Dynamic simulation in the process of pressurized denitration based on oxy-fuel combustion

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Abstract. Oxy-fuel combustion is considered as one of the most promising technologies for capturing CO_2 from coal-fired power plants. It will greatly reduce the cost of gas purification if we remove NO_x in the process of compression, which is the characteristic of oxy-combustion. In this paper, simulation of denitration process of oxy-fuel combustion flue gas was realized by the Aspen Plus software, systematically analyzed the effect of temperature, pressure, initial concentration of O_2 and NO in the denitration process. Results show that the increasing of pressure, initial concentration of O_2, initial concentration of NO and the decrease of temperature are all beneficial to the denitration process.

1. Introduction

NOx can be removed effectively in the process of compression in oxy-fuel combustion, thus this method can save the cost of denitration equipment. However, most of current studies are experimental researches. The object of study has some limitation due to the limitation of experimental conditions. Besides, the reaction mechanism of removal process of NOx is comprehensive, the specific reaction mechanism has not yet been determined. Besides, current studies always focus on studying the effects of different reaction conditions on the removal of NO_x, but the research of integrated optimization choice of optimum research conditions is relatively less[1,2]. In this paper, a reliable model is established by Aspen Plus software according to dynamic data existed in the literature and some experimental data. Then by monitoring gas-phase NO_x concentration, we analyze the effect of different reaction pressure, temperature, initial O_2 and NO concentration on the process of NO_x absorption[3-5].

2. Experimental and system flow set-up

The experiment apparatus is shown in Figure 1. This apparatus can be divided into three parts: the synthetic flue gas system, the reaction system and the gas analysis system.

Synthetic flue gas system is made up of gas cylinders, pressure- reducing valve and mass flow controllers. Flue gas mainly consists of CO_2, O_2, NO and SO_2. The gas flow is controlled by using a mass flow controller to realize precise control and maintain the stable of system flow[6-8]. The body of reaction system is a flip-style magnetic seal lifting autoclave. Temperature and pressure of autoclave are monitored by the external pressure gauge and thermometer. In order to control the flue gas entering or leaving the autoclave, some stop valves are provided in import and export. Synthesis flue gas enters the bottom of the autoclave to react with the deionized water which is pre-loaded[9,10]. The composition of export flue gas is tested by multifunction flue gas analyzer.
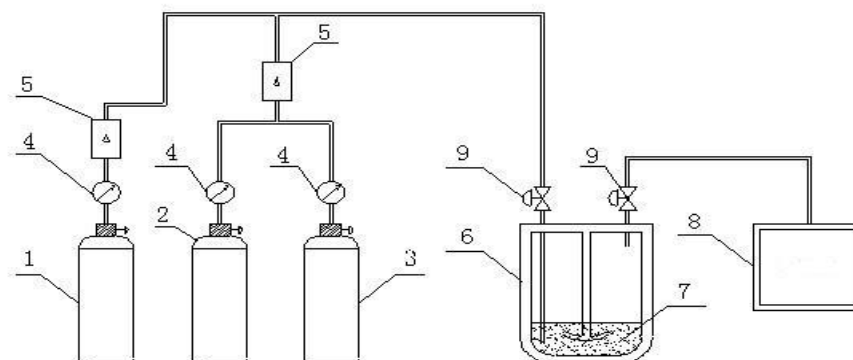
Figure 1. Simplified process flow diagram of the experimental apparatus.
1 O_2 cylinder; 2 CO_2 (or N_2) cylinder; 3 mixed gases cylinder; 4 pressure reducing
valve; 5 MFC; 6 autoclave; 7 deionized water; 8 flue gas analyzer; 9 stop valve.

According to the apparatus or conditions, a series of RBATCH module based on principle of dynamic are used to realize the simulation. The three RBATCH modules are used to simulate the processes of CO_2 cleaning, flue gas booster and constant pressure reaction respectively. Export gas of RBATCH3 occurs flash in the circumstance of export pressure and temperature, and the concentration of NO can be test in gaseous after dehydration.

The components of flue gas are defined in simulation under the same components of experiment, and the productions are HNO_2 and HNO_3. We use the model of ELECNRTL to consider the effect of molecules-molecules, electrolyte-electrolyte and electrolyte-molecules, due to the electrolyte in system participated in the reaction. Aspen Plus automatically calls the internal parameters. In the method of calculating gas-liquid balance activity coefficient, Henry's law can be used to describe the condition of dissolved gas or other supercritical components. The specified Henry components of simulation process contain NO, NO_2, O_2, CO_2, HNO_2 and HNO_3.

3. Simulation verification

The flue gas and operating conditions of experiment are consistent with the simulation. The experimental research and process simulation based on Aspen of pressurized denitration process at different conditions in reaction kettles, Denitration conditions and the experiment and simulation results are shown in Table 1.

We can find that the NO removal rates in simulation results coincide well with the experiment. The maximum relative error is only 1%, so the model and mechanism used in simulation is reliable and feasible. Theoretical support is provided to promote the industrial application of denitration way.

Table 1. The simulation results compared with the experimental results.

