Experiment and Mechanism Analysis of Selective Non-Catalytic Reduction with the Compound Reducing Agents in a Lab-scale CFB Reactor

IOP Conf. Series: Materials Science and Engineering **484** (2019) 012012 doi:10.1088/1757-899X/484/1/012012

Experiment and Mechanism Analysis of Selective Non-Catalytic Reduction with the Compound Reducing Agents in a Lab-scale CFB Reactor

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Abstract. The conventional SNCR technology with reducing agent ammonia has been utilized in power industry extensively. In this paper, a new denitrification method with the compound reducing agents contain ammonia and reducing gas was discussed. The SNCR experiment with H_2 and CH_4 as the additives was carried out in a lab-scale CFB reactor which imitated flue gas environment in CFB boilers, meanwhile the mechanism modelling including the reaction of gas additives was adopted to simulate the experimental process. The validations of mechanism modelling and parameter optimizations were discussed by the comparisons of experimental and computational results. The compound reducing agents with H_2 and CH_4 additives can expand the adaptive temperature window of denitrification reaction and reduce the optimal reaction temperature. Hence the NOx removal efficiency of conventional SNCR can be improved significantly, and the effect of H_2 additive is better than that of CH_4 additive. The optimal reaction temperature in simulation is about 800°C with the H_2 concentration of 300 ppm, while 760°C under the concentration of 900 ppm. The minimal NOx residual concentration is estimated to approach 75 mg/m^3 at 800°C by using the H_2 compound reducing agent.

1. Introduction

In China, the nitrogen oxides (NOx) emission has been one of the major environmental concerns nowadays and the new national standard of air pollution prevention (GB13223-2011) has been already released and implemented. Thus, the control of NOx emission has become a priority aspect of environmental protection. Among various technologies, selective non-catalytic reduction (SNCR) is known to be an effective and feasible approach, especially in Circulating fluid bed (CFB) boilers, because of its low investment cost and very considerable denitrification efficiency.

Since the Thermal De-NOx was firstly patented by Lyon in 1975, various studies of SNCR technology have been carried on by researchers worldwide. One of the most important characteristics of SNCR is the narrow operating temperature window, which is usually located in the range of 1120-1380 K [1-7]. Nevertheless, this operating temperature range could be expanded or lowered by some gas additives with the common reducing agent ammonia [8-10]. It is essential to explore the influence of these compound reducing agents, ammonia with various reducing gas, on the conventional SNCR process in the CFB flue gas environment and its optimum mechanism of SNCR conditions.

For that reason, a lab-scale electricity-heated tubular flow reactor was used to simulate the CFB boiler and the compound reducing agents contain ammonia and gas additives such as H_2 or CH_4 were injected into this system for SNCR experiments. Moreover, the reaction mechanism was analysed by a business chemical dynamics software. In the comparison of simulation results and experimental data, the influence of H_2 and CH_4 addition on SNCR process in CFB boilers was given. As a result, the denitrification reaction characteristics of the conventional SNCR and the SNCR with the compound reducing agents could be investigated and the differences between H_2 and CH_4 on the reaction were analysed.

2. Experiment and Mechanism

2.1. Experiment

The experiments was performed in the experimental device as shown in figure 1, which was consists of serval parts such as pre-heater, electricity-heated tubular flow reactor, cyclone separator, simulated flue gas system, reductant injection system and gas monitoring system. The simulated flue gas was premixed by nitric oxide, nitrogen, oxygen and carbon dioxide from the gas cylinders and sequentially flowed through the pre-heater, tubular flow reactor and cyclone. The flow of flue gas was 0.5m^3/h and its component was set to 268 mg/m^3 NOx, 5% O_2 and 15% CO_2. The electricity-heated tubular flow reactor was made by a corundum tube with the length of 1.2m and inner diameter of 6 cm and the thermocouple was installed at the outlet of reactor to measure and adjust the flue gas temperature inside the reactor within the range of 700-1000°C. The reducing agents were delivered by the constant flow pump BT100-02 and injected at the inlet of cyclone, where the flue gas contains NOx was mixed sufficiently with these reductants due to the gas vortex inside the cyclone. At the outlet of cyclone, the compound of flue gas was measured by the Testo 340 analyser, which has an accuracy of 1 ppm or 0.1% respectively. Besides, various amounts of H_2 or CH_4 were added into the compound reducing agent to explore the effect of H_2 or CH_4 additives on denitrification efficiency and optimal reaction temperature window.

