

## **DESTRUCTION OF VOCS USING NON-THERMAL PLASMAS**

Dr. Mark P. Cal and Martin Schluep

Department of Environmental Engineering  
New Mexico Tech, Socorro, NM 87801  
tel. (505) 835-5059  
e-mail: mcal@nmt.edu

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## **Abstract**

Volatile organic compounds (VOCs) emitted to the atmosphere can cause adverse effects on human health and participate in photochemical smog formation reactions. Title III of the 1990 Clean Air Act Amendments (CAAA) requires that the U.S. EPA promulgate emission standards for 188 hazardous air pollutants (HAPs) associated with about 300 major source categories. Many DOE and industrial facilities throughout the U.S. will need pollution abatement systems for HAPs in order to comply with the 1990 CAAA.

Nonthermal plasmas are an excellent source of gas-phase free radicals ( $O\bullet$ ,  $OH\bullet$ ,  $H\bullet$ ) and other active species useful for destroying pollutants. While there has been extensive research on using plasma-based air pollution control technologies to remove gas-phase species such as  $SO_2$  and  $NO_x$ , research on destroying VOCs with plasmas is in its early stages. This research uses a cylindrical dielectric barrier discharge (DBD) plasma reactor to destroy HAPs, such as benzene and methyl-ethyl ketone (MEK).

The plasma reactor consists of a center discharge electrode surrounded by a dielectric barrier (quartz tube) and an outer electrode. An AC voltage of up to 30 kV is applied to center electrode creating discharge pulses which generate gas-phase free radicals capable of destroying pollutants. The goal of this research is to evaluate destruction removal efficiencies for various HAPs (benzene, MEK, etc.) as a function of discharge voltage, residence time, gas-phase oxygen and water concentrations, and pollutant concentration.

## **Introduction**

Title III of the 1990 Clean Air Act Amendments established a list of 188 potentially hazardous air pollutants (HAPs) associated with approximately 300 major source categories. This legislation affects thousands of government, commercial and industrial facilities in the U.S., requiring them to use pollution abatement systems for HAPs in order to comply with the 1990 CAAA. HAPs will need to be controlled according to maximum achievable control technology (MACT) standards. Many of the regulated HAPs are volatile organic compounds (VOCs). VOCs have been conventionally removed using adsorption, incineration or condensation processes. Adsorption works well for low concentrations of some VOCs, and incineration or condensation processes are typically used for high concentrations of VOCs. If multiple pollutants are present in a gas stream at varying concentrations, multiple control technologies may be needed, adding to the cost and complexity of the process. It would be highly desirable to have a control technology capable of removing multiple gas-phase pollutants, thereby reducing cleanup costs and process complexity.

Non-thermal plasmas are an excellent source of gas-phase free radicals ( $O\bullet$ ,  $OH\bullet$ ,  $H\bullet$ ) and other active species, which are useful for destroying pollutants. Using NTPs for gas-phase pollution control shows much promise, but it is still in its early stages of research and development. NTP may offer several advantages for controlling HAPs when compared to traditional systems, such as adsorption, absorption, and incineration. Advantages NTPs have over conventional technologies includes:

- NTPs completely oxidize organic pollutants to  $CO_2$  and  $H_2O$  at high destruction removal

efficiencies (DREs).

- Plasma reactors have low energy requirements, when compared to incineration. Energy costs are also favorable when compared to adsorption and absorption, because of the relatively low pressure drop through a plasma reactor.
- NTPs operate at near-ambient pressures and temperatures.
- Sorbents and catalysts are not used in NTP processes, which minimizes costs and reduces solid wastes.
- NTPs can be combined with other treatment technologies, such as adsorption or absorption, which may be a favorable combination.
- NTPs have the ability to simultaneously destroy organic (benzene, MEK, toluene, etc.) and inorganic pollutants (NO, SO<sub>2</sub>).

Potential source categories for pollutant destruction using non-thermal plasmas include:

- Painting and coating operations
- Semiconductor and electric component manufacture
- Pharmaceutical processing
- Dry cleaning operations
- Processing of other chemical waste streams
- Commercial and residential indoor air

Since, NTPs have the potential to simultaneously destroy a wide variety of gas-phase pollutants, this reduces the cost and complexity of remediating gas streams containing multiple pollutants.

