Destruction of Benzene with Non-Thermal Plasma in Dielectric Barrier Discharge Reactors

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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. Environmental Protection Agency (EPA) promulgate emission standards for 188 hazardous air pollutants (HAPs) associated with about 300 major source categories. Many industrial facilities throughout the U.S. will need pollution abatement systems for HAPs in order to be in compliance.

Non-thermal plasma can be used to generate gas-phase free radicals ($O(^1D)$, $O(^3P)$, OH•) at low temperature (293 K), which can then be used to destroy pollutants, such as benzene. The destruction of benzene was examined in planar dielectric barrier discharge plasma reactors as a function of applied voltage, benzene concentration, residence time and relative humidity. Near complete destruction of benzene (> 99%) was achieved in both wet and dry gas streams.

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 to comply with the Amendments. HAPs 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 is highly desirable to have a control technology capable of removing multiple gas-phase pollutants, thereby reducing cleanup costs and process complexity.

Non-thermal plasma (NTP) is a source of gas-phase free radicals ($O(^1D)$, $O(^3P)$, OH•) and other active species, which are useful for destroying pollutants. When compared to traditional systems, such as adsorption, absorption, and incineration, NTP may offer several advantages for controlling HAPs, including:

- NTP oxidizes 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 may also be favorable when compared to adsorption and absorption, because of the low pressure drop through a plasma reactor.
- NTP reactors operate at near-ambient pressures and temperatures.
- Sorbents and catalysts are not used in NTP processes, which minimizes costs and reduces solid waste.
- NTP reactors can be combined with other treatment technologies, such as adsorption or absorption, which may be a favorable combination.
- NTP reactors can simultaneously destroy organic (benzene, MEK, toluene, etc.) and inorganic pollutants (NO, SO_2).

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 chemical waste streams
- Commercial and residential indoor air

NTP reactors are capable of treating both small and large gas volumes, making them suitable for use with a wide variety of industrial and commercial processes. This research investigated the use of non-thermal plasma generated in a dielectric barrier discharge reactor to destroy benzene. The oxygen and hydroxyl radicals generated in the NTP react with the pollutants in the gas stream, resulting in near complete oxidation of organic compounds to CO_2 and H_2O, and the conversion of species such as Cl, S, and N to the acids, HCl, H_2SO_4, and HNO_3, respectively. Because NTP processing may be able to simultaneously remove many different types of pollutants, including VOCs, SO_2, NO, and 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]. Previous research has examined using NTPs to destroy SO_2 and NO_x [2], and to destroy hydrocarbons, chlorocarbons, chlorofluorocarbons [3-7].

Non-thermal Plasma

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 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. Electrons in non-thermal plasmas are very energetic (1-10 eV), allowing them to create free radicals ($O(^1D)$, $O(^3P)$, OH•, and H•) from gas-phase species, such as H_2O and O_2. 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 layers having a high dielectric constant (pyrex, quartz, ceramics, etc.) that 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 short lifetime microdischarges 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 8 to 30 kV at frequencies between 50 Hz and several thousand Hz, 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.

Plasma Chemistry and Radical Generation

Active species can be formed through a variety of reaction pathways in a silent discharge plasma, as illustrated below.

