Simultaneous removal of SO₂ and NOx from biomass flue gas by ozone oxidation + wet scrubbing method

Zhenghui Xu¹,²,³, Xiang Xiao¹,³, Ping Fang¹,³*, Jianhang Huang¹,³, Haiwen Wu¹,³ and Dongyao Chen¹,³

1. South China Institute of Environmental Sciences, the Ministry of Ecology and Environment, Guangzhou 510655, Guangdong, China;
2. Key Laboratory of Poyang Lake Environment and Resource Utilization, Ministry of Education, School of Resources, Environmental and Chemical Engineering, Nanchang University, Nanchang 330031, China;
3. The Key Laboratory of Water and Air Pollution Control of Guangdong Province, Guangzhou 510655, China;

corresponding author’s e-mail address: fangping@scies.org

Abstract: In this work, factors affecting NO and SO₂ removal were systematically investigated, including O₃/NO ratio (V/V), different oxidant types, NaOH and KMnO₄ concentrations. Results indicate that the degree of oxidation cannot be pursued too much and the best O₃/NO ratio (V/V) is 0.5. The increased amount of KMnO₄ and NaOH promoted the removal efficiency of NOx. The key to the removal of NOx by KMnO₄ was mainly that when the KMnO₄ was 0.013 mol/L, the removal efficiency of SO₂ and NOx reached 100% and 93.75%, respectively. This indicates that the technology can not only efficiently remove NO and SO₂, but also has a great application prospect.

1. Introduction

The use of biomass instead of fossil fuels to provide energy can alleviate the global warming problem that the international community faces, because biomass combustion does not cause a net increase in CO₂ emissions. [1-3]. At the same time, reducing the reliance on fossil fuels can also reset the energy used in biomass to produce renewable electricity, transportation and heat. [4,5]. In recent years, the general increase in the probability of using biomass for industrial production can also be attributed to the above reasons. Boiler is an important energy user in the industrial production process. At present, the substantial increase in biomass boilers has resulted in increased emissions of pollutants (such as NOx, SO₂). For the development of control technologies for SO₂ and NOx, great progress has been made globally. Wet absorption is widely used in desulfurization because of its simple structure, high desulfurization efficiency and reliability. However, the low solubility of NO limits the appearance of high NOx removal efficiency. [6-8]. O₃ oxidation has the advantages of high oxidation efficiency without secondary pollution..

This experiment will study the optimal oxidation degree of O₃ oxidation combined with wet absorption. It is necessary to quantitatively oxidize a part of the NO in the flue gas to NO₂ in order to find a ratio of O₃/NO (V/V) that is favorable for absorption, so as to reduce the oxidation cost and achieve a higher absorption effect. By determining the optimal reaction conditions, it provides...
constructive guidance for the practical application of O₃ oxidation combined with wet absorption technology to remove SO₂ and NO simultaneously.

2. Experimental setup

2.1. Materials
NO (10.02%), N₂ (99.999%) and SO₂ (4.01%) purchased from Guangzhou Zhuozheng Gas Co., Ltd. were the three kinds of gases that need to be used. Sodium chlorite (> 78.00%, AR), sodium persulfate (≥98.00%, AR), potassium ferrate (≥ 98.58%, AR), potassium permanganate (≥ 99.50%, AR), all of them were got from Guangzhou chemical reagents.

2.2 Data analysis

\[
\eta(\%) = \frac{N_{\text{int}} - N_{\text{out}}}{N_{\text{int}}} \times 100\% \quad \text{(1)}
\]

\[
\eta(\%) = \frac{NO₂_{\text{int}} - NO₂_{\text{out}}}{NO₂_{\text{int}}} \times 100\% \quad \text{(2)}
\]

\[
\eta(\%) = \frac{NOX_{\text{int}} - NOX_{\text{out}}}{NOX_{\text{int}}} \times 100\% \quad \text{(3)}
\]

3 Results and discussion

3.1 Influence of O₃ / NO ratio (V/V)
Ideally, NO is converted into NO₂ as much as possible or dissolved in water with high-valent nitrogen oxides. However, the excessive amount of NO₂ will release NO after dissolving in water. Therefore, this study explored the effect of different O₃ / NO ratio (V/V) on NOx average removal efficiency, and ozone concentration changed from 40 ppm to 200 ppm. Figure 1 showed that when O₃ / NO ratio was changed from 0.2 to 0.5, the average removal efficiency of NOx gradually increased. The average NOx removal efficiency as high as 81.42% occurred when the ratio was 0.5. The continued increase in the ratio had a negative effect on the NOx removal efficiency. This may be because the increase in O₃ concentration caused more conversion of NO into NO₂, which promoted the reaction (4), but the reaction (5) occurred when NO and NO₂ were present in the solution at the same time. This showed that higher ratio did not mean better outcome, there was an optimal range for the ratio. Based on comprehensive economic factors, it was known through experiments that the optimal O₃ / NO was about 0.5.

\[
3\text{NO}_2 + 2\text{OH}^- = \text{NO} + 2\text{NO}_3^- + \text{H}_2\text{O} \quad \text{(4)}
\]

\[
\text{NO} + \text{NO}_2 + 2\text{OH}^- = 2\text{NO}_2^- + \text{H}_2\text{O} \quad \text{(5)}
\]

Figure 1. Effects of different O₃ / NO ratios (V/V) on NOx average removal efficiency. [KMnO₄] = 0.006 mol / L, [NO] = 200 ppm, [SO₂] = 150 ppm, [NaOH] = 0.025 mol / L.
3.2 Influence of the oxidant type
Adding different oxidants is an effective way to eliminate NO. In this study, four oxidants Na$_2$S$_2$O$_8$, NaClO$_2$, K$_2$FeO$_4$ and KMnO$_4$ were selected. Figure 2 was the effect of different oxidants on NOx removal efficiency. It can be seen that different oxidant solution has different removal effect on NOx due to the different oxidizing capacity. The capacity on the NOx removal of four oxidant solutions was KMnO$_4$ > NaClO$_2$ > K$_2$FeO$_4$ > Na$_2$S$_2$O$_8$, with the average NOx removal efficiencies being at 49.61%, 44.18%, 32.10% and 19.02%, respectively. The removal efficiency of NaClO$_2$ at the beginning of the reaction was close to KMnO$_4$, but the stability of the whole reaction process was lower than that of KMnO$_4$. Therefore, considering various factors such as the cost of oxidant, KMnO$_4$ was selected as the best additive.