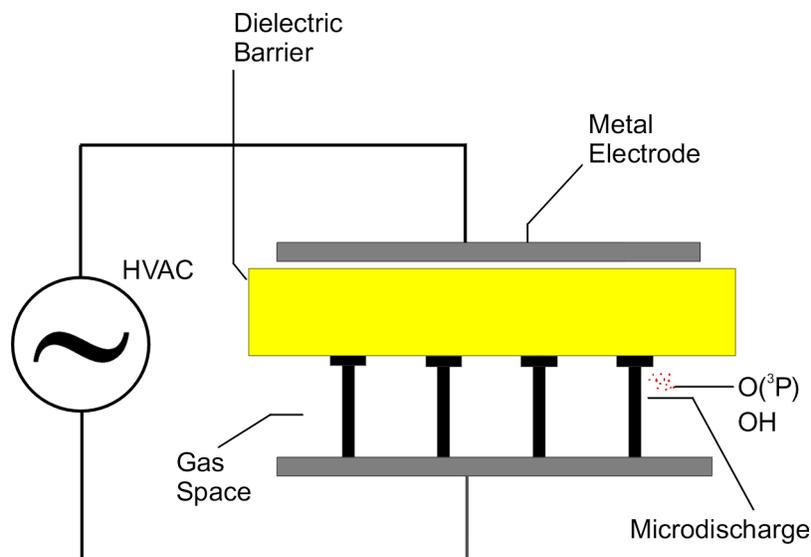
## **Background**

Recent experimentation using non-thermal plasmas (ambient temperature and pressure) for the removal of gaseous pollutants has shown great success. NTP generate free radicals capable of completely oxidizing organic pollutants to CO<sub>2</sub> and H<sub>2</sub>O. NTP are capable of treating both small and large gas volumes, making them suitable for use at a wide-variety of industrial and commercial processes. This research investigated the use of silent discharge plasmas (SDP) to destroy VOCs. SDP uses electrical energy to create large quantities of highly reactive free radicals (O•, O(<sup>3</sup>P), OH•, and H•) in a gaseous medium at near ambient temperature. These radicals react with the pollutants in the gas stream, resulting in near complete oxidation of organic compounds to CO<sub>2</sub> and H<sub>2</sub>O, and the conversion of species such as Cl, S, and N to acids, i.e., HCl, H<sub>2</sub>SO<sub>4</sub>, and HNO<sub>3</sub>, respectively. Because NTP processing may be able to simultaneously remove many different types of pollutants, e.g. VOCs, SO<sub>2</sub>, NO, sulfonated and chlorinated organic species commonly found in industrial gas streams, it is particularly attractive for many present and future environmental applications. It should work well for both high (> 1000 ppmv) and low (< 100 ppmv) concentrations of pollutants [1]. To date, much research has examined using NTPs to destroy SO<sub>x</sub> and NO<sub>x</sub> [2], and some research has been performed using NTPs to destroy hydrocarbons, chlorocarbons, chlorofluorocarbons [3-7].

### Non-thermal Plasmas

A plasma is a gaseous state of matter where molecules or atoms are broken apart to form ions. Non-thermal plasmas are characterized by conditions in which plasma species are not in thermal equilibrium. In a non-thermal plasma, electrons, ions and neutral species have different temperatures and kinetic energies, with the electrons having the highest temperature due to their smaller mass. The electrons present in non-thermal plasmas are very energetic (1-10 eV), allowing them to create free radicals ( $O\bullet$ ,  $O(^3P)$ ,  $OH\bullet$ , and  $H\bullet$ ) from other species in the gas-phase. These free radicals can then be used to destroy pollutants.

Silent electrical discharges are commonly created in a dielectric barrier electrode arrangement. One or both metal electrodes are usually covered with dielectric layers with a high dielectric constant (pyrex, quartz, ceramics, etc.) which separates them from a thin gas layer. The dielectric can also be placed between the electrodes to separate two gas layers. The geometry is commonly either planar or cylindrical. Silent discharge plasma (SDP) refers to a discharge occurring in an open space between two insulated electrodes connected to a source of high voltage alternating current. The discharge consists of a large number of microdischarges of short lifetime but with high instantaneous current. The dielectric barrier configuration provides a self-terminating electrical discharge, which is relatively independent of the drive voltage waveshape. Without the barrier and at gas pressures of about one atmosphere and a gap spacing of a few millimeters, only a few localized intense arcs would develop in the gas between the metal electrodes. With a dielectric present between the electrodes and with voltages between about 10-30 kV at frequencies between about 50 Hz to several thousand kHz, substantial quantities of plasma are created by a large number of microdischarges in the gas. Each microdischarge is a source of non-thermal plasma which is characterized by energetic electrons capable of generating highly reactive free radicals in the gas. An example of a planar, single-dielectric barrier discharge reactor is shown in Figure 1.