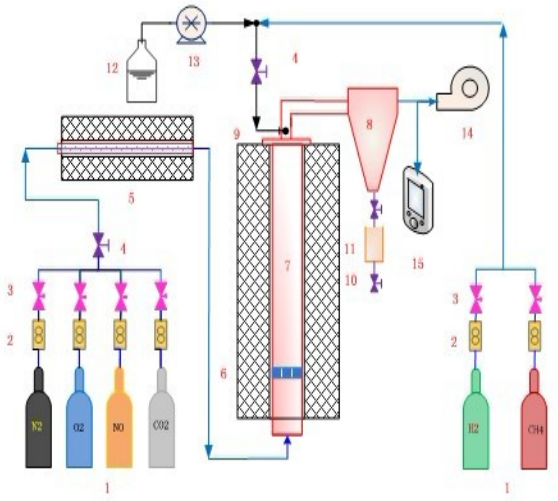

Figure 1. Schematic diagram of the experimental system

Note: 1-simulated flue gas; 2- flowmeter; 3- needle valve; 4-control valve; 5-preheater; 6-distribution plate; 7-electricity-heated tubular reactor; 8-cyclone; 9-injection;10- butterfly valve; 11- container; 12-ammonia; 13-constant flow pump; 14- fan; 15-analyzer.

2.2. Mechanism

In past decades, various reaction mechanisms and models have been implemented by researchers worldwide to investigate the SNCR process. In this work, the simulation process of SNCR was performed by a business chemical dynamics software and the Perfect Stirred Reactor (PSR) model was

adopted in the simulation, in which the adiabatic closed system and the sufficient mixture of various reactants were assumed, and heating process of gas was also ignored.

Among the reaction mechanisms described in literatures [11-14], the racial reaction mechanism of SNCR with gas additives introduced in the literature [13] was selected to simulate the SNCR process with the compound reducing agents in this study. The racial reaction mechanism includes 461 reversible reactions and 66 chemical species, including the oxidation mechanism of H_2 and CH_4 [14], and the interaction mechanism between these gas additives and nitrogen oxides.

The calculation condition of reaction simulation was set as same to the experiment. The flue gas in this simulation containing 5% O_2, 268 mg/m^3 NO (i.e. 200 ppm) and 15% CO_2 was balanced by N_2. The compound reductants were composed by 300 or 400 ppm NH_3 (i.e. NSR=1.5 or 2), 300 or 900 ppm gas additives (CH_4 or H_2). Residence time of flue gas in the reactor was set to 0.6 s and the pressure of CFB reactor was set to 1 atm. The comparison of results in mechanism simulations and experimental data was given in this paper. The characteristics of denitrification reaction in the conventional SNCR and the SNCR with different compound reductants were also analysed.

3. Results and Discussion

3.1. Validation and Parameter Optimization

The reaction temperature, flue gas residence time and normalized stoichiometric ratio (NSR) are three important indexes of SNCR process, and the optimal values for these parameters were determined according to the experimental data and calculation results. As shown in figure 2, the calculation results agree well with the experimental data, which illustrate the mechanism modelling chosen in this study is suitable to simulate the SNCR process. It is also explicit that the denitrification efficiency in the simulation is higher than the experimental data, because the ideal mixture of NH_3 and flue gas was assumed in the theoretical calculation, while it cannot occur in the actual experiment.

