# Wet plasma reactor for remidiation of SO 2

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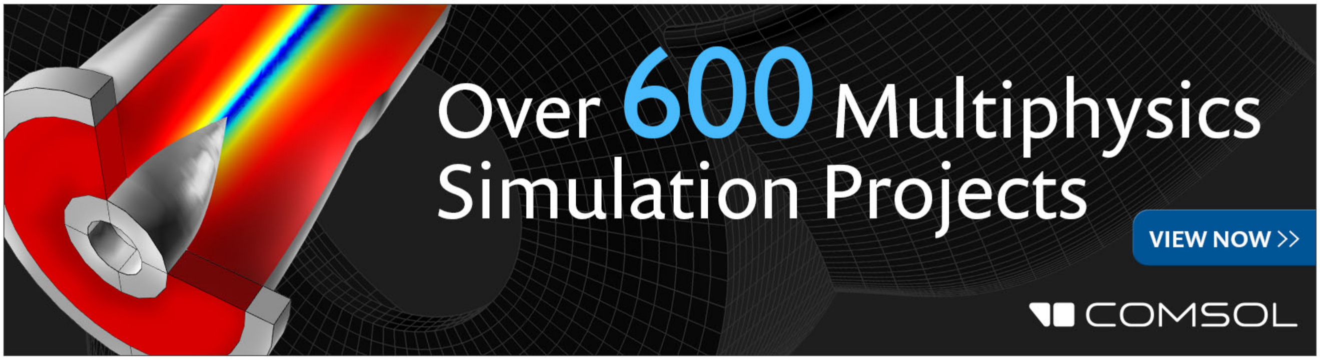

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# Wet plasma reactor for remidiation of $SO_2$

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In pollution control applications, the presence of water in the electrical discharge enhances oxidation of pollutants. The results of an electrical discharge in gas when it flows through a heterogeneous mixture of water and dielectric pellets are reported. The discharge in the wet plasma reactor is more uniform compared to dry dielectric-barrier reactors. The electrical characteristics of such a discharge are discussed. Also the results of removal of $SO_2$ with the wet reactor are reported. The wet reactor was found to be 5–10 times more energy efficient in removing $SO_2$ compared to conventional dry plasma reactors. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1426692]

The use of nonthermal plasma for pollution control is an active research area. To name only a few, nonthermal plasmas have been used for flue gas treatment,[1,2] volatile organic compound (VOC) removal,[3] and vehicle exhaust pollution control.[4,5]

At atmospheric pressures, there are two popular methods of generating plasmas: (1) Corona in dc or pulsed form, and (2) barrier discharge with ac sources. Corona discharges are due to inhomogeneous electrode geometries such as a point electrode and a plane. Although corona discharges have found numerous applications,[6,7] they are limited due to the low active volume available for processing the gas. The barrier discharge, also known as a silent discharge or a partial discharge, is widely used in commercial ozone synthesis and excimer-UV generation.[8,9]

The conventional barrier discharges are in air gaps. However in a wet-barrier discharge a considerable portion of the air gap is filled with water and dielectric beads to disperse the water. The electric discharge takes place in the gas bubbles formed in this mixture. Having water in the discharge has several advantages: (1) It improves the removal efficiency by chemically and physically enhancing the removal mechanism, and (2) it prevents the fouling of the dielectric surface due to contaminants. The discharge in the wet plasma reactor behaves like a partial discharge in voids. In this letter, we present some basic characteristics of the wet plasma scrubber followed by results of removal of $SO_2$.

The schematic of the wet-plasma reactor is shown in Fig. 1(a). The configuration is a cross flow reactor with the water coming down and the gas moving up. It consists of a cylindrical glass dielectric (1.6 cm internal diameter, and 1.5 mm thickness) with the inside filled with glass pellets. The size of the glass pellets is in the range of (4–5 mm). The inner electrode is a 6 mm diameter stainless steel rod and the outerelectrode is a conducting film on the outersurface of the dielectric. The plasma is created in the gas, liquid, and solid mixture between the beads. This produces a heterogeneous medium with the plasma created in gas bubbles as it flows through the volume of the reactor. Due to the small dimension of the gas bubbles, the microdischarges in the bubble do not reach the arc phase. Hence the discharge does not show the filamentary behavior typical of dielectric-barrier discharge.