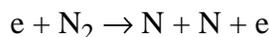
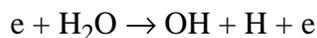
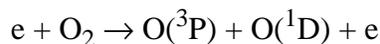
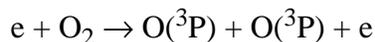


**Figure 1. Planar, Single Dielectric Barrier Discharge Reactor.**

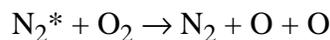
### *Plasma Chemistry and Radical Generation*

Active species can be formed in a variety of ways in a silent discharge plasma. Radicals can be formed by electron impact or by quenching, as outlined below.

#### **Electron Impact**



#### **Quenching**



Once active species have been created, they can then react with pollutant molecules. The probability that a radical will react with a pollutant molecule depends on the reaction kinetics, i.e. competition between interaction with the pollutant and radical-radical loss reactions. Even for small molecules, the reaction mechanisms for pollutant destruction can be complex. Complex molecules often undergo a series of intermediate reactions before they are completely destroyed in a plasma. At high plasma electron temperatures, the decomposition of a gas-phase chlorocarbons like trichloroethylene is dominated by free radicals [6].



Strongly electron-attaching molecules, like  $CCl_4$ , are preferentially decomposed by dissociative attachment at low plasma electron temperatures, but direct electron-induced dissociation and radical attack dominate at high electron energies [8]. For  $CCl_4$ , dissociative attachment is more advantageous than radical attack, because Cl and ClO radicals resulting from  $O\cdot$  and  $OH\cdot$  reactions with  $CCl_4$  participate in a circular kinetic reaction, which allows for the reforming of  $CCl_4$ .

Some of the more commonly formed hazardous chlorinated byproducts like phosgene ( $COCl_2$ ) are unstable and are quickly destroyed by reactions with liquid water or water vapor. In practice, a water-based scrubber can remove phosgene and neutralize acids which are formed from the decomposition of chlorinated hydrocarbons.

Since the mechanisms of plasma destruction of pollutants can be very complex, much research still needs to be done in this area. Fortunately, it is not necessary to completely understand the mechanisms of plasma destruction of pollutants to gain valuable information about the pollutant destruction process.

### *Previous Research*

Chang et al. (1991, 1992, 1993) evaluated the effectiveness of using dielectric barrier discharge (DBD) plasmas for the generation of gas-phase radicals to remove SO<sub>2</sub> and NO from gas streams using a laboratory-scale reactor [2,9,10]. They determined that the removal efficiencies of SO<sub>2</sub> and NO are dependent on applied voltage over the voltage range of 21-25 kV, inlet concentrations of SO<sub>2</sub>, NO, and H<sub>2</sub>O<sub>(g)</sub>, and gas stream temperature. Removal efficiencies for 1000 ppmv inlet SO<sub>2</sub> concentration varied between about 0% and 80%, depending on H<sub>2</sub>O<sub>(g)</sub> concentration, gas temperature, gas residence time, and applied voltage. Removal efficiencies for 250 ppmv inlet NO concentration varied between about 10% and 95%, depending on H<sub>2</sub>O<sub>(g)</sub> concentration, gas temperature, gas residence time, and applied voltage. Chang et al. results indicate that dielectric barrier discharge plasmas have potential to remove both SO<sub>2</sub> and NO from gas streams at concentrations typically found in fossil fuel combustors.

Relatively few studies have examined the destruction of volatile organic compounds with gas-phase radicals generated with plasmas or corona discharges. Chang and Lee (1995) examined the destruction of formaldehyde (HCHO) with a dielectric barrier discharge system similar to the one used for their SO<sub>2</sub> and NO removal experiments [11]. As with the SO<sub>2</sub> and NO experiments, they found operating parameters that affected HCHO destruction included gas concentration, applied voltage, and gas residence time in the dielectric barrier discharge system. In their experiments, they were able to achieve HCHO destruction efficiencies as high as 97% with an inlet concentration of 100 ppmv HCHO. They also noted that it was a promising technology for the destruction of other VOCs.

