ABSTRACT

A model has been developed to predict the performance of a dielectric-barrier discharge for various parameters. The model calculations have been compared with experimental results and are in close agreement for both SO₂/NO removal. The reaction scheme shows that OH is the most important radical for SO₂ removal with the final product being H₂SO₄. Whereas for NO removal both oxidation by OH to form HNO₃ and reduction by N to form N₂ are important channels.

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EXECUTIVE SUMMARY

The primary objective of the proposed research is to investigate a novel scheme for the simultaneous removal of SO$_2$/NO$_x$ using a non-thermal plasma technique (dielectric-barrier corona discharge). Since the proposed approach also has the potential to remove volatile organic compounds (VOC) and hazardous trace elements, a study will be done on the removal of elemental mercury.

A model has been developed to predict the performance of a dielectric-barrier discharge for various parameters. The model calculations have been compared with experimental results and are in close agreement. These results have been submitted for publication to the Journal of Applied Physics.

![Graph showing percentage removal vs. energy density](image)

*Fig. 1. The removal of SO$_2$ as a function of energy density. Initial concentration of SO$_2$ is 670 ppm. The flow rate is 6000 SCCM and the power frequency is 500 Hz.*

The experimental results show that the removal efficiency increases with increasing energy density. However, it eventually saturates at higher energy densities. In the simulation, the critical reduced field is used for all calculations although the applied voltage may be different, because the global electric field is around the critical field as the result of the balance between ionization and attachment processes. The two simulation results also show an increase in removal efficiency with increasing energy density. But if
the simulated gas temperature is fixed at 400 K, the removal efficiency does not saturate as it did in the experimental results. The saturation can be explained if there is a gas temperature increase at higher energies. The dotted line shows the simulation results with a temperature increase as a function of energy density given by:

\[ T = 400 + 2 \times (<e> - 100) \times 1.8 / 2.3 \]

Here \(<e>\) is the energy density and the unit is mJ/cc. This relation was found by trial-and-error.

The major end product of the removal of SO\(_2\) is H\(_2\)SO\(_4\). The evolution of SO\(_2\) and H\(_2\)SO\(_4\) in the discharge for the initial gas mixture of 80% N\(_2\), 6% O\(_2\), 5% H\(_2\)O and 9% CO\(_2\) at 400K and concentration of SO\(_2\) of 670 ppm is given in Figure 2. The discharge is pulsed at 500 Hz with an energy density of 200 mJ/cc. The reaction product accumulates with each pulse in the gas stream. For these conditions, about 65% of SO\(_2\) is converted into H\(_2\)SO\(_4\).
OBJECTIVES

The primary objective of the proposed research is to investigate a novel scheme for the simultaneous removal of SO$_2$/NO$_x$ using a non-thermal plasma technique (dielectric-barrier corona discharge). Since the proposed approach also has the potential to remove volatile organic compounds (VOC) and hazardous trace elements, a study will be done on the removal of elemental mercury. Specifically, the following will be done to accomplish the above stated objectives.

1. *Optimization of the discharge for the removal of SO$_2$ and NO$_x$ without additives:*

2. *Study the reduction of NO$_x$ with ammonia injection into the plasma:*

3. *Study of the removal of mercury and volatile organic compounds (VOC):*

INTRODUCTION AND BACKGROUND

In a plasma, chemical reactions can take place which is ordinarily not possible without a catalyst. We have conclusively demonstrated that plasma chemistry alone is sufficient to convert SO$_2$ to H$_2$SO$_4$, the plasma being produced by a dielectric-barrier discharge. We get nearly 80% removal of SO$_2$ in a flue gas containing 775 ppm (parts per million) of SO$_2$ and 99% for SO$_2$ in concentrations of 300 ppm. However, many questions have to be answered before this technique can be put to practical use.

Theory and experiments suggest that chemical reactions in the plasma are favorable for the removal of SO$_2$/NO$_x$. In a dielectric-barrier discharge, the dissociation of water and oxygen by electrons produce hydroxyl radicals and oxygen atoms, and the reactions are shown below,

\[
O_2 + e \rightarrow O + O(1D) + e \rightarrow HO \rightarrow OH + OH \\
H_2O + e \rightarrow H + OH + e.
\]

The O and OH radicals react with SO$_2$ to form H$_2$SO$_4$, and the reaction scheme is shown below;

\[
SO_2 + O \rightarrow SO_3 \\
SO_2 + OH \rightarrow HSO_3 \\
SO_3 + H_2O \rightarrow H_2SO_4 \\
HSO_3 + OH \rightarrow H_2SO_4
\]

The H$_2$SO$_4$ forms droplets which can be removed from the gas stream by an electrostatic precipitator.

For the removal of NO, the following reaction scheme is proposed

\[
NO + O + M \rightarrow NO_2 + M \\
NO_2 + OH \rightarrow HNO_3
\]
The HNO₃ produced as an end product of the reaction may be removed by injection of NH₃ or Ca(OH)₂ to form NH₄NO₃ or Ca(NO₃)₂ respectively. The particles thus formed can then be removed from the gas stream by an electrostatic precipitator.