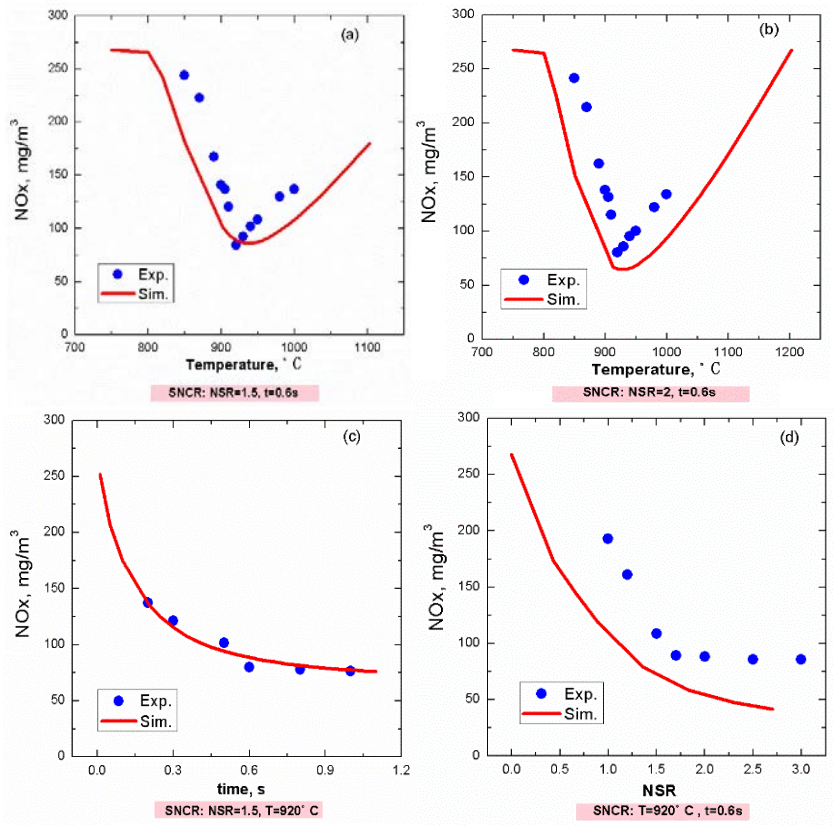

Figure 2. Comparisons of experiment data and simulation results in conventional SNCR without compound reducing agents

In the comparisons of figure 2(a) and 2(b), the optimal reaction temperature in SNCR simulation is close to the optimal temperature of 920°C observed in the experiment, and the optimal temperature window in experiment is narrower than that in simulations. As is well known the flue gas temperature in the furnace of conventional CFB Boilers is almost in the range of 850-900°C. Obviously, the optimal temperature in this study is slightly higher than the actual operational temperature of CFB boilers. However, the initial concentration of NOx emission decreases with the decreasing flue gas temperature under the CFB combustion conditions [15]. Figure 2(c) shows the relationship between the NOx residual concentration and the flue gas residence time while the reaction temperature and NSR was 920°C and 1.5 respectively. The efficiency of denitrification can reaches 50% when the residence time rises to 0.3s, and the residual concentration of NOx approaches the minimum value 70 mg/m^3 once the residence time exceeds 0.6s. Meanwhile, the simulation results agree well with the experimental data in this situation. Figure 2(d) illustrates the relation of the NOx residual concentration and NSR when the reaction temperature and residence time was 920°C and 0.6s respectively. The denitrification efficiency increases with the ascending NSR, but the growth rate of denitrification efficiency decreases significantly when the NSR exceeds 1.5. The denitrification efficiency in the experiment is lower than that in the simulation, which is attributed to the ammonia solution used in experiments and the amount of ammonia involved in actual reaction is lower than that in the theoretical calculation.

3.2. Effect of H_2 on the SNCR

Figure 3 indicates the relationship between NOx residual concentration and the reaction temperature in different concentrations of H_2 additive, and the variation trend in simulation is resemble to that in the experiment. Both in the condition of 300ppm and 900 ppm H_2 addition, the predictive results of NOx residual concentration is slightly lower than the experimental data. For example, in simulation the minimal NOx residual concentration reaches 75 mg/m^3 at the optimal temperature of 800°C, but the concentration only get 95 mg/m^3 at the actual optimal temperature of 870°C in the experiment under the H_2 concentration of 300 ppm. It is obvious in the Figure 3 that, the adaptive reaction temperature window shifts towards the lower temperature section with the increase of H_2 concentration. The optimal reaction temperature in simulation is about 800°C under the H_2 concentration of 300 ppm, while it is 760°C under the H_2 concentration of 900 ppm, and these two values are less than the temperature without the H_2 addition, 920°C. Moreover, the experimental data of NOx residual concentration in the situation of 300ppm H_2 addition deviate from the calculation results under the optimal temperature (T<870°C), while the similar deviation appears when the reaction temperature exceed the optimal value (T>750°C), as shown in figure 3(b) and (c).

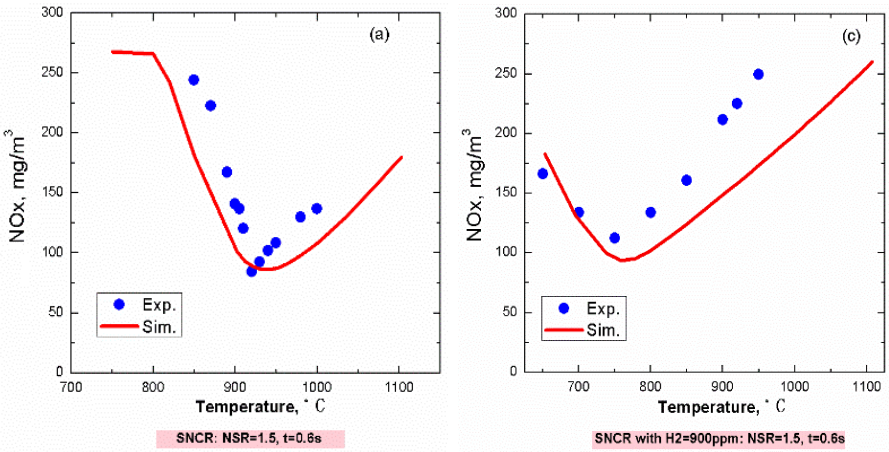

Figure 3. Comparison of experiment data and simulation results in the denitrification reaction with H2 additive