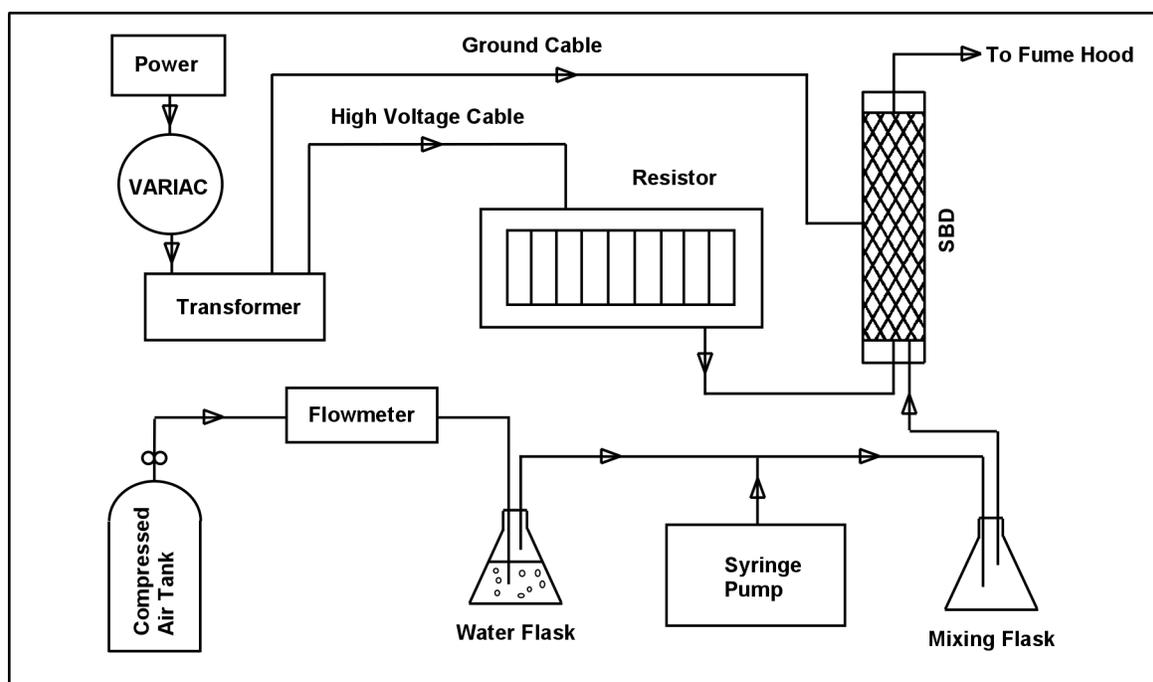
Nunez et al. (1993) used corona destruction technology to examine the destruction of low concentration VOC-laden gas streams [1]. Corona discharges can break molecular bonds, such as C=C, C-C, C-H, C-O, etc., and can form gas-phase radicals from molecules such as O<sub>2</sub>. Their reactor system consisted of a packed-bed corona reactor which made use of a bed of ferroelectric pellets across which an 5-20 kV AC field is generated. For inlet VOC concentrations of about 100 ppmv, destruction ranged from a low of about 15% for methane to nearly 100% for benzene and toluene. Other compounds, such as methylene chloride, hexane, methyl-ethyl ketone, and cyclohexane, had destruction removal efficiencies ranging from 50-80%. The corona destruction process, while similar to the DBD plasma process, has two important differences: 1) it uses a packed-bed system which would have a much larger pressure drop and therefore greater power consumption than the DBD system, and 2) the ferroelectric pellets may degrade over time, which would increase operating costs, because the pellets would need to be replaced.