![Figure 2. Effect of oxidant type.](image)

3.3 Influence of NaOH
Figure 3 showed the effect of KMnO$_4$ on NOx removal efficiency under the condition of changing NaOH concentration. It can be seen that the addition of NaOH had promoted the removal efficiency of NOx, and as the concentration of NaOH added increased, the removal efficiency of NOx increased, with the average NOx removal efficiencies being at 56.65%, 81.41%, 85.91% and 87.69%, respectively. When NaOH was 0.05 mol / L, the NOx removal efficiency can reach 88.89%, which can be attributed to the presence of SO$_2$. When increasing the concentration of NaOH, it can promote the conversion of SO$_2$ to Na$_2$SO$_3$ to a greater extent, thereby generating more sulfite which can react with NO$_2$. At the same time, HNO$_2$ in solution can react with NaOH to generate NaNO$_2$, which can effectively prevent the decomposition of HNO$_2$. When NaOH concentration was more than 0.025 mol / L, the trend of increasing NOx removal efficiency gradually became slow. Therefore, the optimal NaOH concentration for subsequent experiments was chosen to be 0.025 mol / L. The efficiency of SO$_2$ removal will not be discussed in subsequent experiments, because the removal efficiency was 100% throughout the experiment.
3.4 Influence of KMnO₄ concentration

Figure 4 showed the results of different KMnO₄ concentrations on NOx removal efficiency. The increase of KMnO₄ concentration had a positive effect, with the average NOx removal efficiencies being at 79.44%, 84.44% and 92.86%, respectively. When KMnO₄ concentration was 0.013 mol / L, NOx removal efficiency obtained can reach 93.75% due to the increase of the collision probability. In conjunction with Figure 3, when KMnO₄ concentration exceeded 0.006 mol / L, the NOx increasing trend gradually slowed down. Therefore, the KMnO₄ concentration can be selected as 0.006 in practical applications.

4. Conclusion

This study successfully proved a technology (ozone oxidation + wet scrubbing) that can simultaneously remove SO₂ and NOx. After discovering that the SO₂ removal efficiency can reach 100%, the key factors affecting NO removal efficiency were explored. The conclusions were as following:

(1) Ozone oxidation can significantly increase NOx removal. However, the degree of oxidation cannot be pursued too much and the best O₃ / NO ratio (V/V) is 0.5.
(2) The capacity on the NOx removal was KMnO4> NaClO2> K2FeO4> Na2S2O8.
(2) The increase of NaOH concentration will lead to an increasing trend of NOx removal efficiency.
Under the condition of KMnO4 concentration of 0.013 mol / L, the removal efficiency of NOx and 
SO2 reached 93.75% and 100% respectively, which can prove that KMnO4 played a key role.

Acknowledgments
This work was supported by the Project of Science and Technology Program of Guangdong Province
(2018B020208002), the National Natural Science Foundation of China (NSFC-51778264), the
Central-Level Nonprofit Scientific Institutes for Basic R&D Operations (PM-zx703-201904-080), the
youth Top-notch Talent Special Support Program of Guangdong Province(2016TQ03Z576),
Outstanding Young Scientific and Technological Talent Support Program of South China Institute of
Environmental Sciences.

References
[1] Adler, PR., Grosso, SJD., Parton, WJ. (2007) Life-cycle assessment of net greenhouse-gas flux for
bioenergy cropping systems. Ecol Appl., 17:675–91
[2] Mann, M., Spath, P. (2001) A life cycle assessment of biomass cofiring in a coal-fired power plant.
Clean Technol Environ Policy., 3:81–91.
[3] Dias, GM., Ayer, NW., Kariyapperuma, K., Thevathasan, N., Gordon, A., Sidders, D.,
Johannesson, GH. (2017) Life cycle assessment of thermal energy production from short-rotation
willow biomass in Southern Ontario Canada. Appl Energy., 204:343–52.
[4] Demirbas, A. (2005) Potential applications of renewable energy sources, biomass combustion
problems in boiler power systems and combustion related environmental issues. Progr Energy
Combust Sci., 31:171–92.
[5] Chen, X. (2016) Economic potential of biomass supply from crop residues in China. Appl Energy.,
166:141–9.
[6] Zhu, H. S., Mao, Y. P., Yang, X. J.; Chen, Y.; Long, X. L.; Yuan, W. K. (2010) Simultaneous
absorption of NO and SO2 into FeII–EDTA solution coupled with the FeII–EDTA regeneration
catalyzed by activated carbon, Sep. Purif. Technol., 74: 1–6.
[7] Long, X., Xin, Z., Chen, M., Li, W., Xiao, W., Yuan, W. (2008) Kinetics for the simultaneous
removal of NO and SO2 with cobalt ethylenediamine solution. Sep. Purif. Technol., 58: 328–334.
[8] Jin, D. S.; Deshwal, B. R.; Park, Y. S.; Lee, H. K. (2006) Simultaneous removal of SO2 and NO by
wet scrubbing using aqueous chlorine dioxide solution. J. Hazard. Mater.,135: 412–417.