

SIMULTANEOUS REMOVAL OF SO₂ AND NO_x USING AMINE-BASED AQUEOUS SOLUTION IN A PILOT-SCALE LIQUID COLUMN TOWER

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ABSTRACT

Simultaneous removal of SO₂ and NO_x using wet-scrubbing method was reported in many literatures but experiments on pilot-scale device were merely reported as an important step in scale-up process. In this paper, the experiments were carried out in a self-designed pilot-scale liquid column tower in a continuous model to investigate NO_x and SO₂ removal efficiency using a novel mixture amine-based aqueous solution. Operating parameters, such as swirl plate, superficial velocity, liquid-gas ratio, NO_x concentration and SO₂ concentration were widely studied and optimized in separate denitrogenation and simultaneous removal process, respectively. The positive influence of swirl plate was intensively discussed and the effect of removal NO_x was enhanced by a half due to the additive swirl plate. The optimal operation condition for denitrogenation was summed as followed: the superficial velocity was set as 1.5 m/s, the liquid-gas ratio was set as 14.3 L/m³ and the swirl plate was added for the mass-transfer enhancement. The effects of the SO₂ and NO_x concentration on the removal efficiency were tested. Accordingly, the experiments revealed that the SO₂ in off gas improved the denitrogenation efficiency a lot in the pilot-scale device and the simultaneous desulfurization and denitrogenation in one scrubber tower could achieved a desirable efficiency. Overall, the wet-scrubbing method using amine-based aqueous solution has a promising potential in the industrial application as a simultaneous desulfurization and denitrogenation technique.

Keywords: Simultaneous desulfurization and denitrogenation, Pilot-scale, Liquid column tower, amine-based absorbent

1. Introduction

According to new policies in China, many strict requirements on SO₂ and NO_x emission are presented lately and the punishment is sterner than ever (Zhang Q, 2012). Mature treatment method such as wet flue gas desulfurization and selective catalytic reduction are widely applied in industrial setups (Skalska K, 2010) but there are still some problems in the combined technology such as high capital cost, excessively large occupied area, and potential poisoning of catalysts. Thus simultaneous desulfurization and denitrogenation shows a promising prospect to save equipment and energy demanded.

Simultaneous desulfurization and denitrogenation process is a novel conception aimed at absorbing SO₂ and NO_x in one setup. Compared with many techniques, wet-scrubbing method shows its promising prospect due to the feasible application on traditional scrubbing tower. Lots of absorbents such as oxidant, chelates and urea are tested in recently reports (Mondal M K, 2013; Zhao Y, 2014). In those absorbents urea behaving as an environmental-benign absorbent in simultaneous process attracts researchers' attentions (Fang P, 2013). According to Xiong's researches, a kind of amine-based absorbent consisting of urea, NH₄HCO₃ and triethanolamine aqueous solution shows a high removal efficiency in a bench-scale experiment (Xie H Y, 2010; Shi Z, 2011). However, on the other hand, the absorption device plays an important role in the simultaneous absorption. Compared with reported devices, the structure of liquid column tower provides its numerous advantages, such as simple structure and desirable mass-transfer ability

(Li N, 2010). Thus it's necessary to apply mixture absorbent in pilot scale liquid column tower to evaluate its performance in scale-up process.

The main purpose of this paper is to verify the feasibility of simultaneous desulfurization and denitrogenation using amine-based absorbent in the self-designed liquid column tower. The performance of swirl plate is tested and the influence of swirl plate on the separate NO_x removal is discussed. The optimal operation conditions are evaluated based on the comparison between the experiments of simultaneous absorption and separate denitrogenation.

2. Experimental equipment and method

2.1. Reagent:

Urea was used to absorb SO_2 and inhibit the decomposition of nitrous acid. The ammonium bicarbonate (fertilizer, Yuantai Huadian Co.,Ltd., Boai) was added to reduce the capital cost. Triethanolamine ($\geq 99.0\%$, analytically pure, Jiujiu Bioengineering Co.,Ltd., Yangzhou) acted as buffer in denitrogenation process (Xie H Y, 2010). In our lab-scale research, the optimal composition was 5 wt% urea, 5 wt% NH_4HCO_3 and 0.015 wt% triethanolamine so this composition continued to be used in the pilot-scale research (Shi Z, 2011). Reverse osmosis water was used to prepare the solutions.