Researchers at Los Alamos National Labs (LANL) have demonstrated near complete destruction of the chlorocarbons trichloroethylene (C<sub>2</sub>HCl<sub>3</sub>), trichloroethane (C<sub>2</sub>H<sub>3</sub>Cl<sub>3</sub>), tetrachloroethylene (C<sub>2</sub>Cl<sub>4</sub>), carbon tetrachloride (CCl<sub>4</sub>), and chlorofluorocarbons using rectangular planar silent-barrier discharge plasma (SDP) cells [6,7,12]. In LANL field tests conducted at DOE's Savannah River Site in South Carolina, an SDP processor was coupled to a soil vapor extraction unit that pumped volatile compounds out of the soil through wells drilled into the ground. At the site, chlorocarbon concentrations ranged from 700-4000 ppmv, and the SDP was operated at gas flow rates of 30-95 L/min. The LANL tests showed that TCE was easiest to treat, PCE next easiest, and TCA was the most difficult to treat. Removals of 99.999% were approached for TCE over a broad range of energy density (3.71 to 16.14 J/cm<sup>3</sup>), concentrations and flow rates. PCE

treatment achieved 99-99.9% removal over the whole range of test parameters. The best removal achieved for TCA was about 98% at  $13.98 \text{ J/cm}^3$ . Some byproducts were observed and were estimated to be present at concentrations less than about 1 ppmv.

## Experimental Methods

A cylindrical dielectric barrier discharge plasma reactor has been constructed by the author to investigate the destruction of VOCs under various process conditions. The dielectric barrier discharge plasma reactor (DBD) system currently in use is presented in Figure 2.



**Figure 2. Schematic for Cylindrical Dielectric Barrier Discharge Plasma Reactor System.**

The DBD shown in Figure 2 consists of a  $340 \text{ cm}^3$  quartz tube surrounded by an outer electrode of stainless steel wire mesh. The inner electrode is a 3 mm diameter molybdenum wire which runs the length of the reactor. The input voltage to the VARIAC is 116 VAC, and the VARIAC feeds the step-up transformer. Operating voltages for the DBD range from 14-24 kV AC. The gas generation system consists of ultra-zero air flowing over a syringe pump containing the contaminant of interest in liquid form (e.g., benzene). By adjusting the flow rate on the syringe pump and the air flow rate, different gas-phase pollutant concentrations can be achieved. In a typical experiment, gas residence time ranges from about 0.5 to 1.5 minutes, and pollutant concentration is varied from about 100 to 2000 ppmv. Calibration standards from Matheson or MG Industries are used to calibrate the gas chromatograph, so that the influent and effluent pollutant concentrations are known. The syringe pump setup is capable of producing steady gas-phase pollutant concentrations for long periods of time. Reproducibility was measured to be within 2% of the calibration standard.

## Results and Discussion

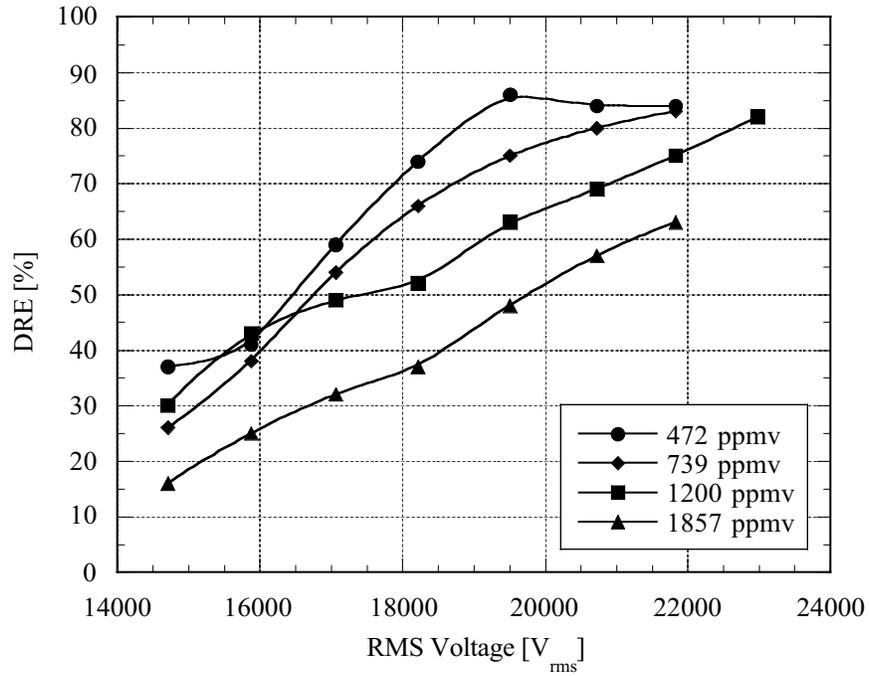
The author has conducted experiments evaluating the destruction of benzene in a cylindrical dielectric barrier discharge plasma reactor. The destruction of benzene was evaluated at various gas residence times, water vapor concentrations, and benzene concentrations, as outlined in Table 1.