Electron impact

$e + O_2 \rightarrow O(^3P) + O(^3P) + e$

$e + O^2 \rightarrow O(^3P) + O(^1D) + e$

$e + H_2O \rightarrow OH\bullet + H\bullet + e$

$e + N_2 \rightarrow N\bullet + N\bullet + e$

$e + N_2 \rightarrow N_2^* + e$

$e + NO \rightarrow N\bullet + O\bullet + e$

Ionization/Clusters

$e + O_2 \rightarrow O_2^+ + e$

$O_2^+ \rightarrow O_2^+(H_2O)$

$O_2^+(H_2O) + H_2O \rightarrow HO_3^+ + O_2 + OH\bullet$

$O_2^+(H_2O) + H_2O \rightarrow HO_3^+(OH) + O_2$

$HO_3^+(OH) + H_2O \rightarrow HO_3^+ + H_2O + OH\bullet$

Quenching

$O^* + H_2O \rightarrow 2OH\bullet$

$N_2^* + O_2 \rightarrow N_2 + O\bullet + O\bullet$

Other

$H\bullet + O_3 \rightarrow OH\bullet + O_2$

$\bullet HO_2 + NO \rightarrow OH\bullet + NO_2$

$H\bullet + O_2 + M \rightarrow \bullet HO_2 + M$

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, that is, 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 gas-phase hydrocarbons is dominated by free radicals [6]. The overall mechanism for benzene destruction by gas-phase radicals is:

$$C_6H_6 + O(^3P) \text{ or } OH\bullet \rightarrow CO_2 + CO + H_2O$$

EXPERIMENTAL

Planar dielectric barrier discharge (DBD) plasma reactors were constructed to investigate the destruction of benzene under various process conditions. The DBD system currently in use is presented in Figure 1. For experiments in this paper, two planar DBD reactors were used with gas gap spacings of 3 mm or 5 mm. The reactors consisted of two aluminum plates each covered with a 3 mm thick pyrex dielectric plate. The plasma was generated in the space between the two dielectric plates by placing a high voltage across the two electrodes. Dimensional information for the plasma reactors is presented in Table 1.

Voltage for the plasma reactors can be varied from 0 to 130 VAC, and frequency can be varied from 45 to 15,000 Hz using a Compact Power Titan Series AC Power System capable of delivering a power load of 1 kVA. The Titan power supply was connected to a

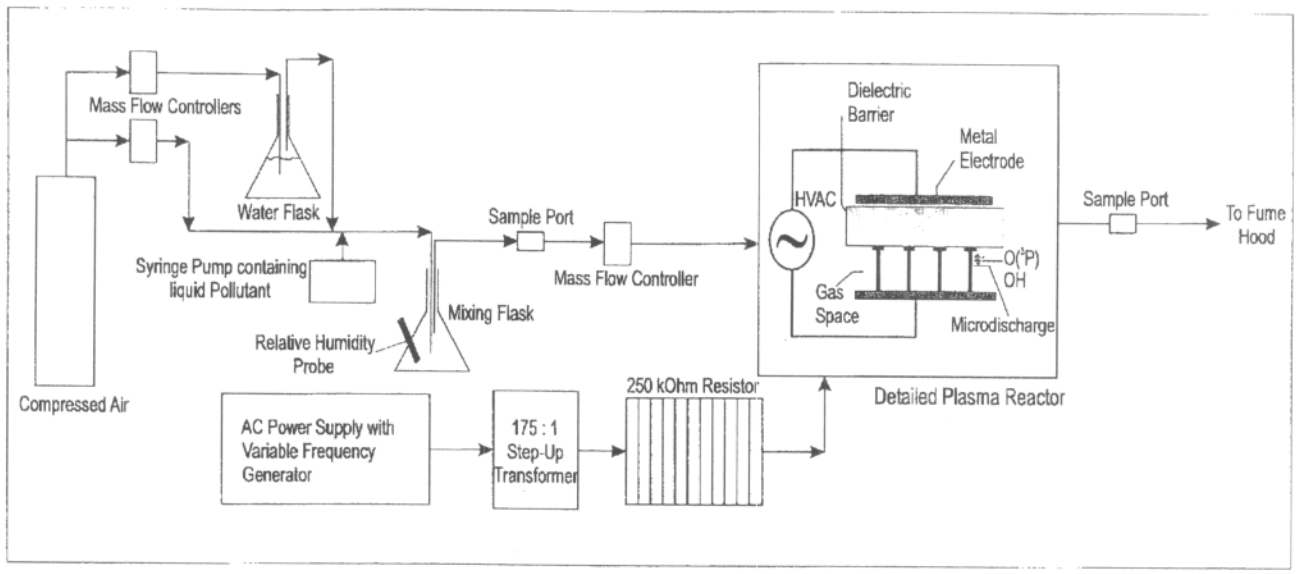

Figure 1. Experimental apparatus for dielectric barrier discharge plasma reactor.