Shown in Fig. 1(b) is a simplified model of the reactor in the presence of water. The glass beads are lumped as uniform glass dielectric, the water drops are lumped as a layer of water dielectric, and the air gaps between the beads and water drops are lumped as the gas gap. The addition of water increases the dielectric constant, which increases the overall capacitance of the reactor. A large fraction of the discharge current is primarily due to the capacitance (displacement cur-

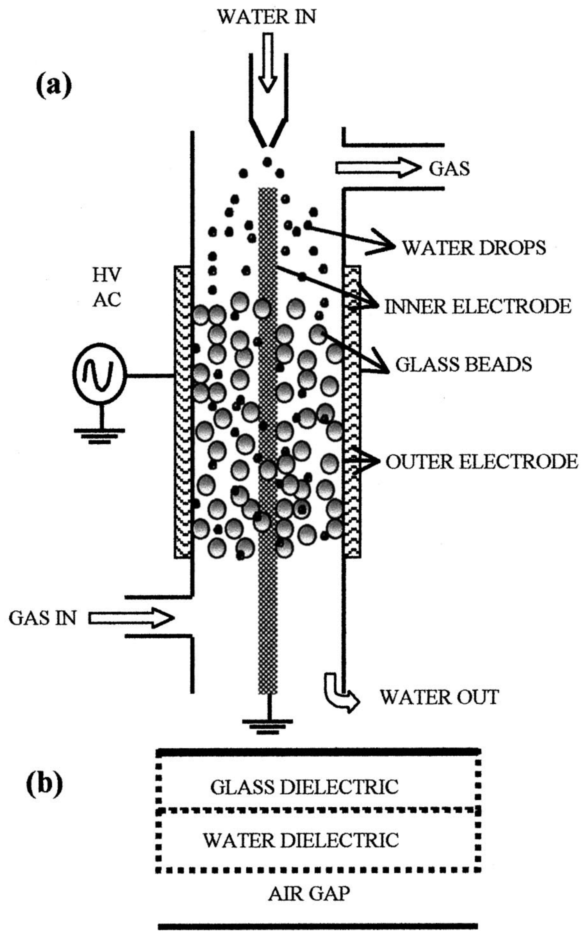

FIG. 1. (a) Schematic of the wet plasma reactor; (b) the equivalent dielectric-barrier discharge representation of a wet plasma reactor.

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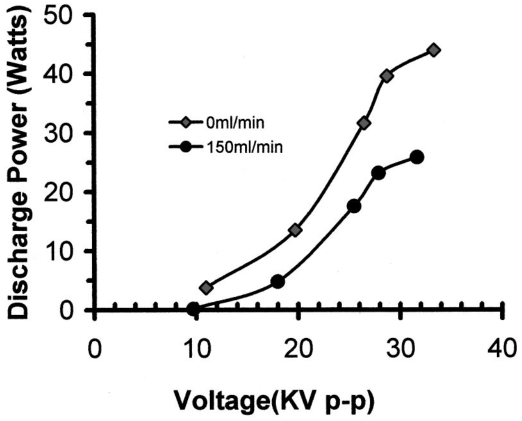

FIG. 2. Discharge power as a function of applied voltage for with and without water flow in the reactor.

rent) of the reactor as is generally the case with dielectric-barrier type discharges. When no water is passed through the system, the capacitive current is slightly lower.

The amount of power deposited to the discharge changes significantly with the addition of water. The discharge power, $P$, in a dielectric-barrier type discharge is given by[10]

$$P=4fV_c'c_d\left(V_p-\frac{(c_g+c_d)}{c_d}V_c\right), \tag{1}$$

where $f$ is the power frequency, $c_g$ and $c_d$ are the gap and dielectric capacitance, respectively, $v_p$, $v_c'$, and $v_c$ are the peak to peak applied voltage, the critical gap voltage required to sustain a discharge, and the critical voltage at which the gap breaks down, respectively. The voltages $v_c$ and $v_c'$ are nearly equal, however we have observed that $v_c'$ tends to be lower than $v_c$.[10] When water is added to the discharge, $c_g$ and $c_d$ change significantly: As shown in Fig. 1(b), the dielectric capacitance which consists of the glass and water in series decreases due to addition of water in the reactor. However the addition of water reduces the gas gap volume, thus increasing the gas gap capacitance, $c_g$. Figure 2 shows the discharge power as a function of the applied voltage with and without water flow. Water flow decreases the capacitance, $c_d$ and increases the term $(1+c_g/c_d)$ causing power to decrease according to Eq. (1).

