Mercury Oxidization in Non-Thermal Barrier Discharge System

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Introduction

In the past decade, mercury pollution in the air has drawn increased attention. Coal-fired utilities are regarded as one of the major mercury emitters. Predominant forms of mercury found in the flue gas from coal-fired utilities are elemental mercury, mercuric oxide and mercuric chloride. Their concentrations in the flue gas vary considerably depending on the rank of coal burnt. The concentration of mercury in the flue gas from typical coal combustors ranges from less than 10 to more than 50 $\mu g/Nm^3$ (1-5 ppbv) with varying levels of oxidized Hg^{2+}. $Hg^0(g)$ is difficult to control and enters the global atmospheric cycle because of its comparatively high vapor pressure and low water solubility. The factors that limit the application of conventional mercury adsorption processes include extremely-low mercury concentrations, different speciation, flue gas residence time and high temperature effects. Conversion of Hg^0 into oxidized Hg^{2+} is the key factor since it is in solid form and therefore more effectively captured. Faced with NO_x, SO_x, PM(particulate matter) and mercury emissions regulations, coal-fired utility sectors are looking for an integrated system that could control as many air pollutants as possible at low cost.

In this study, efforts have been made to investigate a non-thermal plasma dielectric barrier discharge technique, that has been studied for the oxidation of NO, SO_2 and toxic hydrocarbons, to oxidize $Hg^0(g)$ to HgO. The oxidized products can then be treated in the downstream processing in wet ESPs and scrubbers. Barrier discharges are one of the electrical breakdowns that can be classified as non-equilibrium discharges also called non-thermal plasmas. An electrical discharge is a phenomenon wherein free electrons are produced and accelerated under the influence of an electric field. Through collisions with molecules in the gas, electrons cause excitations, ionizations, electron multiplication and the formation of atoms and metastable compounds. It is the formation of atoms and compounds that gives an electrical discharge its unique chemical environment and makes it useful for chemical processing.

The major advantage of the process would be to simultaneously control NO, SO_2, PM and elemental and oxidized mercury from utility plants.

Benchtop Barrier Discharge Reactor System

The reactor geometry used to initiate a barrier discharge in a gas space containing simulated flue gas is one of concentric cylinders. The center and outer cylinders are a solid stainless steel rod and stainless steel tube, respectively. Each of these cylinders serves as an electrode while the outer cylinder also serves as the pressure boundary. A high voltage(up to 25 kV, AC) is applied between the electrodes, with the outer electrode (tube) at ground potential for safety reasons. The inner diameter (ID) of the outer electrode (tube) ranges from 22 mm to 25 mm. The length of the reactor tube is 0.305 m.

Gas enters the inlet plenum of the reactor and exits through the outlet plenum. A view port is installed in the exit plenum in line with the center electrode to observe the discharge. The outer stainless steel electrode for the benchtop reactor is wrapped with copper tubing fed by a constant temperature bath, cooling or heating the electrode as necessary for temperature control.

Mercury and Gas Measurements

Mercury feed is produced by evaporating it under controlled conditions. A commercially-available Jerome 431-X

Mercury Analyzer at the Arizona Instrument, Tempe, Arizona is used. This instrument detects only mercury vapors. It has a Gold Film Sensor and detects mercury in the range of 0.003 to 0.999 mg/m^3. Measurement of other gases, such as SO_2, NO_x, CO_2, H_2O and O_2 are made using individual conventional analyzers.

Mercury Reaction Chemistry

It is reported that mercury can undergo the following reaction:

$$2\ Hg^0\ (g) + O_2\ (g) \Longrightarrow 2\ HgO\ (s,g) \qquad (1)$$

A possible mechanism can be proposed for the non-thermal plasma oxidation of elemental mercury under an electrical field.

$$Hg\ (g) + \text{barrier discharge} \Longrightarrow Hg^*\ (g) \qquad (2)$$

$$O_2 + \text{barrier discharge} \Longrightarrow O + O \qquad (3)$$

$$O_2 + O \Longrightarrow O_3 \qquad (4)$$

$$Hg^*\ (g) + O_3 \Longrightarrow HgO + O_2 \qquad (5)$$

Reaction (5) is the reaction of elemental mercury and ozone, with the formation of mercuric oxide and oxygen. It is of common knowledge that ozone is formed during electrical discharge and will cause oxidization reactions.

Results and Conclusions

Conversion of mercury vapor is measured in terms of inlet and outlet Hg vapor concentrations as follows:

$$\text{Conversion (\%)} = \frac{C_{inlet} - C_{outlet}}{C_{inlet}} \times 100$$

Energy density is the power deposited into a liter of gas mixture at standard conditions (J/L), i.e., discharge power divided by total gas flow rate.

Experiments are conducted by passing a mixture of O_2, N_2 and Hg vapors through the plasma reactor. Inlet and outlet mercury concentrations are measured by the Arizona mercury analyzer. The mercury conversion is found to increase from 0% to about 100% as the inlet oxygen concentration is increased from about 0 % to 0.06% in the inlet gas stream. These results show that mercury present in parts per billion range in flue gas can be fully oxidized with very low concentration of O_2. In these experiments, peak voltage and frequency are varied in the range of 17 to 22 kV and 100 to 150 Hz, respectively. The energy density is found to change from 90 to 300 J/L.

Considerable efforts have been made to adapt the mercury monitor to analyze the mercury concentrations in the presence of ozone which is produced by the barrier discharge. These experiments are conducted at low oxygen input concentrations to use the monitor effectively by minimizing the meter exposure to ozone.