Table 1. Plasma reactor dimensions.

Parameter	Planar (3 mm Gap)	Planar (5 mm Gap)
Gas gap spacing (H)	0.3 cm	0.5 cm
Electrode width (W)	18 cm	18 cm
Electrode length (L)	30 cm	30 cm
Hydraulic diameter (D_h), (2*A/(2*(H+W))	0.30 cm	0.49 cm
Inlet area (A)	5.4 cm^2	9.0 cm^2
Reactor volume (V)	162 cm^3	270 cm^3

175:1 step-up transformer (Corona Magnetics), which delivers a maximum root mean square (RMS) voltage of about 23,000 V in the current configuration. Operating voltages for the DBD ranged from 9 to 20 kVRMS AC, and were measured with a Tektronix high voltage probe (Model P6015A) and a Tektronix oscilloscope (Model TDS 210). The RMS voltage was calculated with the oscilloscope, assuming that the voltage waveform was a sine wave.

The gas generation system consisted of ultra-zero air flowing over a syringe pump containing benzene. By adjusting the flow rate of the pump and the total gas flow rate, different gas-phase pollutant concentrations were achieved. In these experiments, gas residence time ranged from 5 to 32 seconds, and pollutant concentration was varied from 500 to 2,700 ppmv. Calibration standards from Matheson or MG Industries were used to calibrate a Varian gas chromatograph/mass spectrometer (Model 3800 GC/2000 MS), so that the influent and effluent pollutant concentrations were known. The syringe pump was capable of producing steady gas-phase pollutant concentrations over long time periods.

Variation of the inlet benzene concentration was measured to be within 2% of the calibration standard during the course of an experiment. All measurements of the effluent benzene concentration were an average of three measurements taken when the plasma reactor was at steady state. CO and CO_2 were measured with a Liston Scientific NDIR gas analyzer (Model Enviromax). As with the benzene measurements, three CO/CO_2 samples were taken at each voltage and then averaged.

The average power delivered to a silent discharge reactor can be calculated with a formula first derived by Manley [8]. The average discharge power P in watts is given by the following equation:

$$P = 4 f C_d V_i [V_0 - [(C_d + C_g)/V_i]$$

where f is the repetition frequency of the applied voltage waveform in Hz, C_d and C_g are the dielectric and gas-gap capacitance, respectively, in Farads, and V_i and V_0 are the gas discharge ignition and peak applied voltages, respectively, in volts. Both V_i and V_0 are taken from a measurement of the total voltage appearing across the cell, V_{cell}. The power increases linearly with both the applied frequency and the capacitance of the dielectric.

RESULTS AND DISCUSSION

The destruction of benzene in the two planar dielectric barrier discharge plasma reactors was evaluated at several gas residence times, water vapor concentrations, and benzene concentrations (Table 2). Flow through the DBD was laminar with a maximum Reynolds number of 12. Under the reaction conditions, a uniform plasma was developed between the two aluminum electrodes.

Table 2. Experimental conditions for flat plate DBD reactor.