Initial concentration		Tempera ture /℃	Pressure /bar	Residence time /min	Simulation removal ratio of NO /%	Experiment-al removal ratio of NO /%	Relative error of removal ratio of NO/%
NO /ppm	O_2/ %						
279	5	25	10	5	76.0	76.0	0
836	5	25	6	5	83.5	82.7	1.0
836	5	25	10	5	92.5	92.2	0.3
836	5	25	10	10	95.9	95.2	0.7
836	5	30	10	5	91.1	91.0	0.1
836	10	25	10	5	94.4	93.5	1.0
836	5	25	14	5	94.9	95.3	-0.4

3.1. Effect of pressure on the removal of NO

In the process, the absorption reactor temperature is 25℃, initial concentration of O_2 is 5%, residence time of constant pressure in RBATH3 is 5*min*, initial concentration of NO is 836*ppm*. The effect of pressure on the absorption of NO is studied by changing the stop pressure of Rbatch2. Pressure range is 4*bar* to 20*bar*, the simulation results are shown in Figure 2 and Figure 3.
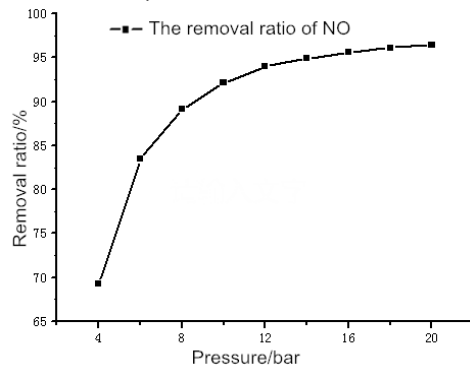

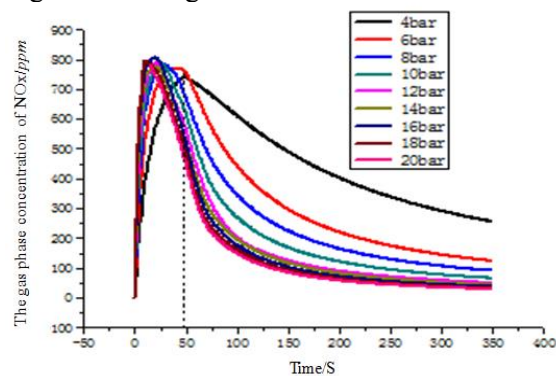**Figure 2.** The removal rate of NO varied with pressure.

Figure 3. The relationship between gas phase NO_x concentration and time in reactor.

Figure 2 shows that removal rate of NO increases with the increase of pressure. And removal rate of NO reachs 96.4% under the pressure of 20*bar*, so the increase of NO will be conducive to the removal of NO. But the effct of increased removal rate of NO is different under different pressure range, the effect is obvious in low pressure, while it becomes more slowly if the pressure is higher than 12*bar*. Figure 3 shows the relationship between gas phase NO_x concentration and time in reactor, the concentration of NO_x increases with pressure at preliminary stage. When the pressure is higher than 12*bar*, the concentration of NO_x begins to drop.

NO_x is absorbed quickly in early stage of constant pressure reaction, and concentration of NO_x gradually reduces with the time. Under the condition of 5*min* residence time, concentration of NO_x is stable in high pressure, but a decline exists in low pressure. So the increase of pressure is conducive to the denitration process of flue gas. But enough residence time is required to reduce the NO_x concentration to a certain extent, and residence time becomes shorter with the increase of pressure.

3.2. Effect of temperature on the removal of NO

In the process, the stop pressure in Rbatch2 is 10*bar*, initial concentration of O_2 is 5%, residence time of constant pressure in RBATH3 is constant, initial concentration of NO is 836*ppm*. The effect of temperature on the absorption of NO is studied by changing temperature from 10℃ to 85℃.
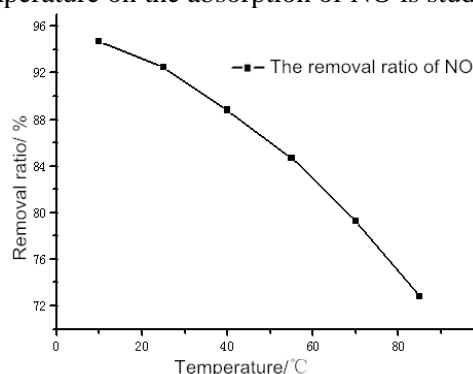

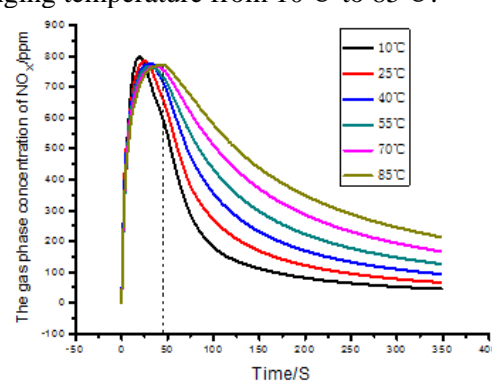**Figure 4.** The removal rate of NO varies with temperature.