3.3. Effect of CH_4 on the SNCR

Figure 4 demonstrates the relation between NOx residual concentration and the reaction temperature in SNCR process with different amount of CH_4 addition. The impact trend of CH_4 additive on SNCR in model simulation is similar with that in experiment. In the simulation, the optimal reaction temperature with CH_4 concentration of 300 ppm is about 820°C, while 800°C for CH_4 concentration of 900 ppm. In the situation of 300 ppm CH_4 addition, as shown in Figure 4(b), the minimal NOx residual concentration is estimated to approach 80 mg/m^3 at the optimal reaction temperature of 820°C, while the experimental value reaches 105 mg/m^3 at 840°C. In general, the simulation results are better than the experimental data due to the ideal gas mixture assumed in the calculations. This phenomenon is mainly caused by the oxidation reaction of CH_4, which also generate OH and promote the reduction reaction of NO_X.

Moreover, in the comparisons of H_2 and CH_4 addition, it can be easily found that the effects of H_2 and CH_4 based compound reducing agents on the conventional SNCR process are different. H_2 additive is more effective to reduce the optimal reaction temperature of SNCR, and the denitrification efficiency of CH_4 additive is lower than that of H_2 additive. It is mainly caused by the differences of generating rate and reaction route of OH in these two conditions.

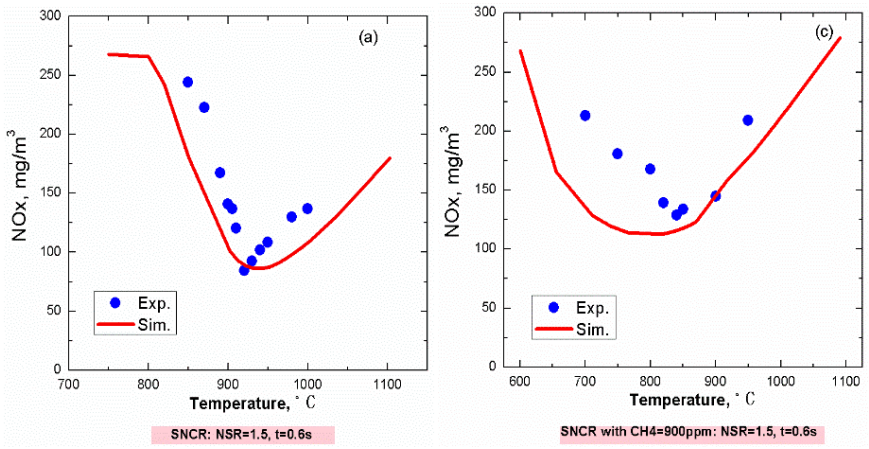

Figure 4. Comparison of experiment data and simulation results in the denitrification reaction with CH4 additive

4. Conclusions

In order to explore the denitrification reaction characteristics of conventional SNCR and SNCR with the compound reducing agents in the CFB flue gas environment, the flue gas SNCR experiment with H_2 and CH_4 as the additives was carried out in a lab-scale CFB reactor which imitated flue gas environment in CFB boilers, meanwhile the mechanism modelling including the elementary reaction of gas additives was adopted to simulate the experimental process. The comparisons of results in mechanism simulations and experimental data were discussed in this paper. By the comparisons, the mechanism model is agreeable to simulate the actual experiment. The compound reducing agents with H_2 and CH_4 additives can expand the adaptive temperature window of denitrification reaction and reduce the optimal reaction temperature. Hence the NOx removal efficiency of conventional SNCR can be improved significantly, and the effect of H_2 additive is better than that of CH_4 additive. In the simulation, the optimal reaction temperature with CH_4 concentration of 300 ppm is about 820°C, while 800°C for CH_4 concentration of 900 ppm. The optimal reaction temperature in simulation is about 800°C with the H_2 concentration of 300 ppm, while 760°C under the H_2 concentration of 900 ppm. These values are less than the temperature without the compound reducing agents. The minimal NOx residual concentration with H_2 compound reducing agent reaches 75 mg/m^3 at the optimal temperature of 800°C and the value approaches 80 mg/m^3 at the optimal reaction temperature of 820°C with CH_4 compound reducing agent.

5. Acknowledgments
The authors greatly acknowledge the financial support of this work by the National Key R & D Program of China (Grant No.: 2016YFB0600202).

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