Parameter	Value
Gas temperature	293 K
Gas pressure	0.85 atm
Gas residence time	5 to 32 sec
Total gas flow rate	0.5 to 2 L/min
Applied RMS voltage	9 to 20 kV_{RMS}
Electrical frequency	1000 Hz
Relative humidity	0 to 90%
Benzene concentration	500 to 2700 ppmv
Reynolds number	3 to 12

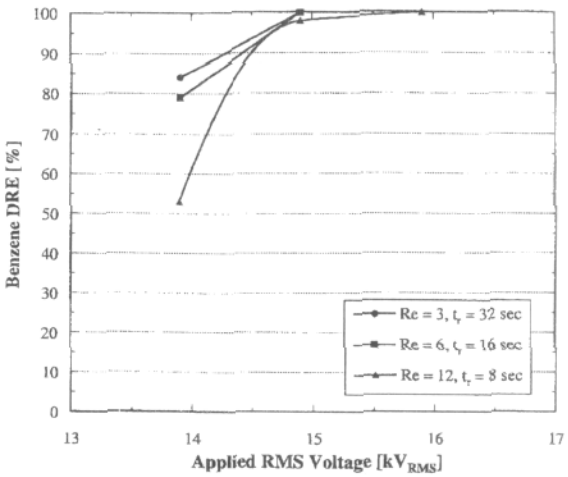

Figure 3. Effect of residence time on benzene destruction. 1,000 ppmv benzene, 0% RH, 1 kHz, 5 mm gas gap.

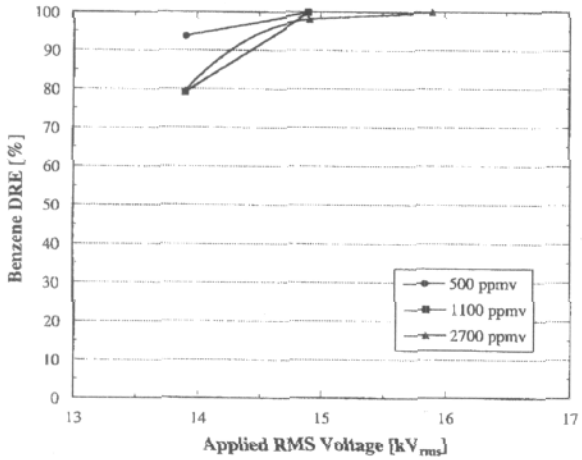

Figure 2. Effect of influent benzene concentration on destruction. 0% RH, 1 kHz, t_r=16 sec, Re=6, 5 mm gas gap.

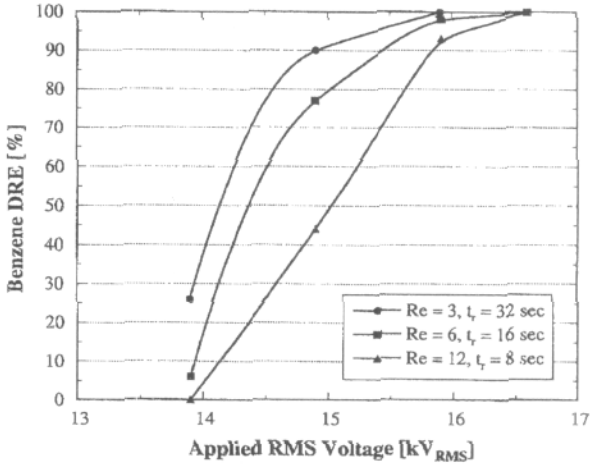

Figure 4. Effect of residence time on benzene destruction. 1,000 ppmv benzene, 90% RH, 1 kHz, 5 mm gas gap.

The DBD reactor was capable of destroying > 99.9% benzene in dry air at a residence time of 16 seconds over the concentration range of 500 to 2,700 ppmv (Figure 2). As residence time was decreased, a higher applied voltage was needed to achieve complete destruction of benzene (Figure 3). In dry air, the main destruction pathway for benzene is reaction with oxygen radicals [O(^{3}P)], since little or no hydroxyl radicals are present. When water vapor is added to the gas stream, hydroxyl radicals are formed which can be used to destroy benzene. Energy is required to disassociate the water molecules, so initially, at lower voltages, benzene destruction removal efficiency (DRE) was lower (Figure 4). With the presence of water in the gas stream, a higher plasma ignition voltage is also required. As voltage or applied power is increased, benzene DRE rapidly increases, until nearly 100% destruction is achieved at between 15.5 and 16.5 kV, depending on the gas residence time.