Figure 5. The relationship between gas phase NO_x concentration and temperature.

Figure 4 shows that removal rate of NO decreases with the gradually increase of temperature. So the decrease of temperature is conducive to the absorption of NO. The remove rate of NO reduces by 22% while the temperature rises from 10℃ to 85℃. Figure 5 shows the concentratrion variety of NO_x in the process of absorption. The gas phase concentration of NO_x almost maintains the stability at the preliminary stage. But in the later stage, the NO_x concentration in high temperature is higher than lower temperature's. The export gas phase NO_x concentration of Rbatch 2 has a certain decline compared with entrance, and the export gas phase NO_x concentration declines with the decrease of temperature, but the amplitude of decrease is not obvious. NO_x is absorbed quickly in early constant pressure reaction stage, and the export NO_x concentration decreases with the incrasing of time. NO_x concentration in low temperature is lower than high temperayure's in constant pressure reaction stage. Under the condition of 5*min* residence time, the NO_x concentration in low temperature has tended balance, while the NO_x concentration in high temperature continues to drop. So the decrease of temperature is conducive to the pressurized denitration process of flue gas. But if we want to reduce NO_x concentration to a certain extent, the enough residence time should be ensured, which will be longer with the increase of temperature.

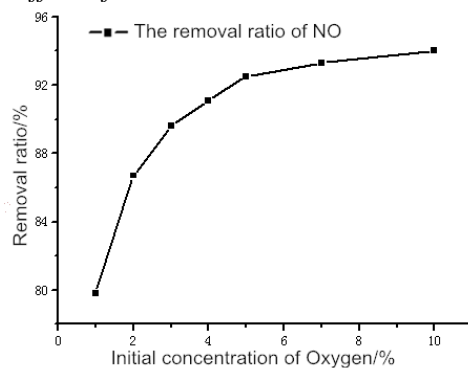*3.3. Effect of initial O_2 concentration on the removal of NO*

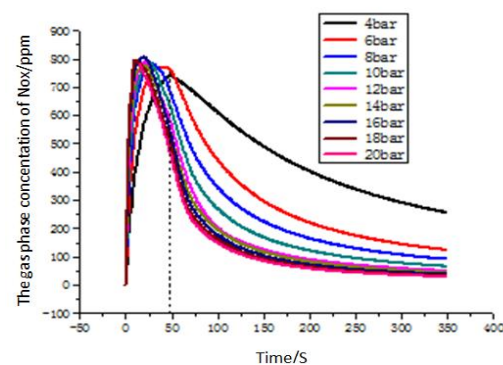**Figure 6.** The removal rate of NO varies with initial O_2 concentration.

Figure 7. The relationship between gas phase NO_x concentration and time.

The stop pressure in Rbatch2 is 10*bar*, the absorption reactor temperature is 25℃, residence time of constant pressure in RBATH3 is constant, initial concentration of NO is 836*ppm*. The effect of initial O_2 concentration on the absorption of NO is studied by changing the downtime. Initial O_2 concentration range is 1% to 10%, the simulation results are shown in Figure 6 and Figure 7.

Figure 6 shows that removal rate of NO gradually increased with the increase of initial O_2 concentration, so the increase of O_2 concentration in flue gas is conducive to the removal of NO. But the effct of increased removal rate of NO is different under different initial O_2 concentration. The removal rate of NO increases rapidly with the increase of initial O_2 concentration when the initial O_2 concentration is lower than 5%. In contrast, the effect of initial O_2 concentration on the removal retio of NO is weak, if the initial O_2 concentration is more than 5%. So when the initial O_2 concentration is 3% to 5%, it is more suitable for pressurized denitration process.

Figure 7 shows the change of NO_x concentration with the absorption time. Concentration of NO_x decreases at preliminary stage, the effect of O_2 concentration on the NO_x is obvious when the initial O_2 concentration is 1% to 5%, while it is more slowly if the initial O_2 concentration is more than 5%. It is accordance with that in Fig.7. Under the condition of 5*min* residence time, the NO_x concentration in high initial O_2 concentration tends balance, while the NO_x concentration in low O_2 concentration continues to drop. So increase of initial O_2 concentration is conducive to the pressurized denitration

process of flue gas. But if we want to reduce NOx concentration to a certain extent, the enough residence time should be ensured, which will be longer with the decrease of initial O_2 concentration.

4. Summary

In this paper, simulation of the pressurized denitration process of oxy-fuel combustion flue gas is provided based on the principle of Aspen Plus intermittent reactors. Results are shown as follows:

(1) Increase of pressure, initial O_2 concentration, initial NO concentration and decrease of temperature are all conducive to the pressurized denitration process of flue gas. The maximum of removal can reach 96.4% in the experimental conditional.

(2) The 3%-5% content of O_2 in flue gas is good for the pressurized denitration process of flue gas. And this concentration range is also the allowable range of O_2 in actual flue gas.

(3) The pressurized process can remove only a little NO, so enough residence time is required to meet the requirement of NOx removal rate. The residence time increases with the decrease of pressure, initial O_2 concentration, initial NO concentration and the increase of temperature.

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