially the technology of removing NOx in coal combustion process.

NH3 is formed during staged combustion of pulverized coal [6], which indicates itself that combustion modification could be an effective strategy for NOx abatement. Hence, Adding NH3 reagent (such as ammonia, urea solution) into the fuel rich zone may be to further reduce NO in staged combustion, which have received little attention in the present literature. Wang [7] reported the NOx reduction by urea solution, which showed that under hypoxic conditions (O2%=0), as the temperature increased, the NOx reduction efficiency increased rapidly. The maximum value of the optimal temperature was higher than in excess of O2(1~8%). In other words, NH3 could react with NOx in fuel-rich conditions, even at the higher temperatures. Fan and William [8-9] also reported this phenomenon in their recent experimental and modeling studies, which were carried out without the addition of any catalytic. According to Javed [10], the rate of NO destruction by ammonia would just be balanced by its formation by oxidation at the temperature of around 1230°C, in excess of O2. Therefore, it can be believed that the temperature balance is increased, if the oxygen concentration is...
decreased. Taniguchi [11] conducted a study to investigate the index for modeling a NO\textsubscript{X} reaction mechanism of combustion of pulverized coal, under various burning conditions. Cremer et al. [12-15] found that when ammonia reagent was introduced into the reduction region of the primary combustion zone in a cyclone-barrel-fired boiler, the NO\textsubscript{X} reduction efficiency improved significantly. Most of the researches focused on the features of NO\textsubscript{X} reduction at relatively lower temperatures, in excess of oxygen. However, there are only few reports, which explain the characteristics of NH\textsubscript{3} reaction with NO at high-temperatures, especially in a pulverized coal furnace.

In the present study, the characteristics of NH\textsubscript{3} reaction with NO in flue gas for typically high-volatile bituminous coal was investigated experimentally and concentrates in the evaluation of the NO\textsubscript{X} emission in reducing region from a novel vertical drop-tube furnace system.

2. Experimental Section
The experimental bench system is shown in Fig.1. The experimental setup consisted of an electric furnace reactor system, reducing agent injection device, pulverized coal feeder, flue gas analyzer, and other affiliated components. The reactor was an corundum tube which had an inner diameter of 50 mm and the length of 2100mm, and reaction zone is 1200 mm. The pulverized coal was fed through a micro-screw pulverized coal feeder, and coal feed rate was 0.2 - 0.5 kg/h for experiments. Pulverized coal and the air of supporting combustion was mixed in the nozzle which used a water-cooled probe to prevent pyrolysis of coal particles before injection. Urea solution, with mass concentration of 5\%, was injected into the reactor by a micro screw peristaltic pump.

![Figure 1. Schematic diagram of the experimental system](image)

The coal used in the tests was high-volatile Shenhua bituminous coal from China. The characteristics of this coal are presented in Table 1. The coal sample was grounded and sieved to a size of 75-90 μm and air-dried at 101°C for 10 h.

| Coal | Ultimate analysis, wt% | Approximate analysis, wt% |
|------|------------------------|--------------------------|
|      | Cad | Had | Oad | Nad | Sad | Mad | Aad | Vad | FCad |
| bituminous coal | 62.74 | 3.82 | 7.78 | 0.7 | 0.5 | 1.03 | 23.43 | 26.88 | 48.66 |

The concentrations of NO, O\textsubscript{2}, CO, and NO\textsubscript{2} were analyzed by a AFRISO-M60 flue gas analyzer, which maximum relative errors for the measured species were ±5% (>100ppm). The on-line data of NO concentration measured was in parts per million [ppm]. For the purpose of comparison, the NO\textsubscript{X}...
The concentration was converted into concentration of NO\(_2\) (mg/m\(^3\), dry 6\%O\(_2\)). The formula for conversion is

\[
[\text{NO}_X, \text{mg/m}^3] = [\text{NO}, \text{ppm}] \cdot \frac{46.0 - 6\%}{22.4 - 21\% - \% \text{O}_2, \text{vol}\%}
\]

\(1\)

3. Results and Discussion

3.1. Influence of SR on NO\(_X\) Reduction

Figure 2. Influence of SR on NO\(_X\) emission without urea solution

Figure 2 shows the influence of SR on NO\(_X\) emission, when no urea solution was injected into the furnace. The results show that the effect of the temperature on NO\(_X\) generation exhibited different characteristics, depending upon the SR. The concentration of NO\(_X\) emission decreased radically with SR at different temperatures. In an oxidizing atmosphere (SR>1.0), higher temperature favored the formation of a larger amount of NO\(_X\). However, under a reducing atmosphere (SR<1.0), the tendency was reversed. It could also be seen that at a higher temperature in the reducing zone, there was a sharper decline in the NO\(_X\) emission as SR decreased.

In order to investigate the effect of SR on NO\(_X\) reduction by urea solution, the experiments were carried out in the SR range of 0.65 to 1.2. Figure 3 shows the influence of the SR in the combustion zone at different NSR and temperatures.

Figure 3. Influence of SR on NO\(_X\) emission with injecting urea solution in reaction zone
As is shown, with decrease of SR in reaction zone, the atmosphere turned into a reducing atmosphere (SR<1.0). The concentration of NOX emission had a obvious decrease. The lower the SR is, the higher the NOX reduction efficiency when the NSR and temperatures were constant. This was due to the fact that when SR of combustion zone decreased, the concentration of O radicals decreased and the concentration CO increased. A small number of O radicals could be prevented from getting oxidized to NOX. The regenerated OH radicals continued to promote the conversion of NH3 to NH2, which reduce NO primarily. The concentration of NOX emissions could be reduced to 50~100mg/m³ in highly reduced atmosphere, with NSR=3 and SR=0.65. There are few studies that reported of SR on NOX reduction by ammonia at high temperature.