A lower plasma ignition voltage can be achieved by reducing the gap spacing between the electrodes. As the gap spacing decreases, the same benzene DRE can be achieved at a lower voltage. Benzene DREs ranged from about 85 to 95% at 14 kV for the 3 mm gap DBD reactor, depending on the relative humidity (RH) of the gas (Figure 5). Complete destruction of benzene was not achieved with the 3 mm gap reactor due to power supply limitations. The maximum output of the power supply (1 kVA) was achieved before there was complete destruction of benzene.

A carbon mass balance was measured for the products exiting and entering the plasma reactor during the oxidation of 1,000 ppmv benzene (Figure 6). The ratio of CO/CO_2 exiting the reactor varied, depending on applied voltage and relative humidity. At 0% RH, the CO/CO_2 ratio was 2:1 at low voltage and 1:1 at higher voltages. At 90% RH, the CO/CO_2 ratio was 1:1 at low voltage and 0.2:1 at higher voltages. Therefore, much less CO was produced with water vapor present in the gas stream. More complete hydrocarbon oxidation can occur when there are higher concentrations of oxygen and hydroxyl radicals present. Complete

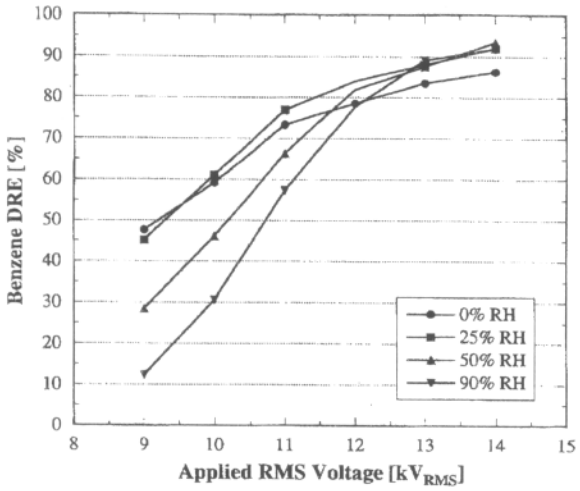

Figure 5. Effect of relative humidity on benzene destruction. 1,000 ppmv benzene, 1 kHz, t_r=5 sec, 3 mm gas gap.

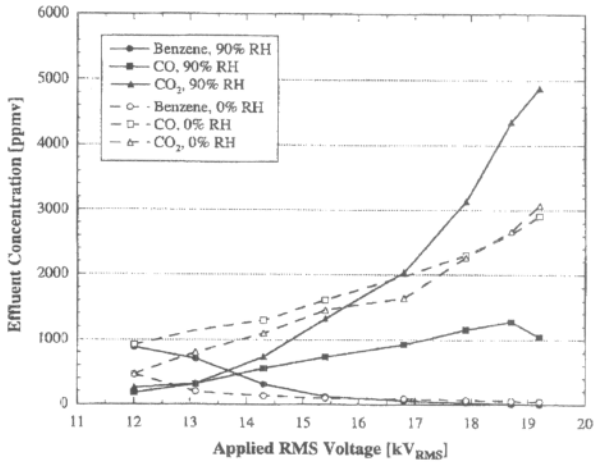

Figure 6. Mass balance for benzene oxidation. 1,000 ppmv benzene, 1 kHz, t_r=5 sec, 3 mm gas gap.