2.2. Experimental equipment

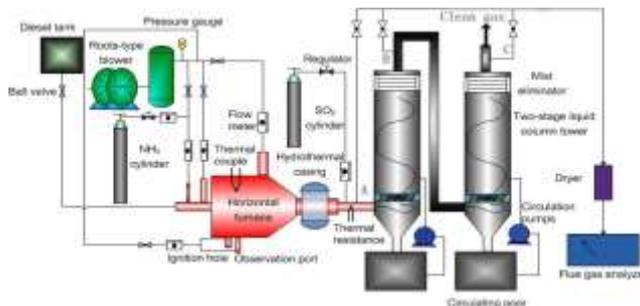


Figure 1: The schematic of the simultaneous desulfurization and denitrogenation system



Figure 2: The schematic of the swirl plate in liquid column tower

From Figure 1, the setup contained gas simulating system, absorption tower, absorbent circulation system and analysis system. The diesel oil and NH_3 gas were burned and mixed completely in the horizontal furnace. The O_2 concentration and NO_x oxidation degree in inlet flue gas was controlled at 4.5 % and 10% by calculations. The hydrothermal casing in the exit of furnace was set to keep inlet gas temperature 165 °C and SO_2 was introduced before the entrance of liquid column tower. The temperature of flue gas was measured by the thermal couple and thermal resistance, respectively. The absorption tower was a self-designed pilot-scale liquid column tower ($\Phi 200$ mm I.D. and 5800 mm H). The swirl plate in Figure 2 was used for gas distributions in absorption tower. The length, height and thickness of stainless steel blades were 193 mm, 50 mm and 2 mm, respectively. The inclination of blades was 30° and those blades were distributed evenly around a stainless steel cylinder. Flue gas flowed through the tower and contacted with absorbent. After flowing through the mist eliminator, the cleaning dry clear gas was introduced to the environment. A, B and C in Figure 1 presented the NO_x and SO_2 concentration at the inlet of the first stage, the outlet of the first stage and the outlet of the second stage measured by gas analyzer NGA2000, respectively. The absorbent was lifted to the nozzles by circulation pumps. The absorbent fell into the circulating pool after contacting with the flue gas and was recycled after mixed with the supplement.

2.3. Data evaluation

After experiments begin, the stable gas samples are recorded at the 10th min after the system runs for half an hour. The removal efficiencies are calculated as follows:

$$E = \frac{C_0 - C_t}{C_0}$$

where C_0 and C_t denotes the concentration at the inlet and outlet, respectively.

3. Results and discussion

3.1. Influence of swirl plate on separation denitrogenation

The benefit of swirl plate on denitrogenation is proved in our experiments. From Figure 3, the efficiency of denitrogenation with the swirl plate is enhanced by about 20% more than that without the swirl plate. The swirl plate has a uniform distribution effect on flue gas. After flowing through the swirl plate, the flue gas is distributed uniformly and spiral through the tower. The spiral flow pattern avoids the bypass which decreases the contact area and the residence time. Thus the swirl plate makes a great contribute to the desirable performance on the denitrogenation process.

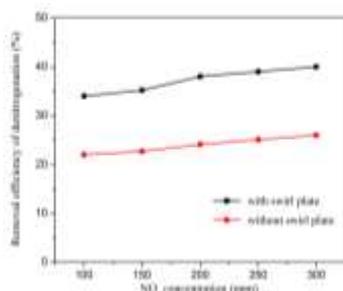


Figure 3. Influence of the swirl plate on separate denitrogenation (gas velocity: 1.5 m/s, liquid-gas ratio: 14.3 m³/L)

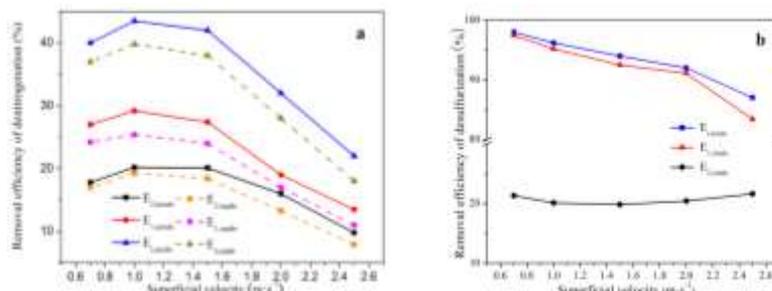


Figure 4. Influence of superficial velocity on removal efficiency (liquid holdup 9.7 m³/h, NO_x concentration: 200 ppm, SO₂ concentration: 1000 ppm)

3.2. Influence of the superficial velocity on removal efficiency

The influence of superficial velocity on separate denitrogenation is illustrated in Figure 4(a). In the range of 0.7 m/s and 1.5 m/s, the denitrogenation efficiency has no significant decrease and keeps around 37% with the increment of superficial velocity. With the superficial velocity increasing, the separate denitrogenation efficiency decreases to about 20%. The trend of denitrogenation in simultaneous removal process is same to that of separate denitrogenation. The denitrogenation efficiency of simultaneous process is higher than that of separate denitrogenation in the same condition by about 4%. From Figure 4(b), when the superficial velocity increases from 0.7 m/s to 2.5 m/s, the desulfurization efficiency decreases by about 8% due to the decreasing residence time.