The proposed reaction scheme is the same as the Thermal DeNOₓ process (Lyon 1987) which takes place in the temperature range of 900-1100 °C. However in a plasma the reactions are possible at temperatures below 300 °C and these reactions are shown below;

\[
\begin{align*}
NH_3 + e^{-} &\rightarrow NH_2 + H + e^{-} \rightarrow NO \rightarrow N_2 + H_2O \\
NH_3 + OH &\rightarrow NH_2 + NO \rightarrow N_2 + H_2O \\
NH_3 + O &\rightarrow NH_2 + NO \rightarrow N_2 + H_2O
\end{align*}
\]

This study will be done for a set of parameters that are typical for coal-fired combustion facility.

The list of chemical substances that must be monitored and controlled under evolving environmental regulations is increasing rapidly. The Clean Air Act Amendments list 190 chemicals, many of which are emitted by fossil fuel-fired boilers. These guidelines will provide the technical basis for selecting appropriate control technology options to meet both current and proposed environmental regulations. Coal contain various mercury compounds, probably bound to sulfur in one way or another. It is very likely that during combustion process (above 700 °C), the compounds are thermally decomposed giving elemental mercury. It is also likely that divalent Hg is reduced on the surface of a burning particle. When the combustion gases are cooled, a small fraction of the mercury is oxidized. Oxidized mercury has its advantages and disadvantages: the disadvantage is that, HgO is more hazardous to the local environment if released to the atmosphere; the advantage is that it is easier to retain in flue gas cleaning system. For power plants with efficient collection systems, it is an advantage to convert elemental mercury to its oxide. In a dielectric-barrier discharge, oxygen atoms are readily created by electron-impact dissociation and the oxidation reaction below 600 °C can be achieved.

RESULTS AND DISCUSSIONS

All the experimental results reported in this section were performed at atmospheric pressures (760 Torr) and inlet gas was at room temperature. The basic composition of the gas consisted of a mixture of 80% N₂, 6% O₂, 5% H₂O and 9% CO₂. The SO₂ concentrations with the discharge turned off and the discharge turned on were measured to obtain the percent \( \eta \) (%) removal from the flue gas stream:

\[
\eta(\%) = \frac{[SO_2]_{off} - [SO_2]_{on}}{[SO_2]_{off}} \times 100
\]
Figure 1 shows the removal of SO$_2$ as function of energy densities. The solid circles in the figure are experimental data, which were obtained from a coaxial geometry dielectric-barrier discharge with an inner electrode of 3.0 mm in diameter, an outer electrode of 2.3 cm, a glass dielectric of 1.5 mm thickness and 5.0 cm length of electrode. The SO$_2$ concentration in the gas mixture was 670 ppm (part per million) and the flow rate was 6000 SCCM (standard cubic centimeter per minute). The power supply frequency was 500 Hz and the power deposited to the discharge was controlled by the applied voltage. The solid line was obtained from the simulation of the experiment and with the temperature of the gas at 400 K. The dotted line was obtained at the same simulation condition of the solid line except that the temperature of the gas was allowed to increase linearly with the energy density.

The experimental results show that the removal efficiency increases with increasing energy density. However, it eventually saturates at higher energy densities. In the simulation, the critical reduced field is used for all calculations although the applied voltage may be different, because the global electric field is around the critical field as the result of the balance between ionization and attachment processes. The two simulation results also show an increase in removal efficiency with increasing energy density. But if the simulated gas temperature is fixed at 400 K, the removal efficiency does not saturate as it did in the experimental results. The saturation can be explained if there is a gas temperature increase at higher energies. The dotted line shows the simulation results with a temperature increase as a function of energy density given by:

\[ T = 400 + 2 \times (\langle e \rangle - 100) \times 1.8/2.3 \]

Here $\langle e \rangle$ is the energy density and the unit is mJ/cc. This relation was found by trial-and-error.

The major end product of the removal of SO$_2$ is H$_2$SO$_4$. The evolution of SO$_2$ and H$_2$SO$_4$ in the discharge for the initial gas mixture of 80% N$_2$, 6% O$_2$, 5% H$_2$O and 9% CO$_2$ at 400K and concentration of SO$_2$ of 670 ppm is given in Figure 2. The discharge is pulsed at 500 Hz with an energy density of 200 mJ/cc. The reaction product accumulates with each pulse in the gas stream. For these conditions, about 65% of SO$_2$ is converted into H$_2$SO$_4$.

Figure 3 shows the removal of SO$_2$ as a function of concentration. Here the solid circles are experimental data and the solid line is obtained from the simulation. The conditions used for the simulation are the same as
the energy density (200 mJ/cc) and temperature of the gas (400 K) are fixed.

Clearly at low concentrations of SO₂ nearly complete removal can be achieved. For a higher concentration of SO₂ (2000 ppm), the radicals required for removal are not sufficient for complete removal and only 30% of the SO₂ is removed. The hyperbolic nature of the curve indicates that at a fixed energy deposition, the percentage removal and concentration of SO₂ is fixed for higher SO₂ concentrations.