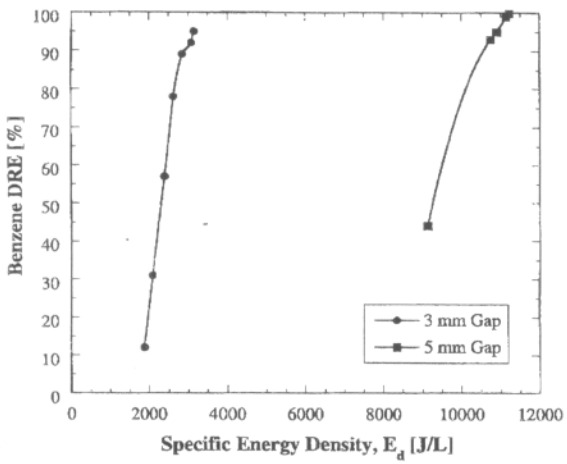

Figure 7. Effect of reactor configuration on energy density. 1,000 ppmv benzene, 90% RH, 1 kHz, 2.0 L/min.

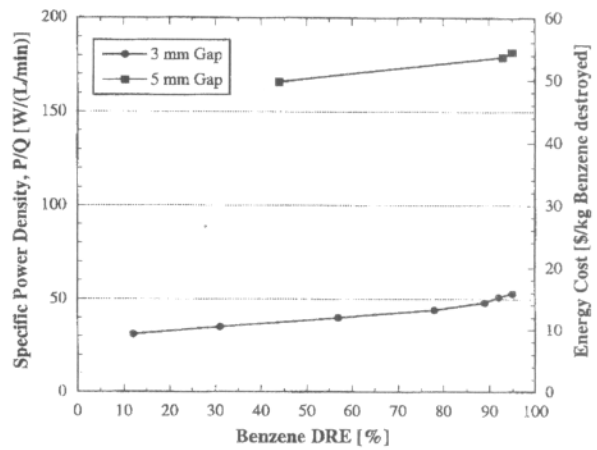

Figure 8. Power density and electrical energy cost. 1,000 ppmv benzene, 1 kHz, 2.0 L/min, 90% RH, 0.06 $/kWh.

closure was obtained on the carbon balance, i.e., 1,000 ppmv benzene was converted to 6,000 ppmv total concentration of CO and CO_2, and no intermediate hydrocarbon byproducts were observed with the GC/MS.

The specific energy density, i.e., the amount of energy deposited to the plasma reactor divided by the total gas flow rate, was calculated as a function of benzene DRE for the two plasma reactors using the equation developed by Manley [8] (see Figure 7). As the gap spacing increases, more energy must be deposited in the gas stream to destroy benzene. Specific power density and energy cost were also calculated, assuming a unit electricity cost of $0.06/kWh (Figure 8). The reactor with the 5 mm gap spacing required about three times the amount of power compared to the reactor with the 3 mm gap to achieve a benzene DRE of 95%.

It should be noted that a yellowish-brown polymer film develops on the dielectric plates over time. The production of the film is greatest at high relative humidities. Eventually, the polymer film needs to be removed from the dielectric plates, because benzene DRE will slowly decrease as the polymer film develops. It was found that a small quantity of water is sufficient to clean the dielectric plates, and that no other solvent or detergent were required. The dielectric plates were normally cleaned after 24 to 48 hours of continuous operation.

CONCLUSIONS

Destruction of hazardous air pollutants with dielectric barrier discharge plasma reactors shows promise as treatment technology. Oxygen and hydroxyl radicals generated in the plasma at low temperature (293 K) can be used to oxidize hydrocarbons to CO, CO_2, and H_2O. Near complete destruction of benzene (> 99%) was achieved in both wet and dry gas streams, but wet gas streams produced considerably

less CO. No intermediate hydrocarbon byproducts were observed with the GC/MS under any conditions, but a polymer film develops on the dielectric plates over time. This polymer film was easily removed with a water wash, but if it was left on the plates, it would slowly lower benzene DRE. Two gas gap spacings were examined for the plasma reactors (3 mm and 5 mm). Both configurations were able to achieve high benzene DREs, but the smaller gap spacing required a lower voltage and shorter residence time than the reactor with the larger gap. The 3 mm gap reactor also required less energy per unit volume to achieve the same benzene destruction as the 5 mm gap reactor.

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