3.3. Influence of the liquid-gas ratio on removal efficiency

The low liquid-gas ratio may not provide enough absorbent to absorb pollutants but the excessive liquid-gas ratio improves the capital cost. Thus, it's meaningful to study this factor in the liquid column tower. The liquid-gas ratio has a significant impact on the separate denitrogenation efficiency in Figure 5(a), especially in the range of 7.7 L/m³ and 14.3 L/m³. The results show that 14.3 L/m³ is an optimal value that a proper liquid volume is provided enough absorbent and contact time to mix with flue gas completely. When the liquid-gas ratio is 16.4 L/m³, the denitrogenation efficiency decreases a little. This is because the excessive liquid-gas ratio provided column higher than the inner height so the flow pattern is changed. The influence of liquid-gas ratio on simultaneous absorption is shown in Figure 5. The NO_x removal efficiency has the same trend and the value is higher than that in separate denitrogenation. In the range of 7.7 L/m³ and 14.3 L/m³, the liquid-gas ratio has a significant impact on SO₂ removal efficiency because of the high solubility of SO₂ in base aqueous solution.

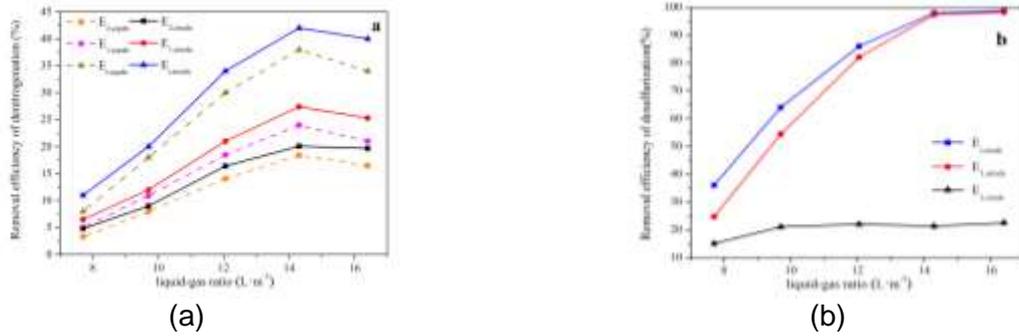


Figure 5: Influence of liquid-gas ratio on removal efficiency (superficial velocity: 1.5 m/s, NO_x concentration: 200 ppm, SO₂ concentration: 1000 ppm)

3.4. Influence of the SO₂ concentration on removal efficiency

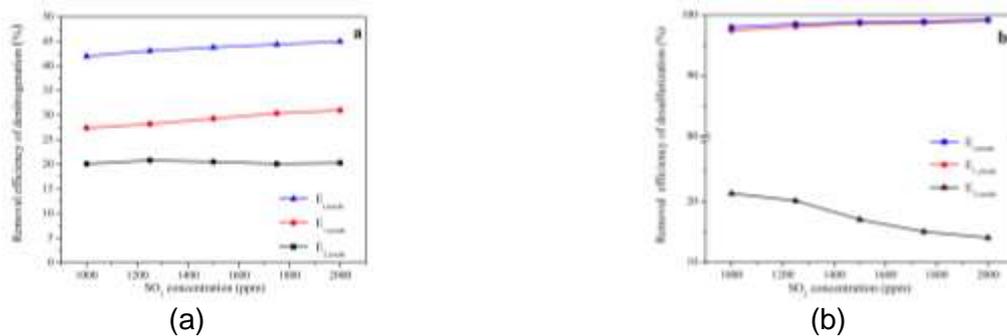


Figure 6: Influence of SO₂ concentration on removal efficiency (superficial velocity: 1.5 m/s, liquid-gas ratio: 14.3 m³/L, NO_x concentration: 200 ppm)

From Figure 6, with the increasing of SO₂ concentration, the desulfurization efficiency is enhanced slightly due to the increasing pressure of SO₂. With the SO₂ concentration increasing from 1000 ppm to 2000 ppm, the denitrogenation efficiency increases by about 3%. According to Fredrik Normann, the additive SO₂ has a positive effect on the NO_x removal (Normann F, 2013). The reason is that the dissolved SO₂ reacts with urea and ammonium bicarbonate to form ammonium sulfite and bisulfite. The former can react with NO to form nitrogen-sulphur matters, e.g., HNO(SO₃)₂²⁻ so that NO is absorbed directly. With the SO₂ concentration increasing, the NO_x removal efficiency in the first stage increases while that of the second stage keeps stable. It can be deduced that a large quantity of SO₂ is absorbed at the first stage tower and the effect of SO₂ on the denitrogenation efficiency is decreased in the second tower. Overall, SO₂ has a positive effect on the NO_x absorption.