**Table 1. Experimental Conditions**

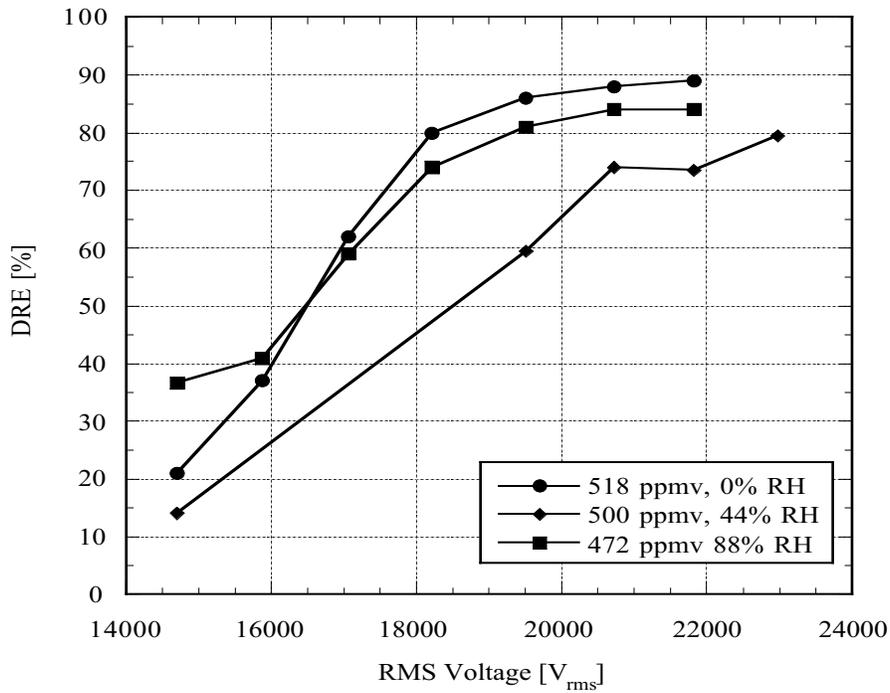
Parameter	Value
Gas Temperature	293 K
Gas Pressure	0.85 atm
Gas Residence Time	0.34 to 1.4 min
Total Gas Flow Rate	250 to 1000 cm <sup>3</sup> /min
Applied RMS Voltage	14 to 24 kV
Relative Humidity	0 to 88%
Benzene Concentration	250 to 2000 ppmv

The relationship between applied voltage and benzene DRE exhibited a near-linear relationship (Figure 3). As benzene concentration was increased, DRE decreased for the same applied voltage. This decrease in DRE with increasing concentration was easily compensated for by increasing the gas residence time. Other experiments showed that at a gas residence time of 1.4 minutes, 95% DRE of benzene was achieved for a wide range of concentrations.

Benzene DRE was also examined as a function of relative humidity (RH) (Figure 4). As RH was increased, more radicals should be generated, and DRE should increase. At approximately 500 ppmv benzene, DRE as a function of voltage for 0 and 88% RH, showed similar results, while the DRE for benzene at 44% RH was significantly less. These results are unexpected, if just approached from the radical generation theory, but it was found that there are side reactions taking place in the plasma reactor that may explain this result. It was noticed that during operation of the DBD, a yellowish-brown polymer film forms on the inside of the dielectric cylinder and on the inner electrode. This polymer film inside the DBD probably acts as a scavenger for radicals, making fewer radicals available to destroy benzene molecules. The polymer film also reduces the number of microdischarges in the plasma reactor, which in turns reduces radical formation. This phenomena will be further investigated, and methods to limit the formation of polymer films will be evaluated. Due to the development of this polymer film, benzene DRE leveled off at 95% even when the concentration was decreased, or when the residence time was increased, or when the applied voltage was increased.



**Figure 3. Destruction Removal Efficiencies for Benzene in Air in Cylindrical Dielectric Barrier Discharge Plasma Reactor at 88% Relative Humidity. Gas residence time = 0.68 min, T = 293 K, P = 0.85 atm.**



**Figure 4. Effect of Relative Humidity on the DRE of 500 ppmv Benzene in Air in Cylindrical Dielectric Barrier Discharge Plasma Reactor. Gas residence time = 0.68 min, T = 293 K, P = 0.85 atm.**

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