The discharge takes place in air bubbles at atmospheric pressures saturated with water (~3.2% at 21 °C). In a barrier type discharge, the field in the air gap is equal to the critical field (the field at which ionization is equal to loss by attachment) required to maintain a discharge. Since water is a highly attaching gas, the addition of moisture increases the critical field. The energetic electrons in the discharge dissociate and ionize the gas components. In an air–water mixture the important electron impact processes are shown below:[4]

$$e+O_2\xrightarrow{k_1}2O(^3P)+e;k_1=1.04\times10^{-9}\ \mathrm{cm^3/s}, \tag{2}$$

$$e+O_2\xrightarrow{k_2}O(^3P)+O(^1D)+e;k_2=4.8\times10^{-9}\mathrm{cm^3/s}, \tag{3}$$

$$e+H_2O\xrightarrow{k_3}OH+H+e;k_3=6.8\times10^{-12}\ \mathrm{cm^3/s}. \tag{4}$$

The reaction rates $k_{1-3}$ are strongly dependent on the gas mixture and electric field. The rates shown for the above reactions are at the critical field (110 Townsend) for an air discharge.[4] The radicals produced by electron impact undergo fast reactions with other radicals and molecules in the discharge to form products with longer lifetimes. Shown below are the reactions that determine the concentration of OH, which is the most important radical for oxidation of pollutants:[1,11]

$$O(^1D)+O_2\xrightarrow{k_4}O(^3P)+O_2:k_4=4.0\times10^{-11}\ \mathrm{cm^3s^{-1}}, \tag{5}$$

$$O(^1D)+H_2O\xrightarrow{k_5}OH+OH:k_5=2.28\times10^{-10}\ \mathrm{cm^3\,s^{-1}}, \tag{6}$$

$$OH+OH\xrightarrow{k_6}H_2O+O:k_6=1.0\times10^{-11}\times\exp(-500/T)\mathrm{cm^3\,s^{-1}}, \tag{7}$$

The final product in the removal of $SO_2$ is $H_2SO_4$. The removal of $SO_2$ takes place primarily through the following reactions:[1,11]

$$SO_2+OH+M\xrightarrow{k_7}HSO_3+M:k_7=5.0\times10^{-13}(300/T)^{3.3}\mathrm{cm^6\,s^{-1}}, \tag{8}$$

$$HSO_3+OH\xrightarrow{k_8}H_2SO_4:k_8=9.8\times10^{-12}\mathrm{cm^3\,s^{-1}}, \tag{9}$$

$$HSO_3+O_2\xrightarrow{k_9}SO_3+HO_2:k_9=4.0\times10^{-13}\mathrm{cm^3\,s^{-1}}, \tag{10}$$

$$SO_2+O+M\xrightarrow{k_{10}}SO_3+M;k_{10}=4.0\times10^{-32}\times\exp(-1000/T), \tag{11}$$

$$SO_3+H_2O\xrightarrow{k_{11}}H_2SO_4;k_{11}=6.0\times10^{-13}\mathrm{cm^3/s}, \tag{12}$$

$$SO_3+O+M\xrightarrow{k_{12}}SO_2+O_2+M;k_{12}=8.1\times10^{-30}\mathrm{cm^6/s}. \tag{13}$$

The reactions shown in Eqs. (8) and (9) are the primary removal pathways. The reactions shown in Eqs. (10), (11), and (12), form an additional removal pathway. Through the reaction shown in Eq. (13), the $SO_3$ is converted back into $SO_2$. Therefore, in order for reactions (9) and (10) to be effective, water has to be present so that reaction (12) can remove $SO_3$.

The results of the removal of $SO_2$ were studied with the wet plasma reactor. A typical removal study on water flow is shown in Fig. 3. The two sets of plots for a starting concentration of 3000 ppm of $SO_2$ in air corresponds to (1) concentration of $SO_2$ in the exhaust as a function of discharge energy, and (2) removal of $SO_2$ per kWh of energy. Removal studies were done for no water flow and with different water flows through the reactor. There is an initial removal of $SO_2$ when water is passed through the discharge without the plasma, which depends on the water flow and is significant. The $SO_2$ gas is partially absorbed by water, and its solubility depends on the temperature. When the discharge is turned on, there is further removal due to the plasma. With increasing flow of water, the fall in the concentration of $SO_2$ is faster as a function of discharge power. The wet plasma reactor was found to be more energy efficient compared to dry