3.2. Influence of NSR on NOX Reduction with Injecting Urea Solution

In order to investigate the influence of NSR on NOX emission at high temperature, the experiments were carried out at different NSR values of 0, 1.0, 1.5, 2.0, 2.5, and 3.0.

Figure 4. Influence of NSR on NOX reduction by ammonia (t=1300°C.)

Figure 4 illustrates the differences in NOX reduction efficiency with variations of NSR, in which baseline conditions for concentration of NOX emission corresponded to the different SR values when temperature is at 1300°C. The efficiency of NOX reduction increased rapidly when NSR increased. However, when NSR>2, the rate of NOX reduction became slowed down. This was due to the fact that the concentrations of NOX and other reactive groups decreased as ammonia content was constantly increased. Thus, the reaction rate gradually slowed down.

3.3. Influence of Temperature on NOX Reduction with Injecting Urea Solution

Figure 5 Influence of temperature on NOx reduction by urea solution at SR= 0.65
The effect of temperature on NO\textsubscript{X} reduction of efficiency while SR=0.65, 0.95 were shown in Figures 5 and Figures 6. It can be observed minimum NO\textsubscript{X} emission occurred at 1400°C, and the NO\textsubscript{X} emission value was lower at SR=0.65 than at SR=0.95. This could be attributed to the fact that the higher temperature in the reducing zone lowered the NO\textsubscript{X} emission with decrease in SR. Those results suggested when O\textsubscript{2} concentration was low in the fuel rich zone; temperature had great effect on the removal efficiency of NO\textsubscript{X}. When SR=0.95, O radicals were relatively high in number, which implied that reactions: NH\textsubscript{2} + O = NH + OH, NH + O = NO + H, HNO + OH = H\textsubscript{2}O +NO, which were the crucial steps that would decrease the reduction efficiency of NO\textsubscript{X}. At higher SR value, as shown in Figure 6(b), NO\textsubscript{x} concentration increased rapidly as temperature increased at different NSR.

4. Conclusion
An experimental investigation was conducted on a vertical drop-tube furnace system, and the conclusion is summarized as follows: SR had an obvious effect on the NO\textsubscript{X} emissions for pulverized coal combustion. The decrease of SR led to a highly reducing atmosphere and increased the reduction efficiency of NO\textsubscript{X} when urea solution participated in the reaction, and vice versa. NO\textsubscript{X} reduction efficiency increased more with increased in NSR, under reducing atmosphere, when the NSR>2, the rate of NO\textsubscript{X} reduction increased is not obvious. Increase of temperature was crucial factor for promoting the NO\textsubscript{X} reduction efficiency in a reducing atmosphere, and reversed results were obtained in a oxidizing atmosphere.

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6. Reference
[1] European union (Large combustion plants) regulations 2012. S.I. No. 566 of 2012.
[2] GB13223-2011, Emission standard of air pollutants for thermal power plants[S], 2011.
[3] Tayyeb Javed M, Naseem Irfan, Gibbs B M. Control of combustion -generated nitrogen oxides by selective non-catalytic reduction. Journal of environmental management 2007, 83: 251-89.
[4] Daood S S, Javed M T, Gibbs B M, Nimmo W. NO\textsubscript{X} control in coal combustion by combining biomass co-firing, oxygen enrichment and SNCR. Fuel 2013, 105: 283-92.
[5] Norbert Modinski. Numerical simulation of SNCR (Selective non-catalytic reduction) process in coal fired grate boiler. Energy 2015, 92: 67-76.
[6] Bose A C. Pulverized coal combustion: Fuel nitrogen mechanisms in the rich post-flame[C] // Symposium. 1989:1127-1134.
[7] Quan Wang, Qingcheng Wang, Jianjun Cai. Experimental study of urea on SNCR removal of NO\textsubscript{x}.Journal of chemical and pharma caceutical research 2014, 6(7): 2541-2546.
[8] Fan W, Lin Z, Kuang J, et al. Impact of air staging along furnace height on NOx emissions from pulverized coal combustion [J]. Fuel Processing Technology, 2010, 91(6):625-634.

[9] William H Sun, Penelope Stamatakis, John E Hofmann. Reaction kinetics of selective Non-catalytic NOx reduction with urea. https://web.anl.gov/PCS/acsfuel/preprint%20archive/Files/38_2_DENVER_03-93_0734.pdf.

[10] Javed M T, Irfan N, Gibbs B M. Control of combustion-generated nitrogen oxides by selective non-catalytic reduction. [J]. Journal of Environmental Management, 2007, 83(3):251-289.

[11] Taniguchi M, Kamikawa Y, Okazaki T, et al. A role of hydrocarbon reaction for NOx, formation and reduction in fuel-rich pulverized coal combustion [J]. Combustion & Flame, 2010, 157(8):1456-1466.

[12] Marc A Cremer, Huafeng D Wang, David E Boll, Edmund Schindler, Edmundo Vasquez. Improved rich reagent injection (RRI) performance for NOx control in coal fired utility boilers. U.S. DOE Conference on SCR and SNCR for NOx control 2003.

[13] Marc A Cremer, Bradley R Adams, David C O’Connor, Venkata Bhamidipati, R Gifford Broderick. Design and Demonstration of rich reagent injection (RRI) for NOx reduction at Conectiv’s B.L. England station. http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.497.5961&rep=rep1&type=pdf

[14] Cyclone boiler field testing of advanced layered NOx control technology in Sioux Unit 1. Final technical report. Reaction Engineering International. Sept. 2006. http://www.osti.gov/scitech/servlets/purl/927774

[15] NOx control options and integration for US coal fired boilers. Final report. Reaction Engineering International, Jun 2006. http://www.osti.gov/scitech/biblio/927773-BjKBpO/