3.5. Influence of the NO_x concentration on removal efficiency

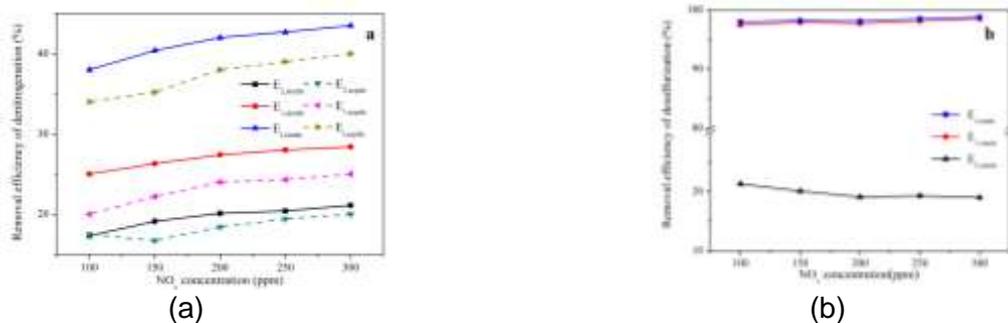


Figure 7: Influence of NO_x concentration on removal efficiency (superficial velocity: 1.5 m/s, liquid-gas ratio: 14.3 m³/L, SO₂ concentration: 1000 ppm)

The influence of NO_x concentration on denitrogenation efficiency is illustrated in Figure 7(a). The denitrogenation efficiency in simultaneous process increases from 38% to 44% with the NO_x concentration in the range of 100~300 ppm. The main reason is that the increasing NO_x concentration enhances the NO_x partial pressure and promotes NO_x absorption. Compared with one-stage tower, the two-stage tower has a great advantage on denitrogenation efficiency improvement. The total denitrogenation efficiency keeps around 37% and increases slowly with the NO_x concentration increasing in Figure 7. The reason is that the SO₂ absorption rate is controlled by gas film mass transfer rate and the change of NO_x concentration is too little to affect SO₂ absorption.

4. Conclusions

In this paper, a pilot-scale liquid column tower system is designed for simultaneous absorption experiments as an important step to apply simultaneous removal of SO₂ and NO_x in industrial setups. The swirl plate has positive influence on the denitrogenation efficiency. The trend of simultaneous absorption is as same as that in the separate denitrogenation experiments. The desulfurization efficiency decreases with the gas velocity increasing while the increasing liquid-gas ratio increases the desulfurization efficiency significantly. The optimal operation condition was 1.5 m/s of superficial velocity and 14.3 L/m³ liquid-gas ratio. The NO_x and SO₂ removal efficiency are enhanced when the concentration of SO₂ in feed gas varies from 1000 ppm to 2000 ppm. With the NO_x concentration increasing, the denitrogenation efficiency has a slight increment while the efficiency of desulfurization changes a little.

REFERENCES

1. Zhang Q, He K, Huo H. Policy: cleaning China's air[J]. NATURE, 2012, 484(7393): 161-162.
2. Skalska K, Miller J S, Ledakowicz S. Trends in NO_x abatement: A review[J]. SCI TOTAL ENVIRON, 2010, 408(19): 3976-3989.
3. Mondal M K, Chelluboyana V R. New experimental results of combined SO₂ and NO removal from simulated gas stream by NaClO as low-cost absorbent[J]. CHEM ENG J, 2013, 217: 48-53.
4. Zhao Y, Han Y, Guo T, *et al.* Simultaneous removal of SO₂, NO and Hg⁰ from flue gas by ferrate (VI) solution[J]. ENERGY, 2014, 67: 652-658.
5. Fang P, Cen C, Wang X, *et al.* Simultaneous removal of SO₂, NO and Hg⁰ by wet scrubbing using urea+ KMnO₄ solution[J]. FUEL PROCESS TECHNOL, 2013, 106: 645-653.
6. Xie H Y, Xiong Y Q, Shi Z F, *et al.* Experimental study on the effects of the characteristics of additives on urea/ammonia solution simultaneous desulfurization and denitrogenation[J]. Proceedings of the CSEE, 2010, 30(23): 51-55(in chinese).
7. Shi Z, Xiong Y, Xie H, *et al.* Experimental investigation on simultaneous removal of SO₂ and NO_x by solutions of urea and ammonium bicarbonate/additives[J]. Journal of Southeast University. Natural Science Edition, 2011, 41(3): 591-596(in chinese).
8. Li N, Zhou Q, Kong D, *et al.* Mass transfer characteristics in double-contact-flow absorber with liquid column/screen flow type: Modeling and experiment[J]. Chemical Engineering Science, 2010, 65(8): 2619-2628.
9. Normann F, Jansson E, Petersson T, *et al.* Nitrogen and sulphur chemistry in pressurised flue gas systems: A comparison of modelling and experiments[J]. INT J GREENH GAS CON, 2013, 12: 26-34.