All the experimental results reported in this section were performed at atmospheric pressures (760 Torr) and inlet gas was at room temperature. The basic composition of the gas consisted of a mixture of 80% N₂, 9% O₂, 2% H₂O and 9% CO₂. The NO concentrations with the discharge turned off and the discharge turned on were measured to obtain the percent η (%) removal from the flue gas stream:

\[ \eta(\%) = \frac{[NO]_{off} - [NO]_{son}}{[NO]_{off}} \times 100 \]

Figure 4 shows the removal of NO as a function of energy densities. The line with solid circles in the Figure are experimental data, which were obtained from a coaxial geometry dielectric-barrier discharge with an inner electrode of 3.0 mm in diameter, an outer electrode of 1.8 cm, a glass dielectric of 1.5 mm thickness and 5.0 cm length of electrode. The concentration of NO in the gas mixture was 320 ppm and the flow rate was 6000 SCCM. The power supply frequency was 500 Hz and the power deposited to the discharge was controlled by the applied voltage. The line with solid boxes was obtained by the simulation of the experiment and with a temperature of the gas at 400K. The line with solid triangles was obtained at the same simulation condition of the line with boxes except that the temperature increases as a function of the energy density:

\[ T = 400 + 2 \times (<e > -30) \]

Here \(<e >\) is the energy density and the unit is mJ/cc.

The experimental data show that the removal efficiency increases in the low energy density range with an energy density increase and peaks at an energy density of about 58 mJ/cc, then it decreases as the energy density increases. It is likely that there is a gas temperature increase during the discharge and the temperature significantly effected the removal of NO. Because some of the energy was used to heat the gas, the experimental data are lower than the simulation data. From the simulation we can see that if the gas temperature remains constant, the percentage removal increases with increasing energy...
temperature remains constant, the percentage removal increases with increasing energy deposition. However, if the gas temperature increases as the energy density increases, the removal efficiency shows a decrease with an energy density increase. The reason that the efficiency decreases with a temperature increase is that many reaction rates for this process are temperature dependent, and the total effect results in a decrease of the removal.

The major end products of the remediation of NO are N₂, NO₂, N₂O, N₂O₅, HNO₂, and HNO₃. The predicted removal of NO and generation of major end products for

\[ Q = \text{energy deposited} \]

Initial gas mixture of 80% N₂, 9% O₂, 2% H₂O and 9% CO₂ at 400K and a concentration of NO of 320 ppm is shown in Figure 5. The discharge was pulsed at 500 Hz with an energy deposition of 100 mJ/cc. The densities of the reaction products HNO₂ and HNO₃, the incremental change in density of N₂ \[ N₂ = N₂(t) - N₂(t=0) \], and the restricted NₓOᵧ product (NO₂, N₂O, N₂O₅) generally incrementally increase with each pulse as the products accumulate in the gas stream. An exception is the reaction product of NO₂ which itself reacts with plasma generated radicals and is ultimately removed. The result is that NₓOᵧ increases with time in the beginning of the process and then decreases with time. For these conditions, about 33% of NO is converted to N₂ through the reduction channel and approximately 28% is converted to HNO₃ through the oxidation channel. Small amount of the restricted oxides of nitrogen are formed. By investigating the pathway which dominated the removal of NO, we found that the percentage removal through the reduction channel increases as the energy density increases.

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PROJECT MANAGEMENT REPORT
March 1 through May 31, 1995

Project Title: COMBINED REMOVAL OF SO\textsubscript{x} AND NO\textsubscript{x} FROM FLUE GAS USING NON-THERMAL PLASMA

DOE Cooperative Agreement Number: DE-FC22-92PC92521 (Year 3)
ICCI Project Number: 94-1/2.1A-4P
Principal Investigator: Shirshak K. Dhali, SIUC
Project Manager: Frank I. Honea, ICCI

COMMENTS

None
# PROJECTED AND ESTIMATED EXPENDITURES BY QUARTER

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*Cumulative by Quarter
CUMULATIVE COSTS BY QUARTER

Combined Removal of So₂ and Noₓ from Flue Gas Using Non-Thermal Plasma

- CUMULATIVE COSTS BY QUARTER
- Combined Removal of So₂ and Noₓ from Flue Gas Using Non-Thermal Plasma
- Total Illinois Clean Coal Institute Award $59,391

Months and Quarters

- Sept 1
- Nov 30
- Feb 28
- May 31
- Aug 31

Cumulative $ (Thousands)

- ○ = Projected Expenditures
- ▲ = Actual Expenditures

Total Illinois Clean Coal Institute Award $59,391
SCHEDULE OF PROJECT MILESTONES

Hypothetical Milestones:

A: Optimization of discharge parameters
B: No\textsubscript{x} removal with NH\textsubscript{3} injection
C: Mercury Removal
D: Technical and Project Management Reports