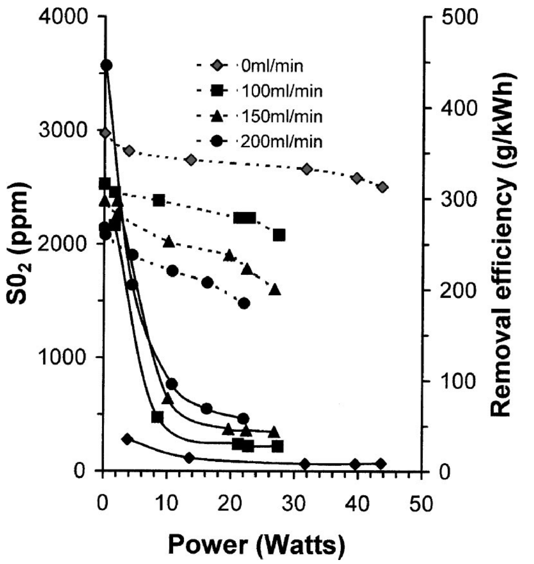

FIG. 3. $SO_2$ removal as a function of power. The dashed lines show the $SO_2$ concentration for various water flows as a function of discharge power. The solid lines show the energy cost for removal for various water flows as a function of discharge power.

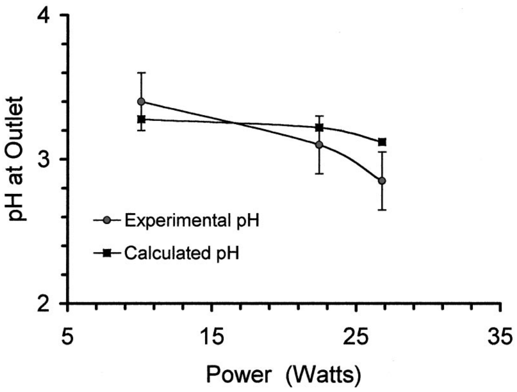

FIG. 4. Water pH at the exit of the reactor.

plasma techniques, and the power requirements were less by a factor of 5–10 compared to dry reactors.[12] Li *et al.* reported $SO_2$ removal in dielectric-barrier type discharges in the order of 10 g/kWh.[12] Also the energy efficiency of the wet reactor was an order of magnitude better compared combined plasma photolysis, which produced removals of the order of few g/kWh.[13]

The addition of water in the reactor causes enhanced production of OH radicals, which improves the removal efficiency. In addition, the $SO_3$ formed is quickly dissolved and removed before the plasma can dissociate it back to $SO_2$. The change in temperature of the water from the inlet to the outlet is only a few °C. However without water flow, the reactor temperature rises by 50–100 °C. Therefore, the wet plasma discharge operates much cooler than dry reactors. From the temperature dependent rates shown for some of the reactions, it can be shown that lower temperatures favor the removal of $SO_2$. The rate $k_6$, which is lower at lower temperatures, reduces the loss of OH with decreasing temperature. The rate coefficient, $k_7$, which determines the removal of $SO_2$, increases at lower temperatures. In dry reactors, acid aerosols on the dielectric foul the reactor, which can cause intense arc-like microdischarges with reduced efficiency for radical production.

The energy efficiency tends to be high at low discharge power as shown in Fig. 2. At such low powers, the concentration of OH is low. Due to the low destruction of OH by reaction (7), the OH utilization for removal of $SO_2$ is very high. However, the percentage removal is low at such low energies and is of little practical importance. Similar results have been reported for $SO_2$ removal at low discharge energies.[11,12]

The solution pH at the exit of the reactor was measured and is shown in Fig. 4. Also shown is the calculated value of pH under the assumption that each $SO_2$ molecule removed produces one $H_2SO_4$. The calculated values agree well with the measured values, thus indicating that the conversion of $SO_2$ to $H_2SO_4$ is the major pathway for the removal of $SO_2$.

Typically in a dielectric-barrier discharge, the power frequency range is from 60 Hz–10 kHz. Since the discharge is highly capacitive, the reactive power increases with frequency. Due to power supply limitation, the highest discharge power achieved decreases as the power frequency is increased. We have observed that the removal efficiency depends on the power input to the discharge, and the power frequency has little influence on the removal.

In conclusion, the characteristics of a wet plasma reactor were discussed. Due to the relative changes in gas and dielectric capacitance, it was found that the power coupled to the discharge decreases due to water flow. In addition, with water flow in the reactor, the removal efficiency of pollutants is enhanced due to lower temperatures and the minimal reactor fouling due to acidic aerosols.

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